STUDIES ON GASEOUS ION CHEMISTRY

A THESIS

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C O N T E N T S

CHAPTER I : GASEOUS ION CHEMISTRY : A REVIEW

A. IONIZATION

Over the past few years a number of methods for ionizing organic molecules have been developed in the field of organic mass spectrometry. The most commonly used techniques are (i) electron ionization (ii) chemical ionization (iii) photo-ionization (iv) field ionization and (v) field desorption. This Chapter deals with some aspects of the formation, rearrangements and energetics of gaseous ions formed by electron and chemical ionization.

1. Electron Ionization

(a) Franck-Condon principle: The collision between electrons of sufficient energy emitted from a tungsten or rhenium filament and the neutral molecules of an organic compound in the vapour state results in the removal of an electron from each molecule (equation 1). The minimum energy required to ionize a

$$M + e^- \longrightarrow M^{+\cdot} + 2e^- \qquad (1)$$

molecule is called its ionization potential (IP). Ionization potentials of most of the organic molecules are between 7 to 10 eV. The electron ionization process is fast. A 50 eV electron has a velocity of the order of 4.2×10^8 cm/s and will pass through molecular diameters of a few Å in about 10^{-15} to 10^{-16} s. This time is shorter than the fastest vibrations of a C-H bond (about 10^{-13} s) in a molecule. Thus, the

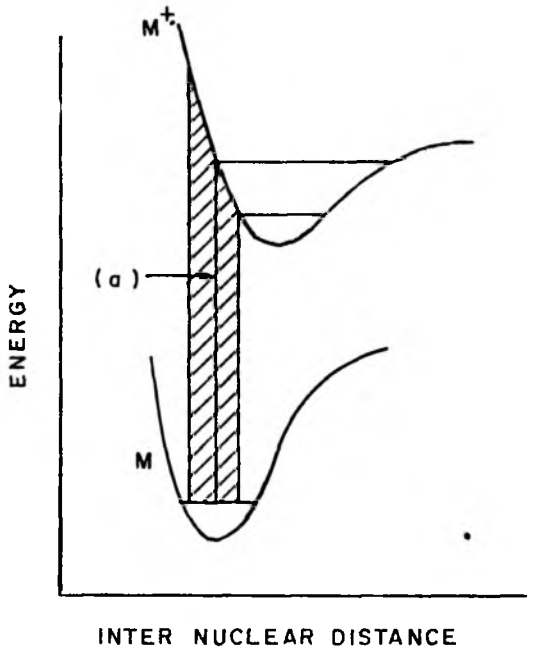
ionization process occurs without changes in internuclear distances. That is, the transition will follow the Frank-Condon rule, which states that the configuration and momenta of the nuclei do not change during the transition. The process is shown in the form of a potential energy diagram in Figure 1A, in which the ionization can be represented by the vertical transition (a). Removal of an electron from the highest occupied molecular orbital is a low energy process, and corresponds to the vertical ionization potential of the molecule.

If the electron energy is raised beyond the IP of the molecule, the molecular ion undergoes fragmentation (equation 2).

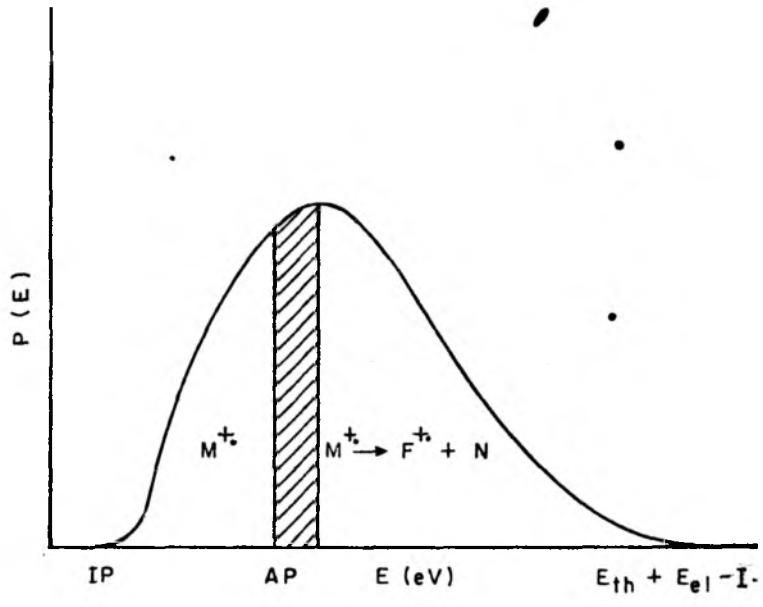
$$M^{+\cdot} \longrightarrow m_2^{+} + N \qquad (2)$$

The minimum energy required for $M^{+\cdot}$ to undergo fragmentation is called the transition state energy of $M^{+\cdot}$ or the appearance potential (AP) of $m_2^{+\cdot}$ ions. The difference between the AP of $m_2^{+\cdot}$ and the IP of $M^{+\cdot}$ is called the activation energy for the fragmentation process.

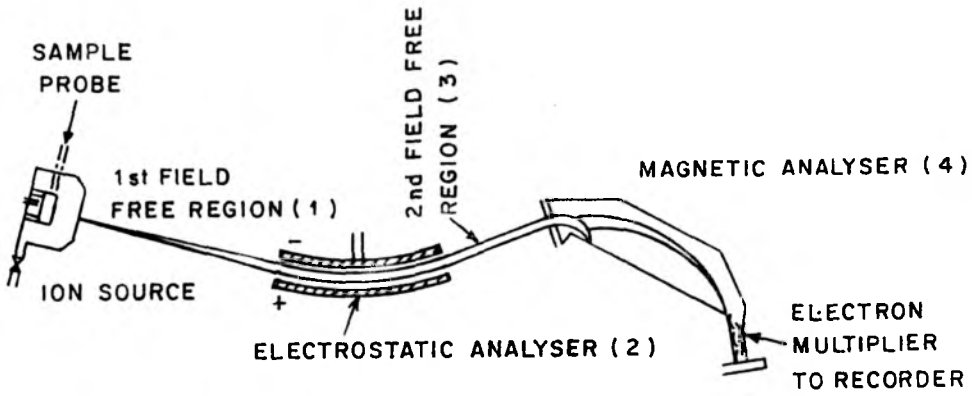
(b) Internal energy distribution in the molecular ion: Quasi-equilibrium theory: Electron ionization produces a molecular ion with a wide range of internal energies extending from zero at the ionization potential (IP) to an upper limit of $E_{th} + E_{el} - IP$; where E_{th} is the thermal energy of the


M+·
(a)
M
ENERGY
INTER NUCLEAR DISTANCE

(A)


P(E)
M+·
M+· → F+· + N
IP
AP
E (eV)
Eth + Eel - I

(B)


SAMPLE PROBE
1st FIELD FREE REGION (1)
ION SOURCE
2nd FIELD FREE REGION (3)
ELECTROSTATIC ANALYSER (2)
MAGNETIC ANALYSER (4)
ELECTRON MULTIPLIER
TO RECORDER

(C)

FIGURE 1.

3

molecule and E_{el} is the electron beam energy. The energy distribution in the molecular ion can be represented as shown in Figure 1B. The energy distribution is a function of IP, electron beam energy and the operating temperature. Due to the absence of collisions the thermodynamic equilibrium and Boltzmann energy distribution in the gas phase are neglected. Hence, Arrhenius type equations cannot be applied. The ions which have the internal energy between IP and the lowest AP appear as stable molecular ions. A given molecular ion will have a certain amount of excitational energy distributed in its electronic, vibrational and rotational degrees of freedom. The various fragmentation processes that occur as a result of high internal energies can be qualitatively explained by the quasi-equilibrium theory[2] of mass spectra. According to this theory, the molecular ions formed initially with varying internal energies do not decompose immediately to various fragments. The molecular ion undergoes more vibrations and the electronic excitation energy is completely distributed into vibrational degrees of freedom. When sufficient vibrational energy accumulates in the reaction co-ordinate, unimolecular decomposition occurs. The rate of decomposition, at a less sophisticated level, is given by the simplified quasi-equilibrium theory expression (equation 3). The rates of

$$K = \nu \left(\frac{E-E_o}{E} \right)^{N-1} \qquad (3)$$

decomposition (K) are described in terms of the internal energy E of the decomposing ion, the activation energy E_o for the fragmentation (AP-IP), the frequency factor ν and the total number of oscillators (N). It has been realized that even this simplified quasi-equilibrium theory rate expression is a poor approximation at the threshold energies. The effective number of oscillators has been found to be much less than the total number of oscillators N = 3n-6, where n is the number of atoms in the molecule.

(c) Decomposing ions, metastable ions and non-decomposing ions: Electron ionization results in the formation of ions with a wide range of internal energies and rate constants (K). The molecular ions having internal energies above the appearance potential decompose in the source to give fragment ions ($K > 10^6\ s^{-1}$). Further decomposition of fragment ions occurs when the internal energy content E is higher than the activation energy E_o ($E > E_o$). This is due to the exponential increase of the rate constant with internal energy E. The ions which have sufficient internal energy to decompose are referred to as decomposing ions. These ions often undergo simple cleavage processes which have higher frequency factors and activation energies. Rearrangement reactions which have low activation energies also compete with these processes.

Depending on the voltages used to accelerate the ions

in the source, they spend approximately 10^{-6} s in the source region. A certain fraction of ions which have relatively low internal energy is accelerated from the source before the decomposition takes place. They can decompose anywhere in the flight path prior to detection, e.g. in the first field free region (1), electrostatic analyzer (2), second field free region (3), magnetic analyzer (4) or after the magnetic analyzer (Figure 1C). Such ions are known as metastable ions. The fragment ions formed from the metastable ions have relatively low energy and are not accelerated after their formation. Consequently they follow a different flight path and are lost. In the normal operation of a double focusing mass spectrometer only ions decomposing in the second field free region (3) are recorded as diffuse metastable peaks at non-integral masses. Metastable ions provide valuable information on the structure and reaction mechanisms of ions having well defined internal energy distributions[3-5].

The molecular ions and fragment ions formed in the source with internal energies less than the lowest fragmentation threshold will not decompose on the mass spectrometer time scale. These ions are in the deep potential well and are carried to the detector and recorded as non-decomposing molecular and fragment ions. The fragment ions may be odd or even electron species depending upon their mechanism of formation from the precursor ions. The structural information

on these ions can be obtained from ion-molecule reactions in ion-cyclotron resonance (ICR)[6] spectrometer or by collisional activation[7] studies.

2. Chemical Ionization

Chemical ionization (CI) is one of the newer soft ionization techniques which was first reported by Munson and Field[8] in 1966. The growing importance of this technique is evident from the increasing number of publications and reviews[9-14]. This technique has been accepted as a complementary to electron ionization. In this technique ion production is based on ion-molecule reactions and charge exchange processes. The molecules under investigation are bombarded with suitable ionized reagent gas. Generally, methane, isobutane, water, ammonia, nitric oxide and rare gases are used as reagent gas. A set of reagent ions are first generated by bombarding a suitable reagent gas at pressures between 0.5 and 1 torr, with high energy electrons. For e.g. methane gas gives the following ions in its plasma (equations 4-9). At normal operating conditions (1×10^{-3} torr)

$$CH_4 + e^- \rightarrow (CH_4)^{+\cdot}, (CH_3)^+, (CH_2)^{+\cdot} \text{ .. etc.} \quad (4)$$

$$(CH_4)^{+\cdot} + CH_4 \rightarrow (CH_5)^+ + CH_3^{\cdot} \quad (5)$$

$$(CH_3)^+ + CH_4 \rightarrow (C_2H_5)^+ + H_2 \quad (6)$$

$$(CH_2)^{+\cdot} + CH_4 \rightarrow (C_2H_4)^{+\cdot} + H_2 \quad (7)$$

$$(CH_2)^{+\cdot} + CH_4 \rightarrow (C_2H_3)^+ + H_2 + H^{\cdot} \quad (8)$$

$$(C_2H_3)^+ + CH_4 \rightarrow (C_3H_5)^+ + H_2 \quad (9)$$

7

95% of the total ion current is carried by $(CH_5)^+$, $(C_2H_5)^+$ and $(C_3H_5)^+$ ions. Their contributions are CH_5^+ (48%), $C_2H_5^+$ (41%) and $C_3H_5^+$ (6 %). Sample molecules are introduced in the usual manner but at a concentration below 0.1% of the reagent gas. Under these conditions the reagent ions react with neutral sample molecules to produce ion molecules which fragment further to give a characteristic CI mass spectrum.

Although detailed mechanism of these ion-molecule reactions is not clearly understood, the simple assumption that $(CH_5)^+$ and $(C_2H_5)^+$ ions act as Brønsted acids with respect to sample molecule M appears to be satisfactory. The ion $(C_2H_5)^+$

$$CH_5^+ + M \rightarrow (MH)^+ + CH_4 \qquad (10)$$

$$C_2H_5^+ + M \rightarrow (MH)^+ + C_2H_4 \qquad (11)$$

$$C_2H_5^+ + M \rightarrow (M + C_2H_5)^+ \qquad (12)$$

can also function as a Lewis acid to form a collision-stabilized complex (equation 12).

In addition to the above acid/base type of substrate ionization, which invariably involves 'closed shell' ions, another type of ion-molecule reaction is of importance. The sample molecules could be also ionized by charge exchange (CE) processes (equation 13). Such ions correspond to the

$$(He)^{+\cdot} + M \rightarrow M^{+\cdot} + He \qquad (13)$$

ions encountered in electron ionization and occur particularly when the reagent gases such as nitrogen or rare gases are employed.

Energetics of CI process

In general, gas-phase ion molecule reactions are appreciably faster than reactions between neutral species. Under chemical ionization the amount of energy transferred to the sample ion is dependent partly on the exothermicity of the ion-molecule reactions employed. Most organic compounds can be considered as Brønsted acids or bases depending on the proton affinity (PA)[15] of the substrate molecule. PA of a molecule is defined as the heat liberated on protonation. Proton affinities of some reagent gases are given in Table I.

Table I

Proton affinities of reagent gases employed in CI.

Reagent gas	Brønsted acid	P.A. K.cal/mole
H_2	H_3^+	101
CH_4	CH_5^+	126
H_2O	H_3O^+	169
CH_3OH	$CH_3OH_2^+$	182
iso-C_4H_{10}	t-$C_4H_9^+$	193
NH_3	NH_4^+	201

Majority of organic compounds have high proton affinities, as compared to conjugate bases of Brønsted acids H_3^+, CH_5^+ and $C_4H_9^+$. The exothermicity of proton transfer will depend on the differences in the PA's of the substrate molecule and that of the conjugate base of the Brønsted reagent acid. Since, the exothermicity of proton transfer reactions to hydrocarbons is low (0–3 eV), the resulting even electron ion, $(MH)^+$ contain little energy in the transition state as compared to those formed under electron ionization. Hence, very intense protonated molecular ions are generally observed in the CI spectra of most of the organic compounds.

The great simplicity and better predictability of CI fragmentation enables its extensive application as a structural tool. In the determination of molecular weight of organic compounds which do not show stable molecular ions in their corresponding EI spectra, the CI has been most valuable[13,16]. This technique is often employed to distinguish between epimeric molecules which give similar E.I. spectra[13,17,18]. Characterization of the components of complex mixtures have been carried out by GC/CIMS analysis[19]. The versatility of CI and its special advantages in the field of biochemistry, pharmacology and medicine have been recognized in recent years[13]. Since this method is useful in the production of carbonium ions, it has been successfully employed to study the gas phase reactions and to compare with known reactions in solution.

B. FRAGMENTATION

When the internal energy of an ion is more than the bond cleavage energy, fragmentation takes place. Mass spectral reactions are unimolecular, competing and consecutive processes. Based on the stabilities of product ion and departing neutral molecule and the fragmentation directing effect of both the radical and charge sites, the gaseous reactions can be classified into three major types as follows:

1. Simple cleavage modes
2. Retro Diels-Alder (RDA) reaction
3. Rearrangement processes.

1. Simple cleavage

A simple cleavage process is the rupture of a single covalent bond to give an ion and a radical. The cleavage can be heterolytic or homolytic. Heterolytic cleavage occurs at cationic centre and the charge is mainly carried by the fragment which has a lower ionization potential (Stevenson's rule). The homolytic cleavage is triggered by a radical site.

(a) Heterolytic cleavage: The dissociation of C-X bond is a high energy process. If it occurs the charge is retained by the carbon atom only. This reaction can be represented by equation 14. Alkyl halides, ethers and mercaptans decompose

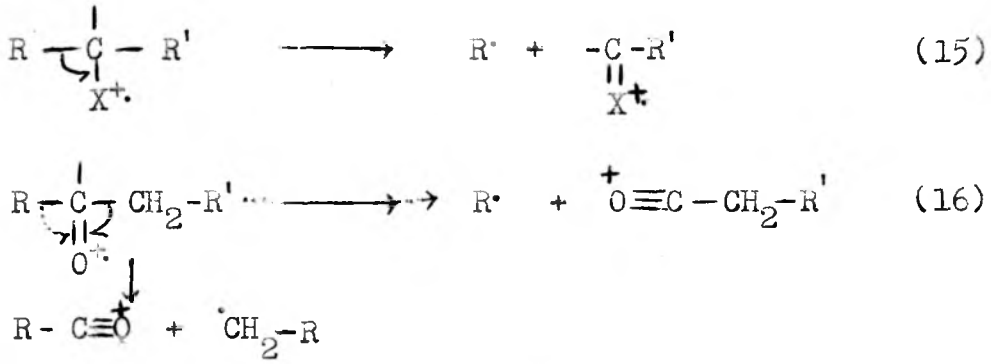
(14)

(X = halogen, OH, SR, OR).

by this fragmentation mode.

(b) Homolytic cleavage: The radical cations have an unpaired electron which can take part in the new bond formation. The excess energy released as a result of bond formation is made available for bond cleavage. Such cleavages which are triggered by radical site proceed at high rates and are more common in electron ionization. They are further divided into α- and β-cleavages.

(i) α-Cleavage: Ions containing a hetero atom which is either singly or doubly bonded to a carbon atom exhibit this type of cleavage. A radical site is first generated on the hetero atom which is followed by a new bond formation with the adjacent carbon (equation 15 and 16). A radical is generally lost. It is a general fragmentation mode observed in



(15)

(16)

alcohols, amines, ethers, sulfides, aldehydes, ketones and esters. Compounds containing C≡N or C=S groups do not show this kind of cleavage. Amino ethers of type $RO(CH_2)_nNR_1R_2$ fragment by α-cleavage to give abundant ions in their EI spectra[20]. This kind of simple fission was also noticed in

the EI spectra of per-O-acetyl-1,1-bis(acylamido)-1-deoxyalditols[21].

(ii) β-Cleavage: Olefinic compounds with isolated double bonds fragment by allylic cleavage[22] (equation 17). It is an example of β-cleavage. The resulting allylic ion

$$R\text{-}\overset{|}{C}\text{=}\overset{|}{C}\text{-}\overset{|}{\underset{|}{C}}\text{-}R' \xrightarrow{e} R\text{-}\overset{|}{C}^{+}\text{-}\overset{|}{C}\text{-}\overset{|}{\underset{|}{C}}\text{-}R' \rightarrow R\text{-}\overset{|}{\underset{+}{C}}\text{-}\overset{|}{C}\text{=}\overset{|}{C}\text{-} + R^{\cdot} \qquad (17)$$

stabilizes by resonance effect. The isomeric olefins may be expected to give different allylic ions by β-fission. But their spectra are often similar[23] indicating that the double bond can migrate. Locating the double bond in simple aliphatic compounds by only EI mass spectrometry is not reliable. Recently, the CI method has been used to locate the double bonds in many linear isomeric olefins[24]. Differences in the EI spectra are however observed when the double bond in an ion is in the vicinity of a functional group. McLafferty has reviewed simple cleavage processes[25]. Cleavage β- to either an aromatic ring or a cyano moiety has been shown to produce abundant ions in the EI spectra of 2-aryl-hydrazonopropandioic acid derivatives[26].

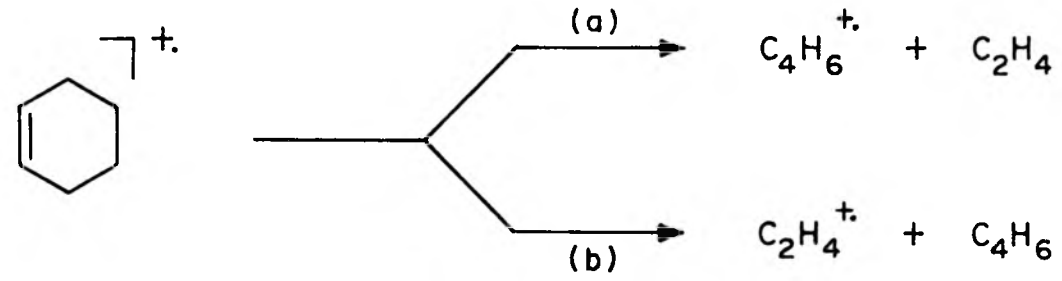
Organic compounds with benzyl groups often undergo β-cleavage to form stable tropylium $(C_7H_7)^{+\cdot}$ ions[27]. The thermodynamic stability of these ions appear to favour this reaction. There are several systematic investigations[28-30] on the formation, structure and reactivity of the tropylium

cation formed from various precursors under EI and CI conditions. Ions formed from C_6H_5-CH_2-Y appear to give mixtures of benzylic and tropylium cations, depending on the nature of the leaving group Y. For e.g. when Y=H, tropylium cation is formed predominantly, while the benzylic cation is the major product when Y = -CH_2Ph. These observations were confirmed by collisional activation (CA) analysis. The formation of $C_7H_7^+$ ions in the CI spectra from C_6H_5-CH_2-Y (Y = halogen, OH, OR) occurs by the heterolytic fission[31] of C-Y bond. The isomerization of benzylic to tropylium cation in the gas phase proposed by McLafferty and Bockhoff[30] is in agreement with Dewar's predictions from MINDO/3 calculations[32].

2. Retro Diels-Alder (RDA) Reaction

The retro Diels-Alder (RDA) reaction[33] is an example of a multi-centred fragmentation mode observed in six membered cyclic olefins. This fragmentation process results in the rupture of two bonds of a cyclic system to give the diene and dienophile ions. The simplest molecule in which this fragmentation takes place is cyclohexene. The diene (m/z 54) and/or dienophile (m/z 28) ions are observed. They arise from different molecular ions of cyclohexene (equation 18). RDA may or may not be accompanied by a hydrogen transfer rearrangement.

Two mechanisms have been proposed for RDA process under



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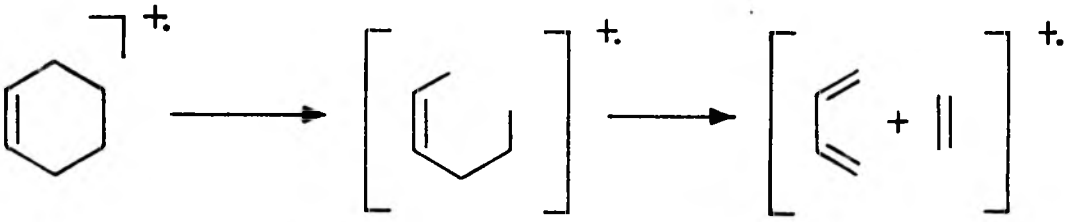

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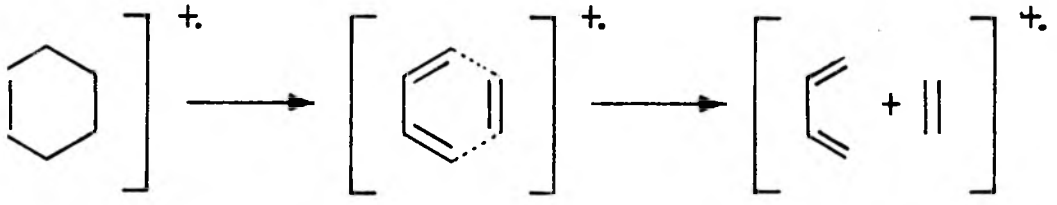


(20)

electron ionization. A stepwise mechanism has been postulated on the basis of thermochemical data obtained for the formation of $C_2H_4^{+\cdot}$ and $C_4H_6^{+\cdot}$ radical cations from cyclohexene[34,35]. The formation of diene and dienophile ions correspond well with the predicted charge distribution in the open chain intermediate (equation 19). Hammerum and Djerassi[36] have shown that the RDA reaction in cis and trans bicyclic Δ^2-octalins is not stereospecific. Similarly, stereochemical differences were not noticed in a series of substituted bi- and tricyclo diketones[37]. These observations have lend additional support to a stepwise mechanism for this process.

The concerted mechanism on the other hand is favoured by Dougherty[38] and others. Based on perturbation molecular orbital (PMO) theory[38], it was proposed that RDA reaction proceeds by a concerted process through a six orbital, five electron transition state (equation 20). It is isoelectronic with the π electron system of the benzene molecular ion. This mechanism resembles the thermal electrocyclic RDA reaction. The concerted mechanism was further supported by Smith and Thornton[39]. They found that in the EI spectrum of 4-vinyl cyclohexene the charge is preferentially retained by the butadiene ion which contains the vinyl group rather than by the other butadiene. This unequal charge distribution in the two diene ions of 4-vinyl cyclohexene was shown to be due to the lower ionization potential of the diene ion which

contains the vinyl group[40]. Elwood and Beynon[41] have observed a correlation between the kinetic energy released in the RDA process of some bicyclic hydrocarbon ions and the activation energies for the formation of similar species by Diels-Alder reaction in solution. This observation favours a concerted mechanism. Mandelbaum and co-workers[42,43] have reported stereospecific RDA reaction in the EI spectra of several tri- and polycyclic unsaturated diketones and diols. Only in the spectrum of the cis isomer the diene ions were formed. Similar stereochemical differences were observed under CI conditions[44]. These workers have suggested that RDA fragmentation proceeds in a synchronous manner. If it is a concerted process it should fulfil the orbital symmetry rules[45] analogous to those established for quasi thermal or quasi photochemical RDA reaction.

Djerassi et al.[46] have studied a series of cis and trans Δ^7-steroidal olefins under EI. It was shown that the RDA reaction in these compounds is controlled by the stereochemistry of the ring juncture A/B. It was proposed that a concerted mechanism operates when A/B ring junction is cis, since the initial ionization does not alter the stereochemistry of A/B ring juncture. The trans isomer in which the initial ionization disturbs the A/B ring juncture, a stepwise mechanism is operating.

The RDA process is accompanied by a hydrogen transfer rearrangement in the EI spectra of some substituted

chromones[47,48]. The evidence was obtained from labelling and high resolution data.

It is known that a double bond can migrate in unconjugated olefins prior to fragmentation[49]. Such migrations have been postulated by Djerassi[50] and Stark[51] to explain the EI fragmentation of some cyclic olefins. The double bond migration is accompanied by a 1,3-hydrogen shift. Williams and Hvistendahl[52] have reported that large release of kinetic energy results for ionic decompositions proceeding through symmetry forbidden pathways. Field ionization kinetics (FIK), collisional activation (CA), kinetic energy release (T), and isotope effect measurements were employed to gain more insight into the RDA fragmentation proceeding the double bond migration in 2-cyclohexen-1-ol[53], tetralin and 1-tetralol systems[54,55].

3. Rearrangements

Rearrangement processes are divided into two types viz., hydrogen transfer rearrangements and skeletal rearrangements. A radical site can form a new bond by abstracting an atom which is not directly bonded to the radical site. This can result in a hydrogen transfer rearrangement. When groups or atoms other than hydrogen migrate, skeletal rearrangement can take place. In skeletal rearrangements the role of radical and charge sites is not clear. They are multicentred low energy processes. Hetero atoms, unsaturation

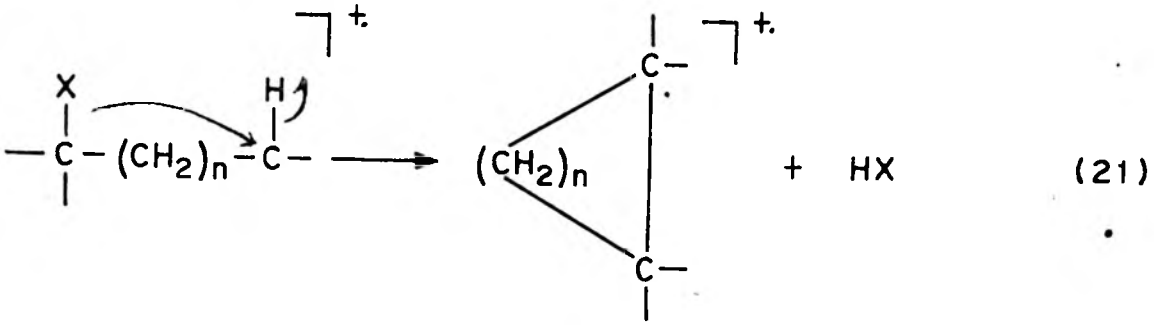
and π- electron system in the molecule favour these reactions. They are regarded as pseudobimolecular reactions since the migrating group acts as a nucleophile which is transferred to an electron deficient centre in the ion.

(a) Hydrogen transfer rearrangements

The intramolecular hydrogen rearrangements in several classes of organic compounds have been reviewed by Bursey and his co-workers[56]. They are classified into four different types.

(i) Scrambling: It is a hydrogen transfer rearrangement process often observed in many aromatic compounds in which an equilibration of atoms takes place. It leads to the cleavage and formation of C-H bonds. Hydrogen, carbon and halogen atoms have been reported to scramble within the molecule prior to fragmentation[57-59]. Extensive hydrogen scrambling has been reported in the $(M-H)^+$ ions of 2-methyl-indazole prior to the elimination of HCN[60]. There are many examples of scrambling in literature.

(ii) Elimination: The fragmentation leading to the loss of neutral molecules such as H_2O, HX, CH_2O, CH_2CO, AcOH and HNO_2 from the molecular ions is well documented in literature[56,61]. It involves the abstraction of a hydrogen by the functional group present in the molecule (equation 21). The charge is generally localized on the carbon atom of the fragment ion. Both the molecular and fragment ions undergo this fragmentation.



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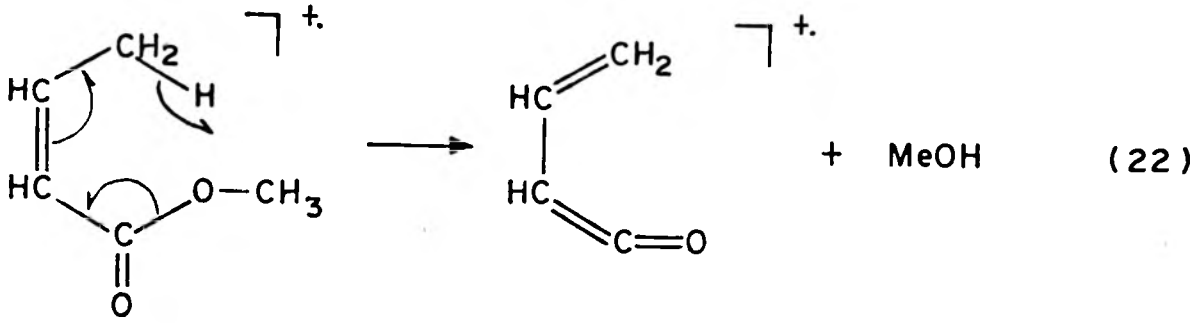

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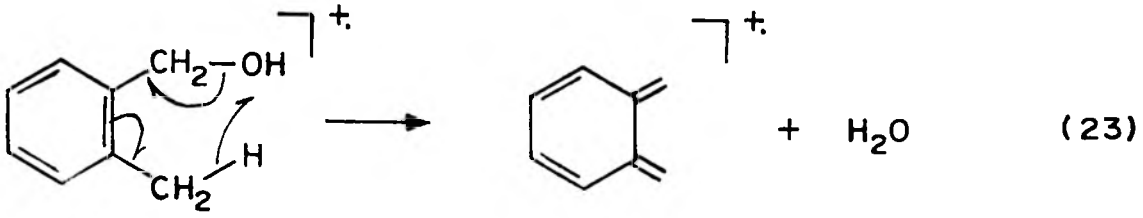

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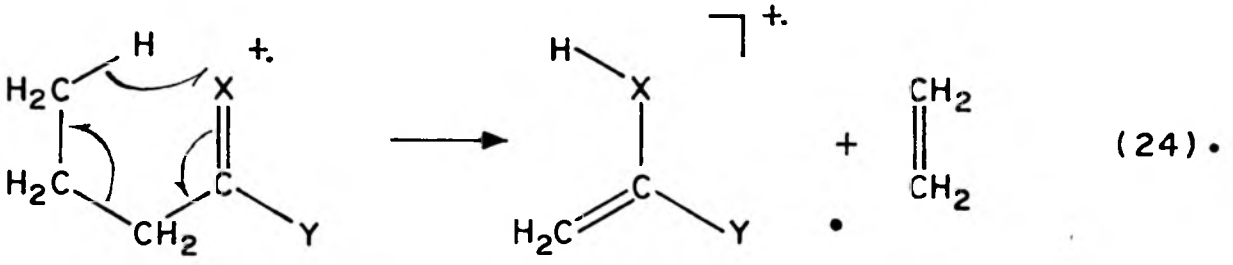

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In acyclic compounds, the loss of water occurs mainly via an 1,4-elimination[56] whereas acetic acid loss proceeds by competitive 1,2- and 1,3-eliminations[62]. In cyclic systems. the reaction can take place by 1,2-, 1,3- and 1,4-elimination processes[63,64]. Elimination reactions in cyclic systems proceed through five or six centred transition states.

Gross and Wojinski[65] have reported a regiospecific elimination of acetic acid from 1-acetoxy tetralin. An 1,4-elimination mechanism was postulated similar to that of water loss from 1-tetralol. These workers have further shown that the molecular ion of 1-acetoxy tetralin expels ketene by a four centred mechanism, which is a common reaction observed in the EI spectra of acetates[56]. Metastable ion characteristics and labelling studies were employed to support their observations. Based on MIKE and CA spectral data Jaudon[66] and Tabet have shown that the loss of ethylene from the molecular ion of α -methyl-decalone occurs by a hydrogen transfer rearrangement. Loss of a neutral molecule of acetaldehyde from the $M^{+\cdot}$ ion of 4,4-dimethyl-2-allyl cyclohexanone proceeds by extensive hydrogen rearrangement processes[67]. The only 1,1-elimination process reported in literature is the expulsion of HCN from the molecular ion of o-nitrobenzyl cyanide[68]. Similar loss was not observed in the corresponding chloro and hydroxy compounds. The elimination reactions are frequently observed in alcohols, ethers, cyanides, halides and esters.

(iii) Ortho effect: Cis olefins and o-substituted aromatic compounds show ortho effect[69] which results in the elimination of a stable neutral molecule. Loss of methanol from the molecular ion of cis methyl crotonate is an example (equation 22). Similarly, expulsion of water from the molecular ion of o-methyl benzoic acid can be explained by ortho effect (equation 23). This phenomenon has been reviewed by Schwarz[70]. It is observed in several systems[71-74]. The unusual fragment ions encountered in the EI spectra of N-benzyl and N,N-dibenzylanthranilic acids[75] have been explained on the basis of ortho interaction of the carbonyl group with the N-benzyl and N,N-dibenzyl moieties.

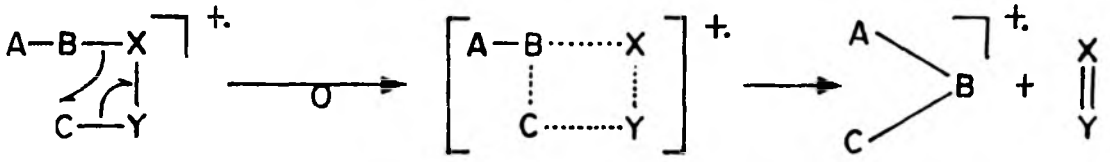
(iv) McLafferty rearrangement: The most extensively studied hydrogen transfer rearrangement under electron ionization is the McLafferty rearrangement[76]. A γ -hydrogen atom is transferred via a six membered transition state to an electron deficient centre. This is followed by a β -cleavage with respect to the functional group (equation 24). A review article[77] has appeared in the literature. It is a characteristic fragmentation mode of ketones, aldehydes, esters, olefins, acids, phenyl ethanols, aryl ethers, nitriles, carbonates, oximes and hydrazones[77]. The structural requirements for this rearrangement are a three carbon side chain, a γ -hydrogen atom with respect to the functional group and a double bond. The double bond could be a carbonyl function, an olefinic double bond or an aromatic system. Djerassi et al.[78] have

reported a double McLafferty rearrangement in dipropyl ketone.

Concerted and stepwise mechanisms have been proposed for this hydrogen transfer process. Dougherty[79], based on the perturbation molecular orbital theory for the molecular ion of 1-pentene has proposed a concerted mechanism. McLafferty and his associates[80] applied Milliken's molecular orbital theory and showed that a stepwise process is operating. The γ -hydrogen is transferred to the carbonyl oxygen which is followed by β -cleavage. The two mechanisms differ in the geometrical arrangement of bonds. A stepwise mechanism is accepted at present since it has received some experimental support[81,82]. Turecek and Hanus[82] have studied McLafferty rearrangement in 2,5-diphenyl-1-hexene and its deuterated analogs. The α-methylstyrene fragment ions were shown to retain the charge with equal probability and give identical metastable spectra. These results have lend additional support to a stepwise mechanism to this rearrangement.

(b) Skeletal rearrangements

In organic mass spectrometry there are many reports[83-85] on skeletal rearrangement processes involving migration of atoms or groups other than hydrogen. In general, a neutral species is expelled in such processes. Stable ions are formed containing new bonds which are absent in the original molecule (equation 25). The transition states for these rearrangements



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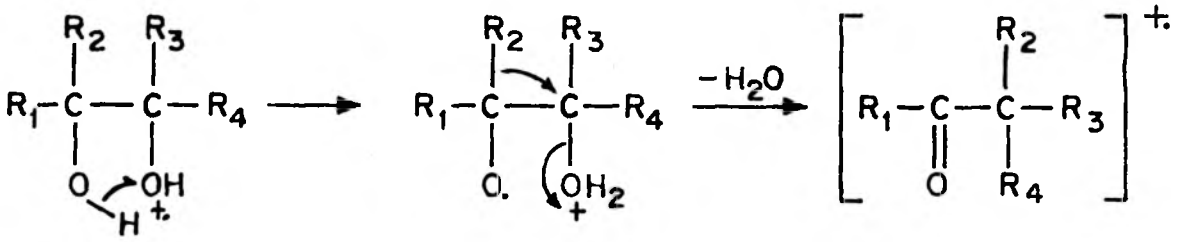

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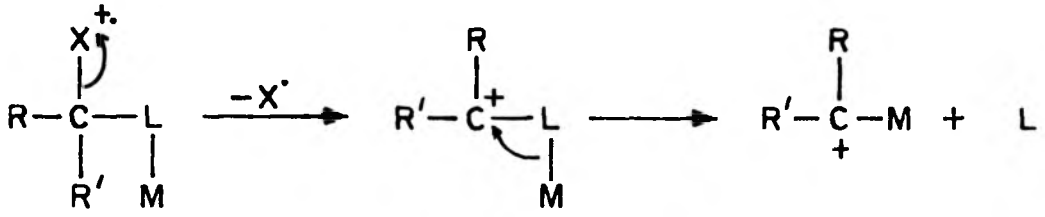

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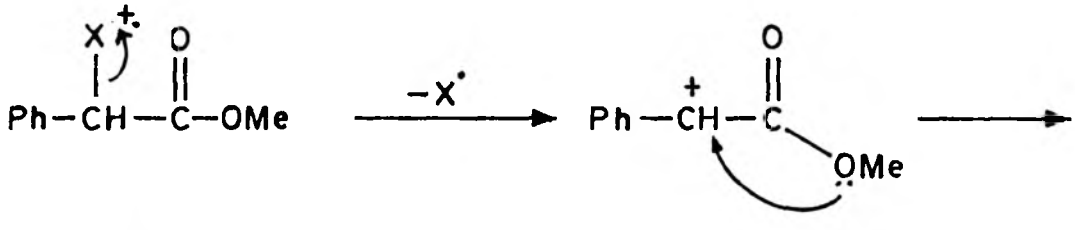
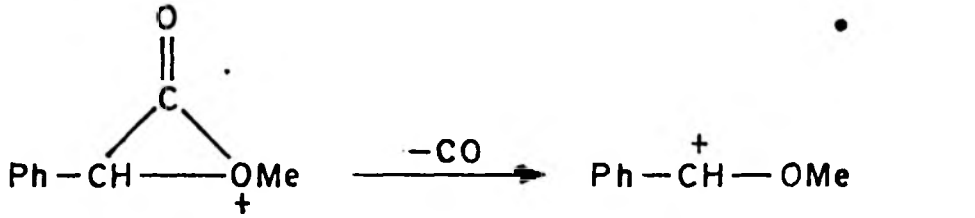




(28)

are usually four or six centred. The relative intensity of the rearrangement ions can vary. In some cases they form the base peak. Williams and Cooks[86] have shown that daughter ions of moderate abundance at 70 eV formed by rearrangement processes become more abundant in low voltage spectra. This is a consequence of the entropy requirement of rearrangements, which results in lower frequency factors than for direct bond cleavages. These fragmentation modes are regarded as low energy processes in which the rates of reaction of each consecutive step are similar. One reason for the observation of such processes appears to be the formation of favoured low energy transition state which results from bond formation and bond cleavage[87]. In skeletal rearrangements hetero atom plays an important role. The stability of neutral species expelled and the product ion formed provides a 'driving force'.

Such processes could be detected from the rearranged ions which contain structural units which are not directly linked in the parent molecule. Indirect methods used for their detection are (i) heats of formation and (ii) ion structures. In practice, it is difficult to ascertain whether rearrangement occurs prior to or during fragmentation, although the available evidence on hydrogen scrambling in aromatic system suggests that they occur prior to fragmentation[88].

It is not certain whether the radical or cationic site provides the driving force for these rearrangements. Many

workers believe that both have some role on rearrangement processes. The rearrangements observed in carbohydrate derivatives[89] revealed that the radical as well as cationic centres would induce these rearrangements. Alkyl migrations in the EI spectra of formaldehyde acetals[90] result in the expulsion of neutral formaldehyde molecule. Elimination of carbon dioxide in unsaturated esters and carbonates is an example. Similarly, thiocarbonates, carbamates and thiocarbamates, cyano acetates expel carbon dioxide by alkyl rearrangements. Rearrangement processes are also observed in aromatic nitro compounds, sulfones and sulfoxides. Pinacol-pinacolone rearrangement[91] of several 1,2 glycols under EI is known (equation 26).

Even electron ions formed under electron ionization, protonated molecular ions and fragment ions produced under CI mode also exhibit skeletal rearrangement processes. The absence of radical site in these even electron ions makes the process simpler. Hence it is possible to compare the structure, energetics and reactivity of such ions with those formed in solution[5]. Migration to cationic centre in the gas phase is regarded as intramolecular nucleophilic substitution (S_Ni) reaction (equation 27). The nature of the migrating group M, leaving group L, and the carbonium ion stabilizing groups R and R^1 determine the reaction. In a systematic study of this reaction Cooks et al.[92] used migrating groups bearing lone pairs or π electrons (e.g. OH, OMe, NH_2, X and Ph) and

leaving groups of type $(CH_2)_nCO$ including CO itself. These compounds showed major peaks in their spectra due to rearrangements (equation 28). In the EI spectra of amidines[93], based on the labelling data it was found that the $(M-CH_3)^+$ ion undergoes a skeletal rearrangement leading to the expulsion of a molecule of HCN.

Skeletal rearrangements involving the migration of trimethyl silyl group to the carbonyl oxygen within the molecular ion of TMS derivatives of acylglycines have been reported[94]. The evidence was obtained from high resolution data. Similar migrations have been reported by Smith and Daves[95] in the EI spectra of some silyl derivatives. Ho and co-workers[96] have observed phenyl migrations to silicon in the EI spectra of α -silyl ketones of type $Me_nPh_{(3-n)}Si-\overset{O}{\overset{\|}{C}}-Ph$. The migration was shown to be accompanied by the expulsion of carbon monoxide from the molecular ions. Four centred skeletal rearrangement processes have been noticed in thioanilides[97] under electron ionization. It was shown to involve loss of a substituted thiophenoxy radical followed by aryl migration from nitrogen to sulfur by a four centred mechanism. Substituent effects were observed on this rearrangement process. Based on ^{13}C labelling data and kinetic energy release measurements, Nibbering and Van den Heuvel[98] have shown that $(C_8H_6O)^{+\cdot}$ ions are formed from 7-exo-phenylbicyclo(3,1,1)heptan-6-one by skeletal rearrangement processes only.

C. METASTABLE IONS

As indicated earlier, the ions which decompose after acceleration outside the ion source but before the detector are referred to as metastable ions. Unlike fragmentation modes occurring in the ion source, metastable transitions take place from a narrow range of ion energies corresponding to rate constants for decompositions between 10^{+4} to $10^{+6} s^{-1}$. Some of the useful information obtained from the studies on metastable ions are (i) ion structure elucidation from metastable ion abundances, (ii) identification of rearrangement processes from kinetic energy release measurements, (iii) measurement of isotope effect, (iv) the determination of the extent of scrambling and (v) collisional activation studies to gain information on ion structures.

1. Detection of metastable ions

In a double focusing mass spectrometer the relation between the mass to charge ratio of an ion m/z, the accelerating voltage V, and the magnetic field strength H, is given by

$$\frac{m}{z} = \frac{H^2 r^2}{2V} \qquad (29)$$

where r is the radius of deflection of mass m in the magnetic field. Generally, ESA voltage, E_o coupled to accelerating voltage V is held in a fixed ratio. If a reaction $m_1^+ \rightarrow m_2^+ + N$ takes places in the second field-free region, the m_2^+ ions possess less kinetic energy than normal m_2^+ ions formed in the source. Hence, they are deflected more readily

when they pass through the magnetic sector. These ions are not recorded at the normal position for m_2^+ in the spectrum, but at $m^* = m_2^2/m_1$[99]. Factors influencing the shapes of metastable peaks have been discussed[100]. The width at half height of the metastable peak has been used to calculate the kinetic energy (T) released during metastable transition using the equation (30) where V is the accelerating voltage,

$$T = \frac{Ve}{4\mu}\left(\frac{\Delta m}{m_2^2/m_1}\right)^2 \qquad (30)$$

e is the electronic charge, $\mu = (m_1-m_2)/m_2$, and T = kinetic energy released in electron volts. Data on kinetic energies released during the decompositions of isomeric metastable ions from various precursors provide evidence for their decomposition through identical activated complexes[98].

If the metastable decomposition $m_1^+ \longrightarrow m_2^+ + \dot{N}$, occurs in the first field free region of the conventional double focusing mass spectrometer, then the kinetic energy of the daughter ions is reduced to m_2/m_1 value of the full accelerating voltage. If the mass spectrometer is set for normal operation, these m_2^+ ions cannot follow the central path along with the ions decomposing in the source. These ions strike the plates and are lost. They can be however made to follow the central path by increasing the ion accelerating voltage by the ratio of masses of the precursor

to daughter ions m_1/m_2. This method of observing metastable transitions developed by Barber and Elliot[102] is called as metastable defocusing technique. This method has the disadvantage that as the ion accelerating voltage is changed the optimum tuning conditions within the source are altered. It is due to the change in the field penetration and also that voltage cannot be changed by more than a factor of four. This limits the ratio of precursor to daughter ions which can be studied. The method has the advantage that mass scale of the instrument is not changed during acceleration so that the magnet current can be set to observe the precursor ion. As the accelerating voltage is scanned, a series of peaks can be observed each of which correspond to a different metastable ion which decomposes to the daughter ion.

Alternatively the daughter ions formed in the first field free region can also be made to follow the central path by reducing the normal electric sector voltage by a factor m_2/m_1 keeping accelerating voltage constant. This gives the ion kinetic energy (IKE)[103,104] spectrum of the compound. In this technique also the main beam of stable ions is not transmitted. The IKE technique has the disadvantage that the mass scale of the instrument changes during the scan of electric sector voltages. It has the advantage that all the products of metastable decompositions without limitation on the ratio of masses of parent to daughter ions can be made to follow the central path through the electrostatic sector. A detector

placed at the exit of the electric sector will plot a complete IKE spectrum of the products of the metastable ion decompositions. IKE spectra were shown to give detailed 'finger prints' and appear to be sensitive to small differences in structure[105].

2. Mass analyzed ion kinetic energy (MIKE) spectroscopy

During the last decade reverse geometry instruments in which the ion beam enters the magnetic field first and then traverses the electric sector have been developed and are commercially available. Such instruments have extended the field of application of many mass spectral techniques.

With the reverse geometry instrument it is possible to focus any ion that is formed in the source by setting the magnetic field. The decompositions of the selected ion, in the second field free region can then be studied by scanning the electric sector voltage. All the daughter ions formed can be detected. Since accelerating voltage and the magnetic field remain fixed, there is no loss in ion extraction efficiency. Focusing conditions are not altered and the mass scale also does not change. The mass scale of the fragment ions formed in this technique is a linear function of electric sector voltage. This technique is called as Mass Analyzed Ion Kinetic Energy (MIKE) or Direct Analysis of Daughter Ions (DADI)[106,107].

3. Linked scan

In double focusing instruments it is possible to scan the products of decompositions of metastable ions by various methods without interference from the stable ions that appear in the normal mass spectrum[108]. These methods are (i) the 1/V scan, in which all precursors of a particular daughter ion are detected and (ii) the linked scan, in which two of the three fields and voltages of the mass spectrometer are varied simultaneously.

There are three types of linked scans to detect the metastable ion decompositions. (i) $V^{1/2}/B$ scan[109], (ii) B/E scan[110], and (iii) B^2/E scan[111] where B is magnetic and E is the electrostatic fields. The former two scans are useful for recording daughter ions from a common precursors. In all these cases the accelerating voltage (V), and electric sector voltage (E) are uncoupled from each other, thus taking advantage of high intensity of first field free region metastable ions. The B/E and B^2/E scans are of great interest since they do not have any restriction over mass range. They also do not alter the ion source focusing during metastable scanning.

4. Metastable peak shapes and kinetic energy release

Metastable peak shapes and kinetic energy released during fragmentation in the field free regions have been shown to provide valuable information on isomerization processes, reaction mechanisms and transition state geometry of organic ions in the gas phase[3,5].

For a reaction $A^+ \rightarrow B^+ + C$, there is a reverse activation energy E_r, which is composed of a translational component E_t and a vibrational component E_i (Figure 2). The contribution from any translational component in the reverse activation energy will be revealed by the product ions B^+ and neutral C repelling each other. Figure 3 illustrates the decomposition of a metastable ion of unit charge and mass m_1 in the second field free region of a conventional double focusing mass spectrometer. A daughter ion of mass m_2 (closed circles) and the neutral species (m_1-m_2, 'open' circles) are produced. Little or no kinetic energy is released in a decomposition if the translational energy E_t is zero. Relatively narrow gaussian metastable peak results in such cases irrespective of orientations (A,B,C,D,E etc.). The metastable peak is observed in the normal mass spectrum at m/z value corresponding to m_2^2/m_1 [112] (Figure 4A). When a relatively large kinetic energy is released during decomposition, the orientation A (Figure 3) gives rise to daughter ions with slightly increased momentum, relative to that if no kinetic energy were released. It is due to the fact that these ions are pushed along the beam. As a result these ions with more momentum are deflected slightly less readily by the magnetic analyzer. They appear at m/z value marginally higher than m_2^2/m_1. On the other hand, decompositions occurring in orientation B (Figure 3) result in the ions with less momentum. These ions are deflected by magnetic analyzer more rapidly

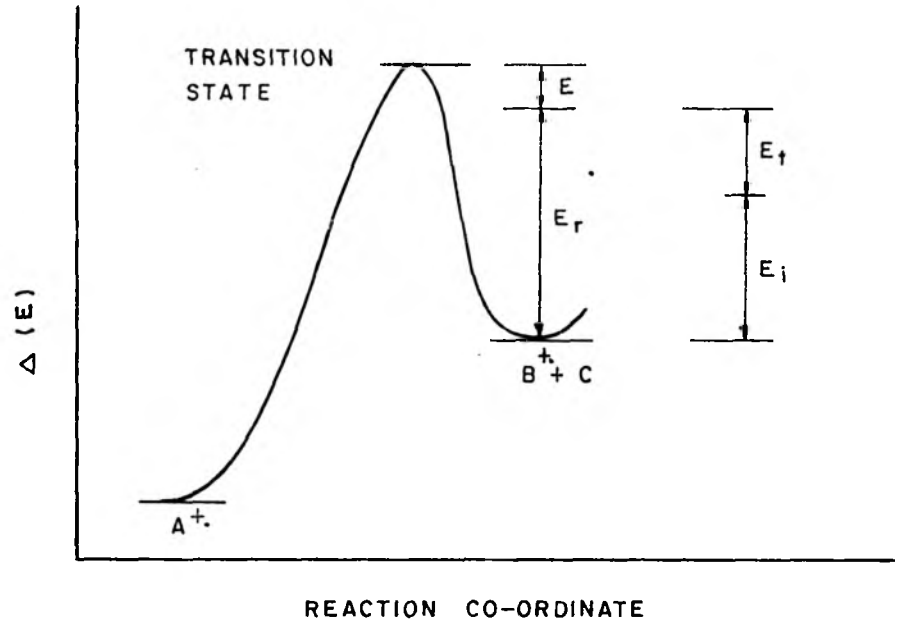


FIGURE 2.

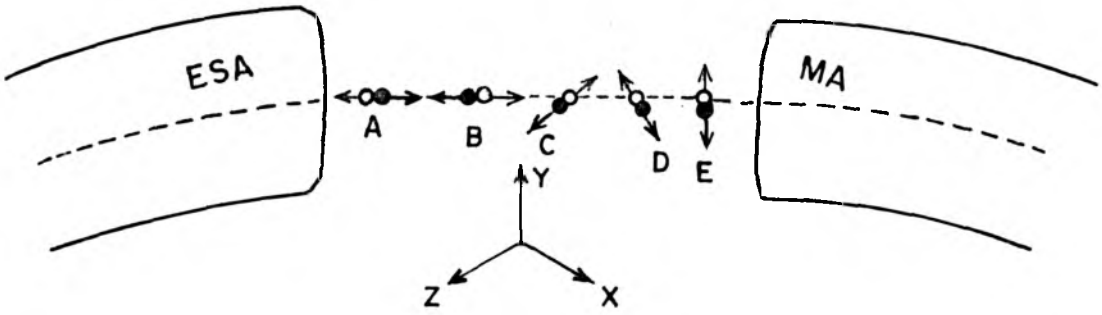


FIGURE 3.

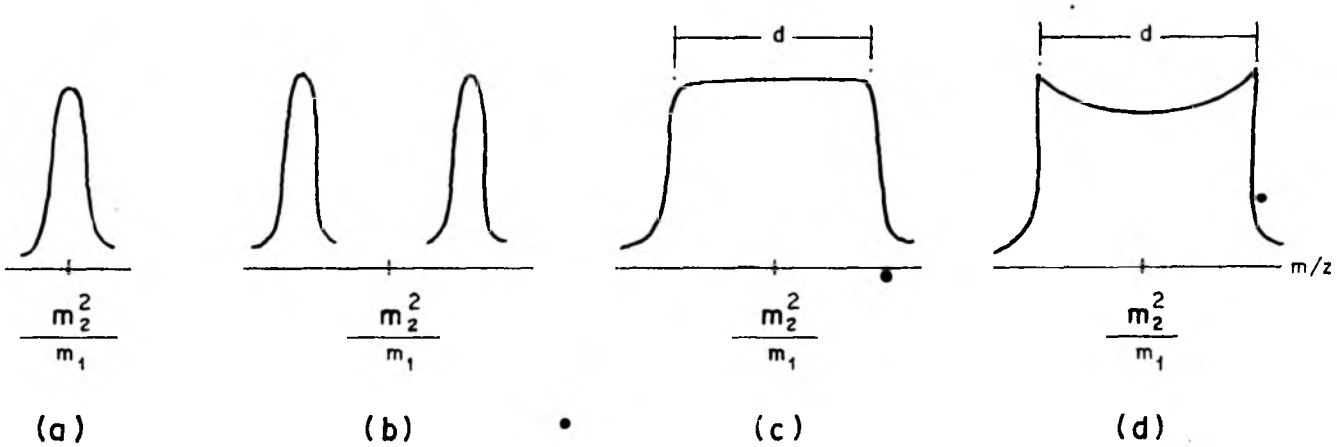


FIGURE 4.

and appear at a m/z value marginally lower than m^2_2 / m_1 (Figure 4B). Decompositions from the intermediate orientations (C,D,E etc., Figure 3) also contribute to give a flat-topped metastable peak (Figure 4C). A dish-topped metastable peak is due to the finite length of the slits[113] through which the ion passes (Figure 4D). The observation of flat-topped or dish-topped metastable peak indicates that large kinetic energy T is released upon decomposition. On the contrary, a gaussian peak reveals that decomposition occurs with little or no kinetic energy release T. Large kinetic energy release is generally associated with rearrangement/isomerization processes proceeding through tight transition states[114-118]. The excess internal energy in the transition state is due to the energy of reverse activation (E°_r) and non-fixed energy which is also called as kinetic shift ($E^{\ddagger}$). As the transition state collapses to products, part of this excess energy is released as translational energy of the product. The decompositions accompanied by low kinetic energy release are attributed to simple cleavage processes.

5. Collisional activation (CA) - MIKE spectroscopy

Collisionally activated decomposition may be defined as the conversion of kinetic energy into internal excitation energy of the reactant ion sufficient to lead to its fragmentation[7]. When non-decomposing ions with a high translational energy collide inelastically with neutral molecules in the collision chamber, part of their translational energy

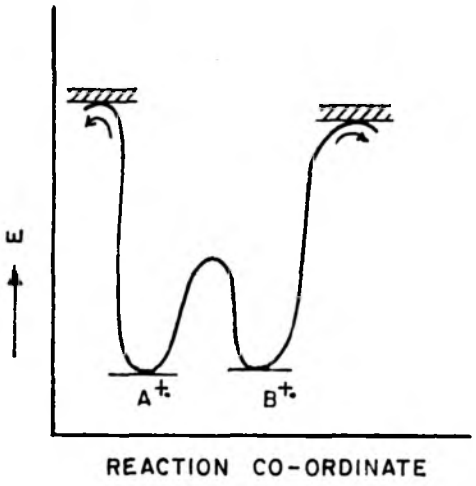
is converted into electronic excitation energy. It is rapidly converted into vibrational energy which in turn distributes itself over the entire ion and leads to fragmentation. This results in the CA spectrum of the compound[7].

Since the place where collissionally activated fragments are formed, is the same as that for metastable decompositions, they are detected by similar scanning methods. However, reverse geometry instruments are more suitable for their detection. MIKE scan can be employed wherein an ion of interest is preselected by the magnetic field. The collision gas helium or nitrogen is introduced at a controlled pressure through a high vacuum valve in the second field free region. A differential pumping system prevents all but small amounts of collision gas from entering the source or electric sector. The peaks due to collisional activation are broad as compared to those obtained by unimolecular metastable ion decompositions.

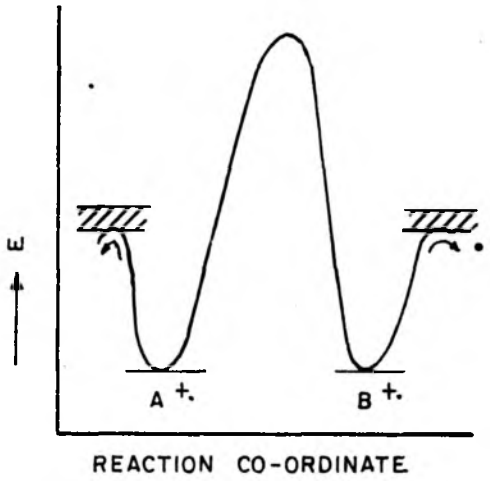
Collisional induced decomposition of organic ions is a new method for investigating structures of ions and mechanisms in organic mass spectrometry. Application of this technique has been discussed by McLafferty[119] in detail.

D. UNIMOLECULAR ISOMERIZATION OF ORGANIC IONS

The metastable ions which decompose in the field free regions of the mass spectrometer undergo 10^8 to 10^9 vibrations in the arrival time of about 10^{-5} to 10^{-6} s. During this time the ions may undergo extensive isomerizations prior to decomposition. The extent of rearrangement of an ion $A^{+\cdot}$ to an isomeric ion $B^{+\cdot}$ depends on the relative barriers viz., activation energy for isomerization (E_i) and the competing energy of activation for fragmentation (E_f). Extensive interconversion between ion structures $A^{+\cdot}$ and $B^{+\cdot}$ is possible when the activation energy barrier for isomerization is lower than the lowest threshold for decomposition process[120] ($E_i < E_f$, Figure 5A). On the other hand, when two isomeric ions are separated by a relatively high activation energy barrier for interconversion, as compared to the energy barrier for their decompositions, fragmentation from both the ions occurs independently[121] ($E_i > E_f$, Figure 5B). The energy required for isomerization from structure $B^{+\cdot}$ to $A^{+\cdot}$ may be more than the energy required for the decomposition of ion $B^{+\cdot}$. As a result, ion $B^{+\cdot}$ decomposes in preference to isomerizing to $A^{+\cdot}$. However, ion $A^{+\cdot}$ may isomerize to $B^{+\cdot}$ by a rate determining step when it reaches a highly excited vibrational level. The ion $B^{+\cdot}$ may rapidly decompose instead of isomerizing back to structure $A^{+\cdot}$. This is because, the energy required for the decomposition of ion $B^{+\cdot}$ is lower than the energy needed for isomerization to $A^{+\cdot}$. It is also due to the relatively large amount of internal energy present in ion $B^{+\cdot}$. There is a rate



(A)



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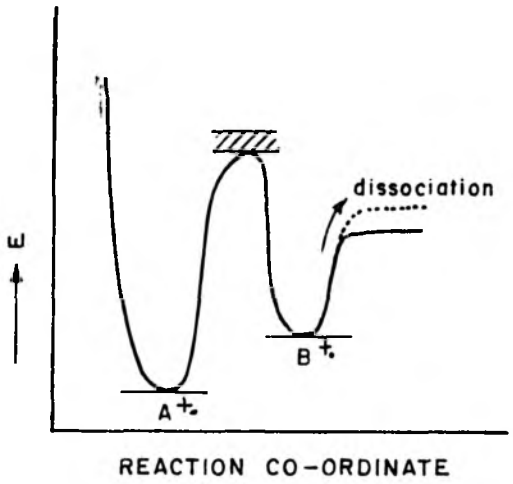

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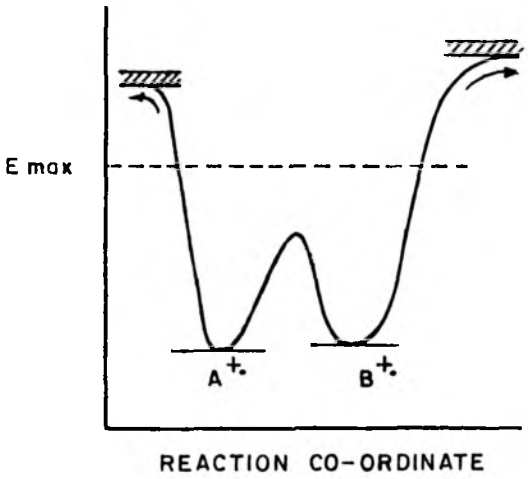

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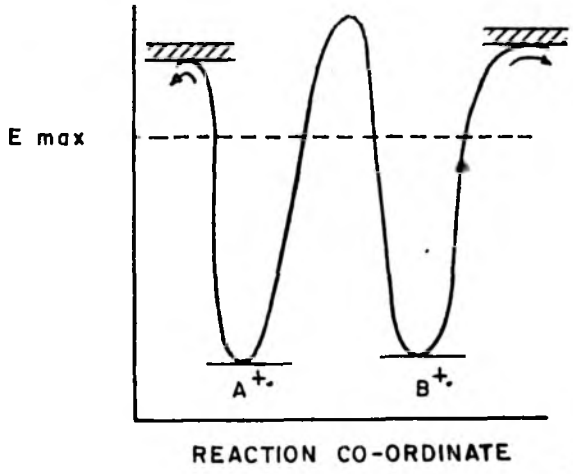


(E)

FIGURE 5.

determining isomerization step[122] and can be represented in a form of potential surface as shown in Figure 5C. Such rate determining steps are regarded as symmetry forbidden processes, though other mechanisms are possible.

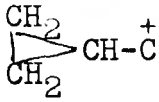
Metastable ion characteristics and kinetic energy release measurements provide information on structure and isomerization of decomposing ions. Mass analyzed ion kinetic energy (MIKE) technique has many advantages in the study of isomerization versus fragmentation behaviour of these low internal energy reactive ions.

As indicated earlier the non-decomposing ions have insufficient energy for decomposition before detection. They have an internal energy distribution and the maximum energy (E_{max}) available in these non-decomposing ions is well below the energy threshold for decomposition (Figures 5D and 5E). However, these ions may also undergo isomerization, if the barrier for isomerization is below the maximum energy (E_{max}) as shown in Figure 5D ($E_i < E_{max}$). When the isomerization barrier is more than the maximum energy (E_{max}) available in the non-decomposing ion, neither isomerization nor decomposition results. The potential surface for such ions is shown in Figure 5E.

Structural information regarding non-decomposing ions can be obtained by ion-molecule reactions, for e.g. by ICR and CA spectroscopy. In the latter technique, the energy is

supplied by collision process. It is believed that CA process corresponds to double excitation since these ions contain high internal energy and decompose spontaneously by simple cleavage processes.

There are a few systematic investigations on the isomerization of ions generated from different precursors. The results suggest that the ions of same molecular formula generated from different precursors may or may not isomerize to a common structure[123-128].

The gas phase isomerization of methoxy and carbomethoxy substituted cycloalkanes having three to seven membered rings[129] have been investigated by field ionization kinetics, metastable ion characteristics and collisional activation spectroscopy. The extent of isomerization to a common intermediate was shown to depend upon the ring size and substituent. Hommes and Terlouw[130] have demonstrated that a number of non-interconverting structures exist for $(C_4H_5O)^{+\cdot}$ ions in the gas phase. Of these four $C_3H_5\text{-}\overset{+}{C}{=}O$ isomeric ions viz., $H_2C{=}\overset{CH_3}{C}\text{-}\overset{+}{C}{=}O$, $H_2C{=}CH\text{-}CH_2\text{-}\overset{+}{C}{=}O$, $H_3C\text{-}CH{=}CH\text{-}\overset{+}{C}{=}O$ and  were shown from their characteristic CA spectra to be stable for $\geq 10^{-5}$ s. In a related study these workers have generated $(C_4H_5O)^{+\cdot}$ ions from a series of acetylenic, allylic and unsaturated cyclic ethers[131]. Based on the CA spectra and kinetic energy release measurements, the following four non-interconverting ionic structures have been assigned to the $(C_4H_5O)^{+\cdot}$ ions.

(i) $HC \equiv C-\overset{+}{C}H-OCH_3$ (ii) $H_2C = C = \overset{+}{C}-OCH_3$ (iii) $\overset{\longleftarrow}{O-CH-\overset{+}{C}H=CH-CH_2}$ and (iv) $HC \equiv C-CH_2-\overset{+}{O}CH_2$.

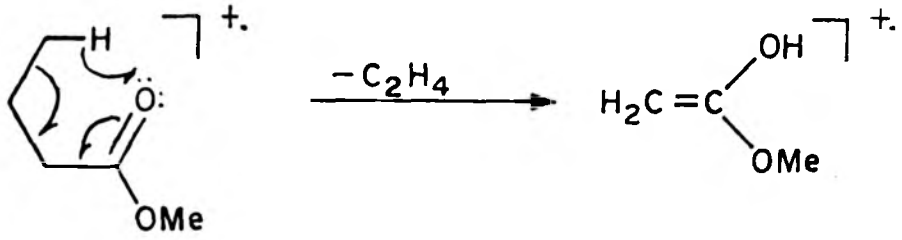
Maquestiau et al.[132], based on kinetic energy release measurements and labelling data have shown that the metastable $(C_6H_5N)^{+\cdot}$ radical cations generated from 26 different precursors isomerize to a common structure prior to fragmentation. The CA spectra of these ions however indicated the existence of several non-interconverting structures. Results obtained by Broer and Weringa[133] have indicated that reactive $(C_2H_5S)^{+\cdot}$ ions with different initial structures isomerize to a common intermediate or a mixture of intermediates before decomposition.

The structure of $(C_2H_3O)^{+\cdot}$ ions in the gas phase has been studied extensively. Based on the data obtained from heats of formation[134] and ion molecule reactions[135] four isomeric structures have been assigned to these ions. Weber and Levsen[136] have reinvestigated this problem by CA spectrometry. The $(C_2H_3O)^{+\cdot}$ ions generated from different precursors gave similar CA spectra indicating their free interconversion to a common structure on CA time scale ($\sim 10^{-5}$ s).

The technique of charge stripping[137] has been applied to the problem of gas phase isomerization of organic ions. It is a process by which singly charged ions having high translational energies are excited by collision to become doubly charged species. Holmes and co-workers[138] have

reported the charge stripping mass spectra for isomeric $(C_5H_8)^{+\cdot}$ and $(C_3H_6)^{+\cdot}$ ions. The loss of water from the molecular ions of cyclopentanol and n-pentanol has been shown to produce mixtures of ionized penta-1,3- and 1,4-dienes. The $(C_3H_6)^{+\cdot}$ ions produced from ionized butane, methyl propane and 2-methyl propan-1-ol were shown to isomerize to propene ion. The ionized tetrahydrofuran, penta-1,3-diene and pent-1-yne isomerize to cyclopropene ion. Similar results have been reported independently by Bowen and McLafferty[139].

Among the gas phase isomerization reactions keto-enol tautomerism is well documented in several isomeric ions. Schwarz and Wesdemiotis[140] have investigated this phenomenon in methyl acetate molecular ion and its enol form. The enol form was generated from methyl butanoate by a MacLafferty rearrangement (equation 31). Based on CA spectral data obtained for these two ions, it was shown the non-decomposing keto and enol forms exist as stable species and do not interconvert on CA time scale. But the kinetic energy release measurements obtained for these decomposing ions have suggested that the enol form isomerizes to keto form by a rate determining step prior to fragmentation. It is a symmetry forbidden process involving a 1,3-hydrogen shift. On the other hand results obtained by Holmes and Lossing[141] from the heats of formation of the methyl acetate and its enol form have shown that they interconvert freely at internal energies corresponding to the decomposition threshold.



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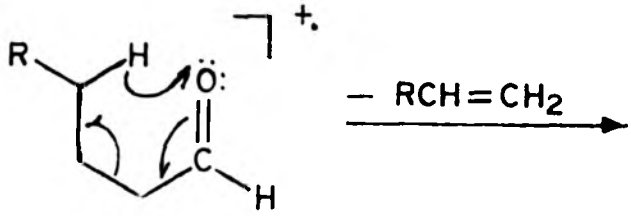

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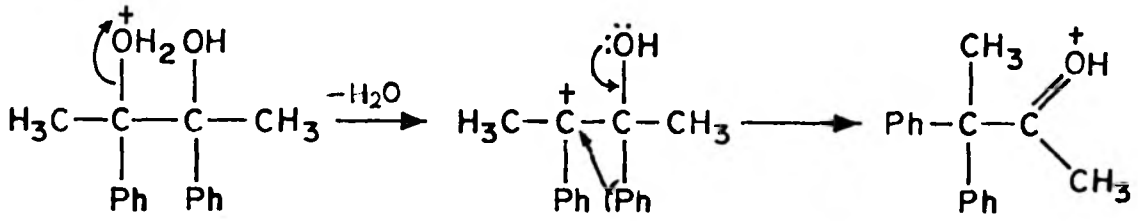

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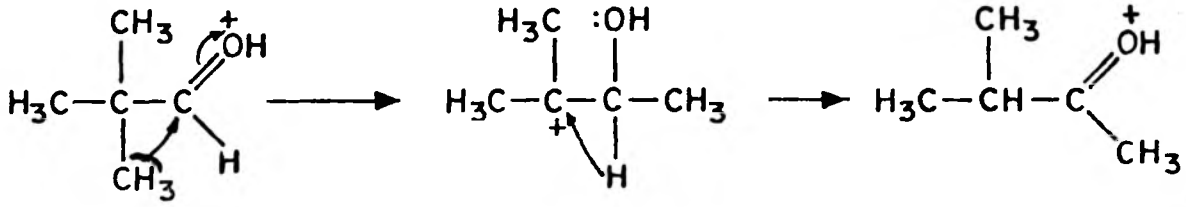
(a) (b) (c)



(34)

Protonated pivaldehyde

Protonated methyl isopropyl ketone

The heats of formation for ionized vinyl alcohol and its keto forms i.e. acetaldehyde have been measured[142]. The ionized vinyl alcohol was generated from the higher straight chain aldehydes by a McLafferty rearrangement (equation 32). The results have indicated that the enol ion is thermodynamically more stable than the corresponding keto form. For the corresponding neutral enol and keto compounds the stabilities are in the reverse order[143]. It was further shown that these two species are not interconvertable upto at least the energy corresponding to their fragmentation.

Holmes and Lossing[144] have obtained the data on heats of formation of thirteen enol ions of aliphatic aldehydes, ketones, acids and esters. The data calculated for enol ions were compared with the corresponding ionized keto forms. The results clearly showed that the enol ions are more stable than keto form by 14 to 31 K cal. mol^{-1}. These data deal only with threshold energetics and give no information on the ratio of the two forms generated at energies above the threshold for keto ion formation. However, from the earlier work[140,141,145] on this phenomenon it appears that the two tautomers may isomerize freely at internal energies below the dissociation threshold.

Gross and co-workers[146] have investigated keto-enol tautomerism in $C_6H_6O^{+\cdot}$ radical cations generated from phenol and bicyclo(2,2,2)oct-2-ene-5,7-dione. They have reported a

maximum energy barrier of 55.2 K.cal mol^{-1} for enol to keto tautomerism of metastable phenol to cyclohexadienone ions. This isomerization was shown to take place by a sigmatropic 1,3-hydrogen migration, a symmetry forbidden process. Splitter and Calvin[147] have proposed the energetics of this reaction which may be accounted for by two consecutive 1,2-hydrogen shifts[148]. The ΔH_f's of the intermediate ions formed by 1,2-hydrogen migration in the phenol ion and enol ion of acetic acid have been calculated to be 220 and 191 K.cal mol^{-1} respectively. These data indicate barriers to the keto-enol tautomerism *via* two stepwise 1,2-hydrogen shifts of 50 and 47 K.cal mol^{-1} respectively. These values are in agreement with the previously reported data[146,149]. Similarly, the tautomerism in the closed-shell systems (i) vinyl alcohol⇄acetaldehyde and $H_3C\text{-}CH=\overset{+}{O}\text{-}CH_3 \rightleftarrows H_3C\text{-}CH_2\text{-}\overset{+}{O}=CH_2$ has been discussed in terms of two consecutive 1,2-hydrogen shifts.

E. ANALOGY BETWEEN MASS SPECTRAL AND CHEMICAL REACTIONS

Information on the structure of some carbonium ions in the gaseous state is now available. If the information is precise and accurate it is possible to suggest a reaction profile as reactant ions pass to product ions through elusive transition states or short lived intermediates. Carbonium ions formed in solution are investigated by the identification of the reaction products and from the low temperature nuclear magnetic resonance (NMR) technique. On the other hand, in the

gas phase, product analysis has been limited to mass measurement. Chemical ionization, ion cyclotron resonance and flowing afterglow techniques have widened the scope of the studies on gaseous ion structures and the mechanisms involved in their rearrangements.

One of the advantages in the gas phase is that there are no solvent effects. Moreover the reactions are intramolecular in nature. In solution, solvent effects are important. Many reactions are intermolecular. There are several instances in literature, where similarities between mass spectral reactions and reactions which occur under pyrolytic, photolytic and solution conditions have been reported. Such similarities must be accepted with care, since the reactions under different conditions are governed by various factors, such as kinetics, energetics and the stabilities of the product ions.

The energetics of isomerisation or other rearrangement reactions of ions in the isolated and condensed phases have been studied. Low temperature NMR studies in super acid media have shown that several rearrangements involving hydride and alkyl shifts and isomerization processes in cyclic and acyclic ions occur with activation energies close to the enthalpy differences involved[150,151]. Based on the quantum mechanical calculations it has been suggested that similar rearrangements may take place in the gas phase[152]. Hence, it is assumed that the symmetry allowed[45] rearrangements

may proceed without significant energy barriers other than those associated with the inherent differences in stability of the ions concerned. On the contrary, 1,3-hydrogen migrations are symmetry forbidden processes and require high activation energies[153]. As stated earlier, the metastable peak shapes give more valuable information on the nature of ionic decompositions in the gas phase. Like solution chemistry, the rate-determining step need not always be the final step but may be a slow prior isomerization. It is then followed by a rapid dissociation. A broadening of the metastable peak would result in such cases. Many examples of this behaviour have been reported in the literature[154-157].

De Jongh and Shrader[158] have reported that the ratio of $(M-Br)^+$ ion to the molecular ion intensity for exo-2-norbornyl bromide is ten times greater than the corresponding ratio of intensities for the endo compound. Since the rate-determining step in the solvolysis of 2-norbornyl derivatives is heterolytic cleavage, these workers have compared the solvolytic and electron impact behaviour of these compounds. The ratios observed in solvolysis of the exo- and endo-2-norbornyl bromides in 80% aqueous ethanol were found to be similar with those obtained in the gas phase. A qualitative similarity in the behaviour of these compounds in both phases was indicated.

The gas-phase pinacol-pinacolone rearrangement has been well studied under electron ionization[91] and chemical ionization conditions[159,160]. It is a well known acid-catalyzed reaction which occurs in solution. High resolution data and labelling experiments have been used to establish the mechanism of this rearrangement under electron ionization[91]. The MIKE/CA techniques have been employed in CI mode. Thus, the CI/CA/MIKE spectra from precursors (a) and (c) (equation 33) have been shown to be similar. It confirms that the reaction sequence (a) → (c) has occurred (equation 33). Similarly, the rearrangement of some protonated aldehydes to isomeric protonated ketones via 1,2-alkyl or aryl migrations is reported[160]. Protonated pivaldehyde is known to undergo skeletal rearrangement in acid solution to give a protonated methyl isopropyl ketone, probably via a tertiary carbonium ion intermediate (equation 34). Such rearrangement has also been shown to take place under CI conditions. The similar CI/CA/MIKE spectra obtained for protonated pivaldehyde and methyl isopropyl ketone ions have confirmed this rearrangement in the mass spectrometer. Glish and Cooks[159], on the basis of MIKE technique in conjunction with labelling data, have demonstrated the Fischer Indole synthesis in the gas phase. It is well documented acid-catalyzed reaction in solution. The protonated molecular ions from phenylhydrazone expel ammonia to form protonated indole ion. The CI/MIKE spectra of $(MH-NH_3)^+$ ions generated

from protonated molecular ions of phenylhydrazone and the $(MH)^+$ ions of indole were shown to be identical. This gave a direct evidence for this rearrangement process in gas phase.

Beynon et al.[161] drew analogy between condensed and gas phases in (i) the cyclization of citronellol to isopulegol and (ii) the formation of dihydropyran by ring expansion of tetrahydrofurfuryl alcohol. These workers have used the CI/MIKE technique. The work of Schwarz et al.[162] on N-benzoyl-α-amino acid methyl esters under CI conditions has provided another example of similarity between the solution and gas phase reactions. The elimination of methanol from $(MH)^+$ ions of esters which lead to a cyclization reaction was compared with similar reaction in solution. The extent of cyclization was shown to be similar to that in the condensed phase. Similar correlation has been observed by Maquestiau and his co-workers[163] for the ring opening of cyclopropane derivatives and for the stereospecific trans position of aromatic oximes. Recently Schwarz and his associates[164] have shown that the gas phase proton catalyzed dehydration of both 2,5-hexanedione and 1,4-diphenyl-1,4-butadienone yields protonated 2,5-disubstituted furans. A similar reaction is known in solution. Many alkyl and aryl migrations in the gas phase parallel known rearrangements in solution.

The analogy between condensed and isolated phases can be established unambiguously provided precise information is available on the structure of the product ions and the mechanism of reactions.

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CHAPTER II : CHEMISTRY OF SOME RADICAL CATIONS AND CARBONIUM IONS IN THE GASEOUS STATE

A. INTRODUCTION

Chemical ionization (CI) has recently assumed a new role in Organic Mass Spectrometry. Unlike electron ionization (EI) the spectra are relatively simple and the protonated molecular ions $(MH)^+$ are significant. This technique has been shown to be useful to study the rearrangements of many gaseous carbocations which are similar to acid catalyzed rearrangements known in solution. Instrumental developments have enabled the choice and application of appropriate newer techniques to gain deeper insight into structure of gaseous organic ions and the mechanism of their reactions. Some of the methods currently used in ion structure determinations, include metastable ion characteristics, thermochemical measurements, isotopic labelling, substituent effects, field ionization kinetics, ion cyclotron resonance (ICR), collisional activation (CA) and mass analyzed ion kinetic energy (MIKE) spectroscopy. This Chapter deals with the chemistry of some gaseous carbonium ions.

B. PRESENT STUDY

The present investigation is a study on chemical ionization (CI) behaviour of a series of di- and tri-aryl

substituted nitrocyclohexenes. An attempt has been made to understand the effect of different functional groups on C-4 of the cyclohexenyl ring, on the fragmentation processes operating in these molecules under CI and electron impact (EI) ionizing conditions. The mass analyzed ion kinetic energy (MIKE) and collisional activation (CA) spectra of some ions generated from 3,5,6-triphenyl-4-nitro-Δ^1-cyclohexene were examined and discussed in the light of previously reported results. The compounds examined are shown in Scheme 1.

C. DISCUSSION

1. Unimolecular Ion Decompositions of some di- and tri-aryl substituted Nitro Cyclohexenes Induced by Chemical Ionization (CI).

CI mass spectra can be interpreted by assuming that the reagent ions protonate specific sites in a molecule and decompose to give specific product ions[1-8]. In general only exothermic ion-molecule reactions proceed at high rates[9,10]. This condition is fulfilled for proton transfer if the proton affinity[11-15] (PA) of the sample under study (M) exceeds that of the conjugate base (e.g. CH_4 or C_2H_4) of the appropriate reagent ion (e.g. CH_5^+ or $C_2H_5^+$). Proton affinity can be defined as the standard enthalpy ΔH° of the reaction:

$$[MH]^+ \longrightarrow M + [H]^+ \qquad (1).$$

The CI mass spectra are characterized by the formation of highly stable protonated molecular ions $(MH)^+$ with very few fragment ions[2-6,16,17]. The molecular weights are determined by the technique of chemical ionization [18-20].

The chemical ionization behaviour of compounds 1-20 (Scheme 1) is discussed in this Chapter. The CI spectra of all the nitro compounds were obtained, using either methane or isobutane as the reagent gas. The general fragmentation modes are presented in the light of their structural and stereochemical features. A comparison is also made with the behaviour of these compounds under electron impact (EI) conditions.

(a) Fragmentation modes under electron ionization

The electron impact (EI) induced decomposition of these compounds 1-16 are reported[21,22]. The major fragmentation modes operating in these molecules under EI conditions are exemplified by compound 3 and are given below. They are summarised in scheme 2.

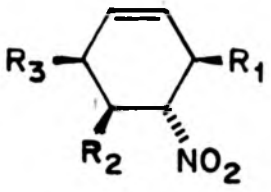
(i) A rearrangement process resulting in the elimination of nitric oxide (NO) from the molecular ion.

(ii) Hydrogen transfer rearrangements leading to the expulsion of HNO_2 and H_2NO_2 from the molecular ion.

(iii) Retro Diels-Alder (RDA) fragmentation. The charge is mostly carried by the diene fragment probably due to its lower ionization potential (IP).

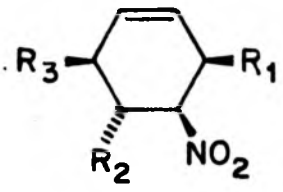
(iv) Formation of ions at m/z 91, 115, 128, 167 and 193 by rearrangements.

The seven isomeric pairs of compounds 1-14 exhibit



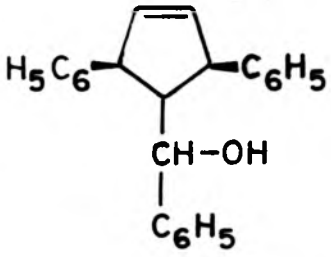
Endo phenyl

(Isomer A)



Endo nitro

(Isomer B)



(21)

1.	$R_1 = R_3$ = Phenyl; R_2 = H	Isomer A
2.	$R_1 = R_3$ = Phenyl; R_2 = H	Isomer B
3.	$R_1 = R_2 = R_3$ = Phenyl	Isomer A
4.	$R_1 = R_2 = R_3$ = Phenyl	Isomer B
5.	$R_1 = R_3$ = Phenyl; $R_2 = -C_6H_4-CH_3(p)$	Isomer A
6.	$R_1 = R_3$ = Phenyl; $R_2 = -C_6H_4-CH_3(p)$	Isomer B
7.	$R_1 = R_3$ = Phenyl; $R_2 = -C_6H_4-Cl(p)$	Isomer A
8.	$R_1 = R_3$ = Phenyl; $R_2 = -C_6H_4-Cl(p)$	Isomer B
9.	$R_1 = R_3$ = Phenyl; $R_2 = -C_6H_4-F(p)$	Isomer A
10.	$R_1 = R_3$ = Phenyl; $R_2 = -C_6H_4-F(p)$	Isomer B
11.	$R_1 = R_3$ = Phenyl; $R_2 = -C_6H_4-Br(p)$	Isomer A
12.	$R_1 = R_3$ = Phenyl; $R_2 = -C_6H_4-Br(p)$	Isomer B
13.	$R_1 = R_3$ = Phenyl; R_2 = 2-Furyl	Isomer A
14.	$R_1 = R_3$ = Phenyl; R_2 = 2-Furyl	Isomer B
15.	$R_1 = R_3$ = Phenyl; R_2 = 2-Thienyl	Isomer A
16.	$R_1 = R_3$ = Phenyl; $R_2 = -C_6H_4$ CN(p)	Isomer A
17.	$R_1 = -C_6H_4-Cl(p)$; R_2 = -phenyl	Isomer A
18.	$R_1 = -C_6H_4-Cl(p)$; $R_2 = -C_6H_4-CN(p)$; R_3=Phenyl	Isomer A
19.	$R_1 = -C_6H_4-Cl(p)$; $R_2 = -C_6H_4-F(p)$; R_3 = Phenyl	Isomer A
20.	$R_1 = -C_6H_4-Cl(p)$; R_2 = 2-Thienyl; R_3 = Phenyl	Isomer A

Scheme 1

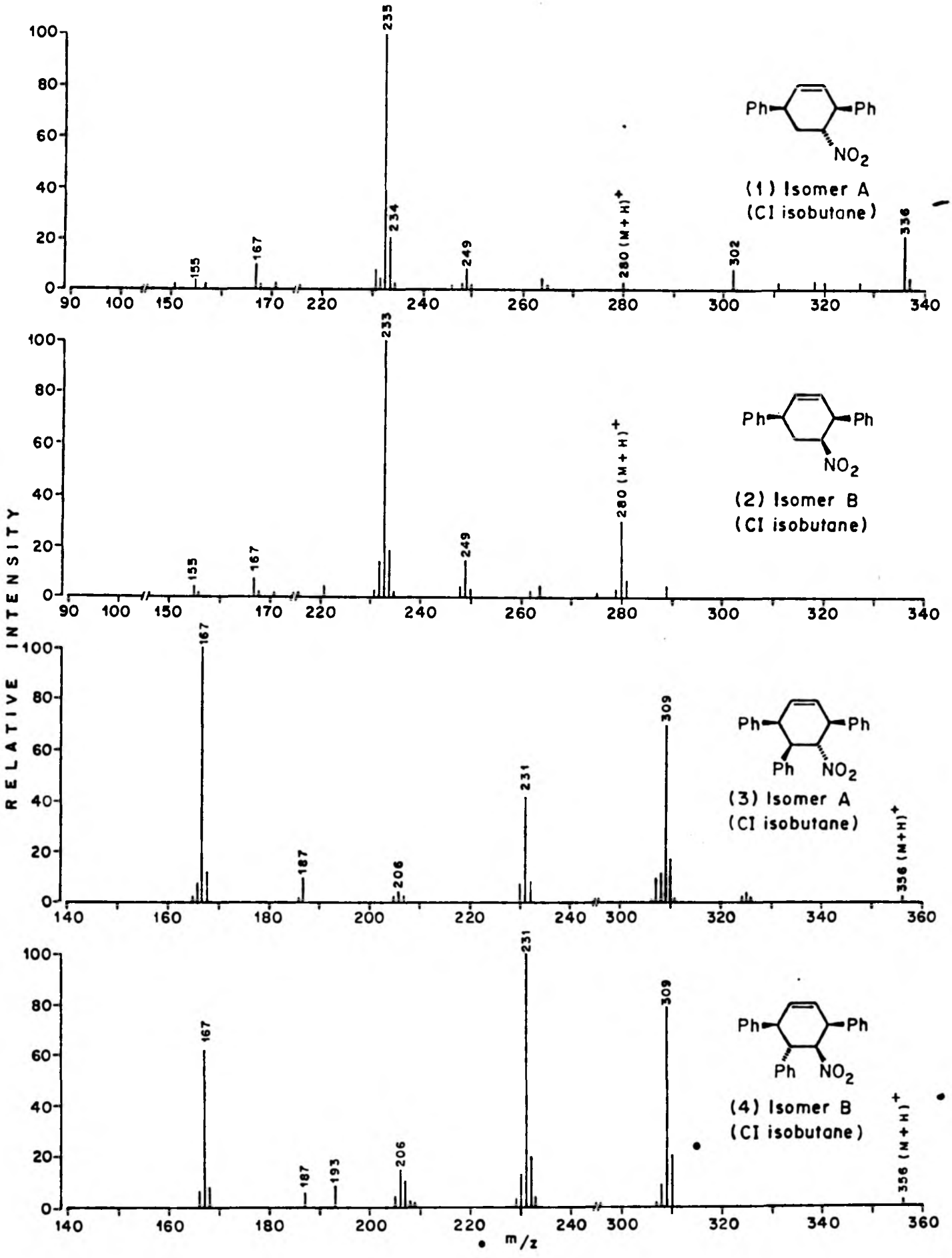

RELATIVE INTENSITY
m/z
(1) Isomer A
(CI isobutane)
(2) Isomer B
(CI isobutane)
(3) Isomer A
(CI isobutane)
(4) Isomer B
(CI isobutane)
Ph
NO2
235
234
233
231
309
167
155
249
280 (M+H)+
302
336
356 (M+H)+
187
206
193

FIGURE 1.

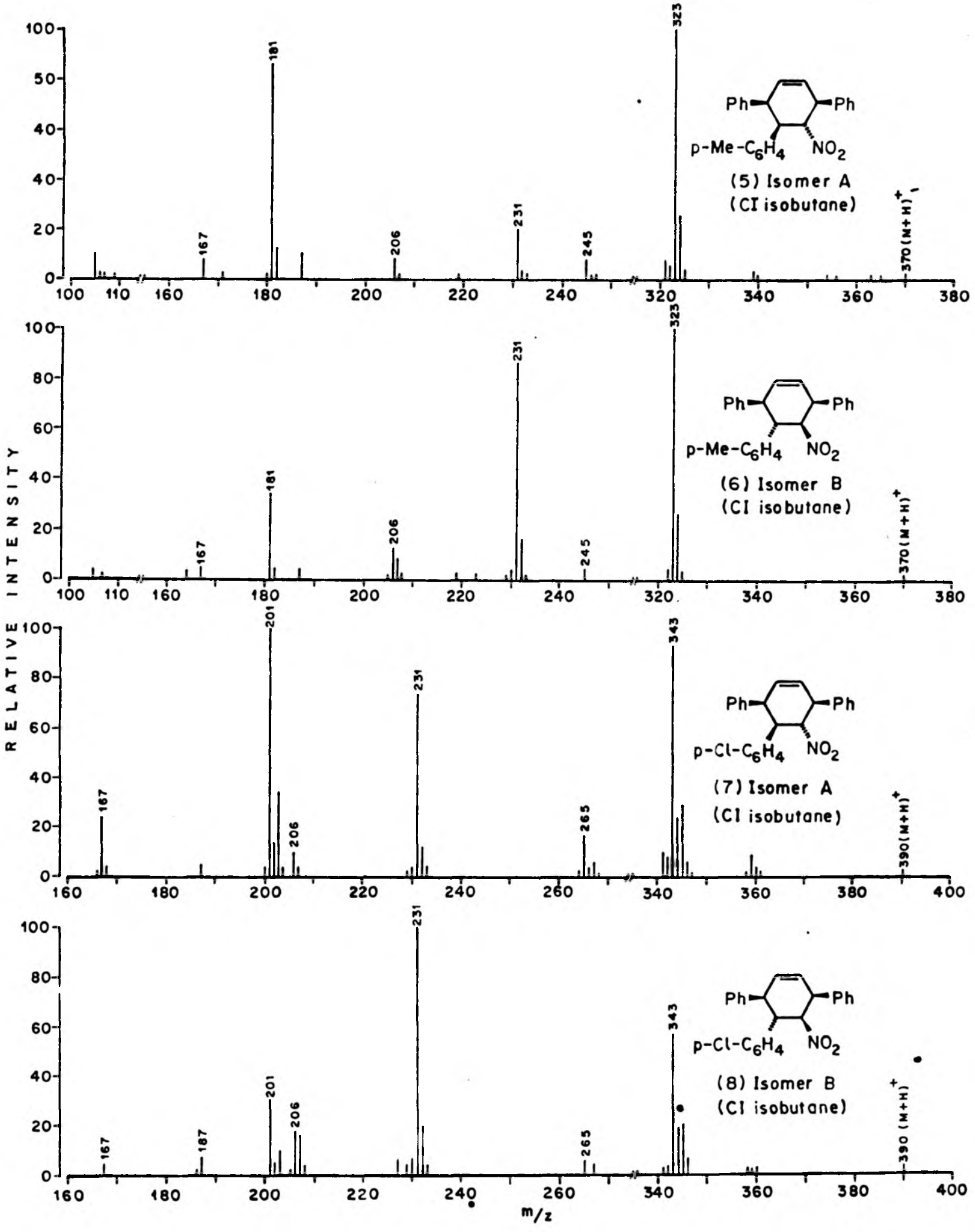

RELATIVE INTENSITY
m/z
Ph
Ph
p-Me-C6H4
NO2
(5) Isomer A
(CI isobutane)
(6) Isomer B
(CI isobutane)
p-Cl-C6H4
(7) Isomer A
(CI isobutane)
(8) Isomer B
(CI isobutane)
370(M+H)+
390(M+H)+
323
231
181
167
206
245
343
265
201
187

FIGURE 2.

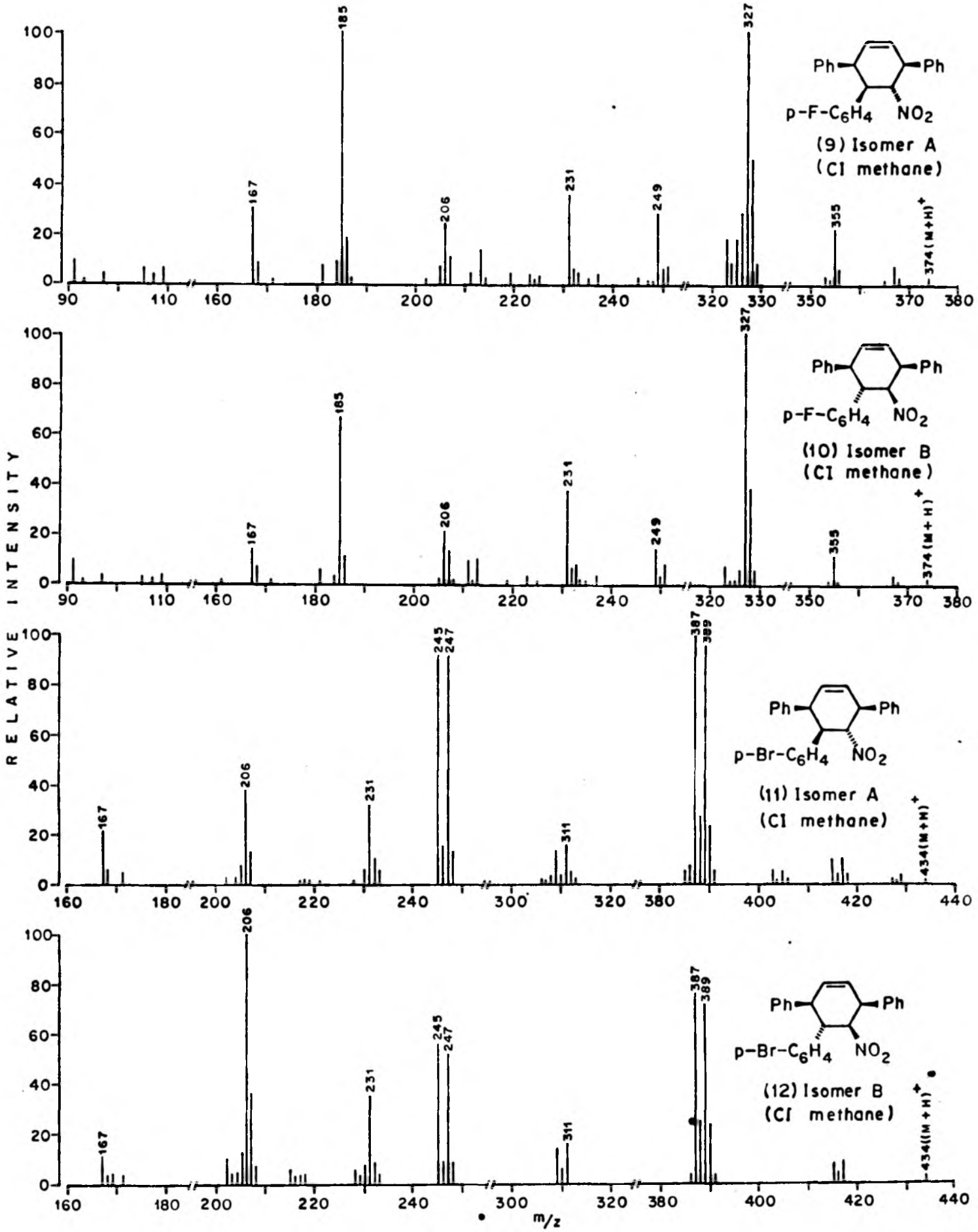

RELATIVE INTENSITY
m/z
(9) Isomer A
(CI methane)
(10) Isomer B
(CI methane)
(11) Isomer A
(CI methane)
(12) Isomer B
(CI methane)
p-F-C6H4
p-Br-C6H4
NO2
Ph
374(M+H)+
434(M+H)+

FIGURE 3.

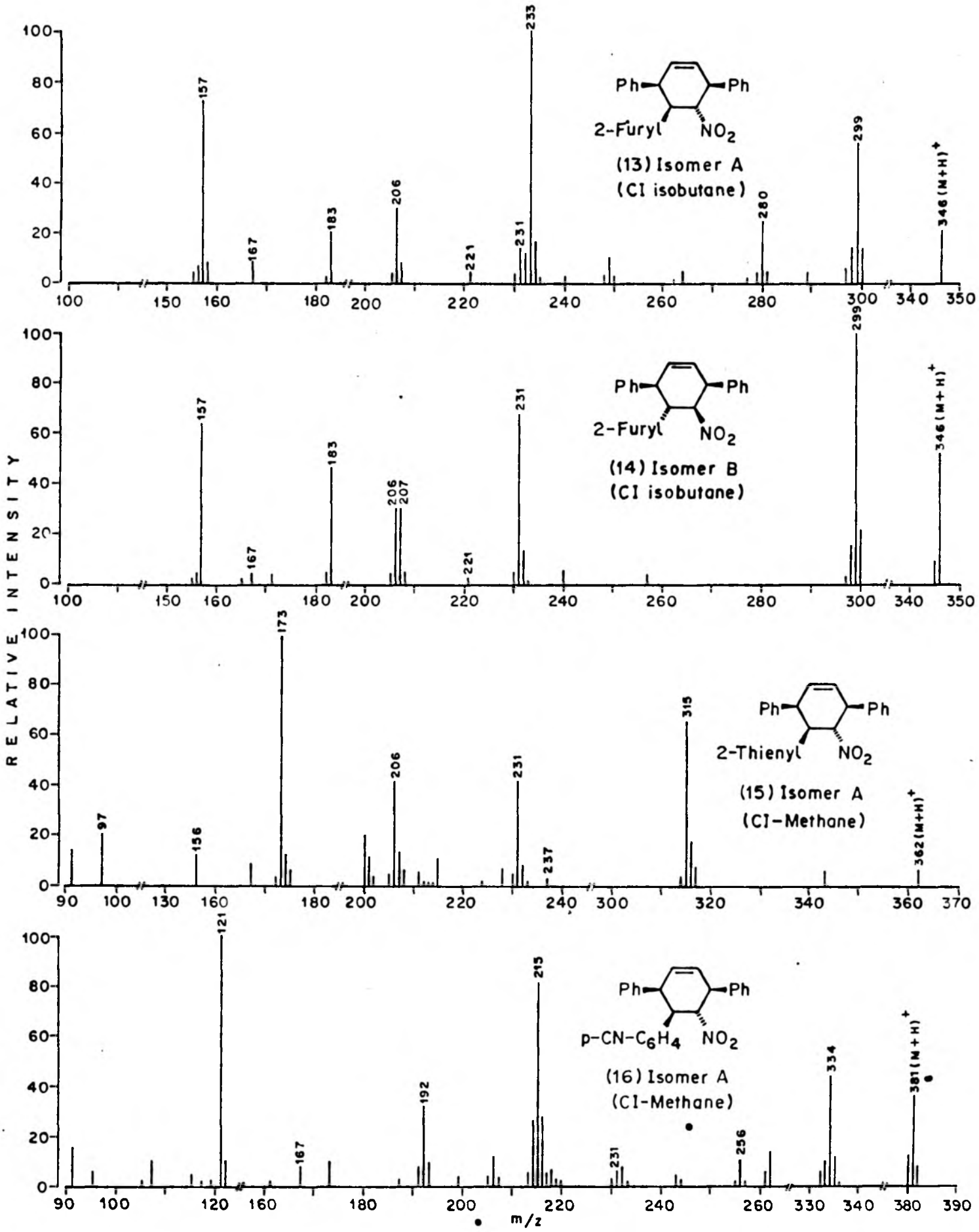

RELATIVE INTENSITY
m/z
Ph
Ph
2-Furyl
NO2
(13) Isomer A
(CI isobutane)
(14) Isomer B
(CI isobutane)
2-Thienyl
(15) Isomer A
(CI-Methane)
p-CN-C6H4
(16) Isomer A
(CI-Methane)

FIGURE 4.

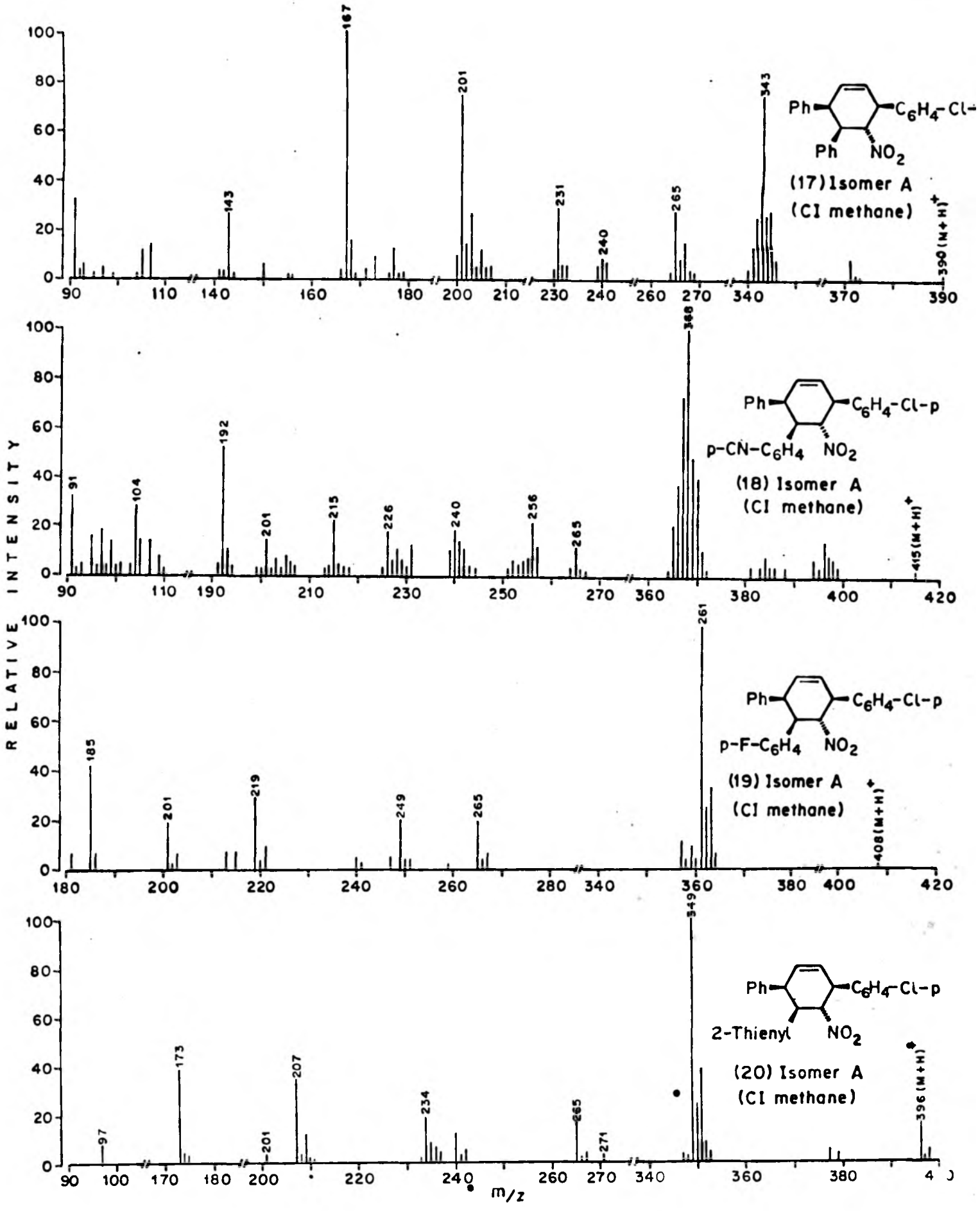
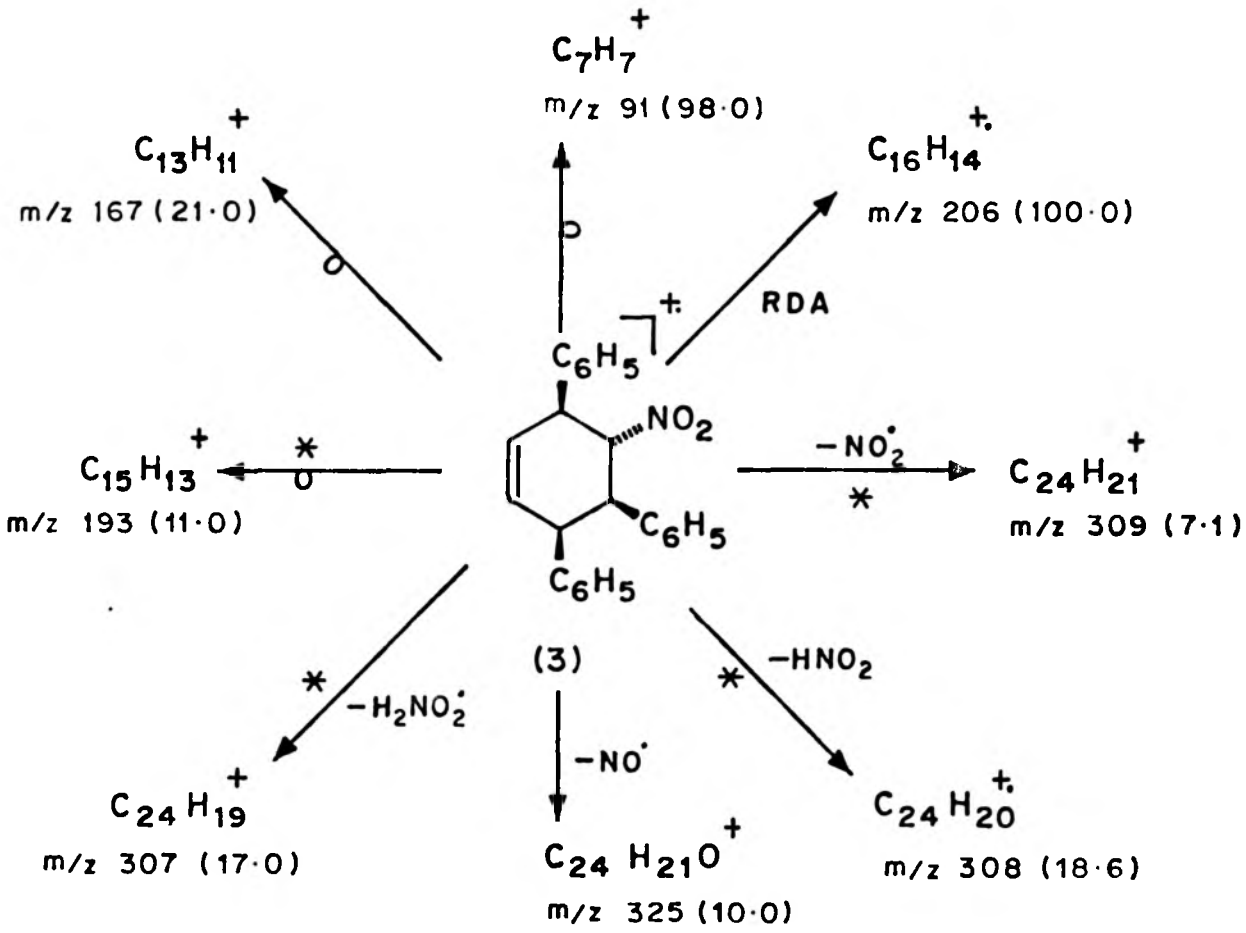
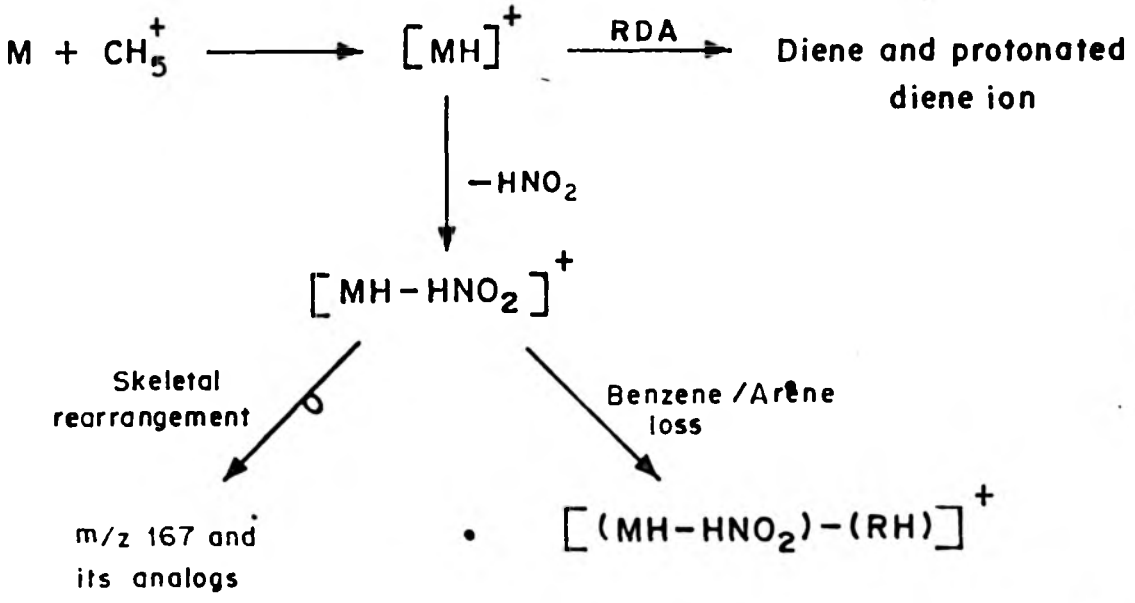

RELATIVE INTENSITY
m/z
Ph
C6H4-Cl-
Ph
NO2
(17) Isomer A
(CI methane)
167
201
343
143
231
240
265
390 (M+H)+
C6H4-Cl-p
p-CN-C6H4
(18) Isomer A
(CI methane)
192
91
104
201
215
226
240
256
265
415 (M+H)+
p-F-C6H4
(19) Isomer A
(CI methane)
261
185
201
219
249
265
408 (M+H)+
2-Thienyl
(20) Isomer A
(CI methane)
349
173
207
97
201
234
265
271
396 (M+H)+

FIGURE 5.



SCHEME 2

* Metastable peaks found in normal 70 eV spectrum. Figures in parentheses refer to the relative intensities of the ions (% to the base peak) in the spectrum.



SCHEME 3

minor stereochemical differences in their fragmentation behaviour under electron impact conditions[21]. The loss of nitric oxide, nitrous acid and H_2NO_2 from $M^{+\cdot}$ ions are more in the endo-phenyl isomers (isomer A). On the other hand the RDA process and the formation of m/z 193 ion are preferred fragmentation modes in the endo-nitro isomers (isomer B). A 1,3-diphenyl-propenyl cationic structure was assigned to the latter ion.

The direct loss of nitro group from the molecular ion is a minor process, which would have resulted in the formation of a substituted cyclohexenyl carbonium ion. Evidences to support the above mentioned fragmentation processes were obtained by metastable ion defocusing and ion kinetic energy (IKE) spectral data[22,23].

(b) Chemical ionization induced fragmentation reactions

The chemical ionization mass spectra of compounds 1-20 (scheme 1) show insignificant protonated molecular ions $(MH)^+$ (% $\leq$ 90 1 to 3.0). This observation is very interesting since the $(MH)^+$ ions are expected to be stable under CI conditions. These ions appear to be unstable and undergo a facile loss of nitrous acid. Some of the major ions observed in the spectra appear to be formed by the following decomposition processes (scheme 3).

(i) The loss of nitrous acid (HNO_2) from the $(MH)^+$ ions.

(ii) A minor retro Diels-Alder (RDA) process to give the diene and protonated diene ions.

(iii) Elimination of neutral benzene/arene from the $(MH-HNO_2)^+$ ions and

(iv) The formation of diphenyl methyl carbonium ion and its analogs by skeletal rearrangement processes.

A comparison of EI and CI behaviour of these compounds showed some salient differences. It is interesting to note that the RDA process is a preferred fragmentation mode under EI conditions, while it is a minor process under CI conditions. The loss of NO, H_2NO_2 from $M^{+\cdot}$ ions, the formation of ions at m/z 193 and 91 (and analogs) are significant processes only under EI conditions. The expulsion of HNO_2 appears to take place by different mechanisms under EI and CI conditions. In the former case a hydrogen transfer rearrangement operates to give a substituted cyclohexadiene ion; while a direct loss of the protonated nitro group by a simple cleavage process, to generate a substituted cyclohexenyl ion is taking place under CI conditions. Similarly, the formation of diphenyl methyl cation (m/z 167) also appears to arise by different routes under the two different ionizing conditions. It is a preferred process under the CI conditions and the precursor is the $(MH-HNO_2)^+$ ion. On the other hand, this rearrangement ion is formed by a different mechanism from $(M-NO)^+$ and $(M-HNO_2)^{+\cdot}$ ions under EI conditions as is evident from

metastable ion defocusing and mass analyzed ion kinetic energy (MIKE) spectroscopic data.

The CI mass spectra of some aliphatic[24] and aromatic[25-29] nitro compounds have been reported in literature. The loss of 30 mass units from $(MH)^+$ ions in the CI spectra of many aromatic nitro compounds[25-27] was believed to be due to the expulsion of nitric oxide (NO), similar to the behaviour under EI conditions[30-32]. Goldsack et al.,[29] have shown that the $(MH-30)^+$ ions are formed by the reduction of the nitro group to the corresponding amino group within the CI source (equation 2). Evidence for this

$$R\text{-}NO_2 \xrightarrow[CIMS]{H_2/(H_3)^+} \underset{(MH-30)^+ \text{ ion}}{RNH_3^+} \qquad (2)$$

chemical reduction within the mass spectrometer was obtained from accurate mass measurements on $(RNH_3)^+$ ions and by using deuterated reagent gas[29]. This may be due to the high pressure conditions existing in the ion source. Beynon and co-workers[33] have observed similar reduction but to a very small extent in the EI mass spectra of some aromatic compounds. They have suggested that this reaction is a catalytic reduction by hydrogen present in the source as adsorbed water. Recently

Maquestiau et al.,[28] have claimed a similar reduction in the case of 6-nitroindazole, which was proved by collision induced dissociation (CID) technique[34]. On the other hand, Thuijl and his associates[35] have observed electrophilic substitution of some substituted aromatic compounds using ammonia as reagent gas. When -CN or $-NH_2$ group is present in the aromatic compound, both methane and ammonia spectra gave $(MH)^+$ ions. But when the aromatic ring has $-NO_2$, halogens or CHO as substituted group stable $(MH)^+$ ions are observed only with methane as the reagent gas. When ammonia $(NH_4)^+$ is used as the reagent gas, these compounds exhibited no $(MH)^+$ ions, but showed anilinium ($PhNH_3^+$) ions.

Aliphatic nitro compounds[24] on the other hand do not show the chemical reduction within the CI source. The di- and tri-aryl nitrocyclohexenes (1-20), examined in the present study also do not exhibit the $(MH-30)^+$ ions in their CI spectra to any extent, indicating the absence of reduction process, which is very significant in aromatic nitro compounds[27-29]. It is interesting to note that many aliphatic nitro compounds exhibit abundant $(MH)^+$ ions, but in the case of aryl substituted alkanes they are less abundant or absent and mostly replaced by $(MH-HNO_2)^+$ ions[24], a situation similar to that observed in the compounds under study. This characteristic feature of the CI spectra of these compounds can be explained by the

very high stability of the resulting benzylic cations (which in turn rearrange to tropylium cations, eqn.3) formed by the expulsion of HNO_2 from $(MH)^+$ ions. This is the basis for the identification of aryl nitro alkanes by

$$C_6H_5\text{-}CH_2\text{-}NO_2 \xrightarrow[(ii)\ -HNO_2]{(i)\ CH_5^+} C_6H_5\text{-}\overset{+}{C}H_2 + HNO_2 \qquad (3)$$

Tropylium cation

CI mass spectrometry. Loss of HNO_2, HNO, NO_2, HNO_3 and H_2O are some of the fragmentation modes of $(MH)^+$ ions reported for some mono-, di- and tri-nitro alkanes[24]. These fragmentation modes and mechanistic aspects proposed are supported by MINDO/3 calculations[36].

(i) Stability of protonated molecular $(MH)^+$ ions

The stability of $(MH)^+$ ions of many organic molecules appear to be governed by various factors. It is known that the product ion stability is one of the driving forces and promotes fragmentation processes[37]. Field and Munson[38] have offered an explanation for the lack of stability of the $(MH)^+$ ions. They have indicated that the protonation of several organic molecules (e.g. esters, cycloalkanes, etc.) results in the rupture of either a C-C or C-X (where X is a heteroatom) bond. The stability of $(MH)^+$ ion is also governed by the ease with which the protonated group 'X' is lost as a stable neutral molecule HX. The rate of this reaction

is inversely proportional to the proton affinity of HX. However, it has been shown by several workers that the stability of $(MH)^+$ ions in disubstituted alkanes and cycloalkanes can be due to the formation of a proton bridge between two functional groups of the molecule[39-44].

Table I shows the relative intensities of protonated molecular ions for compounds 1-20. These ions in compounds 1, 3-12, 15, 17-19 appear to be very unstable. Compounds 2, 13, 14, 16 and 20 exhibit relatively more abundant $(MH)^+$ ions in their spectra. Significant and consistent stereochemical effects are not observed on the stability of $(MH)^+$ ions of many isomeric pairs examined in the present study. Isomers 1,2 and 13,14 show some differences on the stability of their $(MH)^+$ ions which may be due to stereochemical features of the molecules.

The initial protonation of these molecules may be expected to take place either on the C_4-nitro group[24,45], the double bond[46], or on any of the aryl groups[47,48] present on 3,5 and 6 carbon atoms. It is well known that proton affinities (PA) are different for different sites in a multifunctional molecule[49-51]. It is reasonable to assume that in these molecules the preferred site of protonation would be the nitro group[24]. It has a favourable site for attack by Bronsted acids such as CH_5^+ or $C_4H_9^+$ ions present in the plasma of the reagent gas used. The two electronegative oxygen atoms

Table I

Relative intensities of $(MH)^+$ and $(MH-HNO_2)^+$ ions in the Cl spectra of nitrocyclohexenes[a] 1-20. (as % base peak and % of total ionization above m/z 90).

Compd. No.	Reagent gas[b]	$(M + H)^+$ ions		$[(MH)-(HNO_2)]^+$ ions	
		% base peak	% Σ_{90}	% base peak	% Σ_{90}
1	I	3.0	1.3	100	52
2	I	31.2	12.0	100	37
3	I	< 2.0	< 0.5	69	21
4	I	< 2.0	< 0.5	78	21
5	I	< 2.0	< 0.5	100	29
6	I	< 2.0	< 0.5	100	30
7	I	< 2.0	< 0.5	95	18
8	I	< 2.0	< 0.5	56	15
9	M	< 0.5	< 0.1	100	15
10	M	< 0.5	< 0.1	100	21
11	M	< 0.5	< 0.1	100	14
12	M	< 0.5	< 0.1	76	10
13	I	19.5	3.0	57	9
14	I	53.3	7.5	100	15
15	M	6.6	1.3	66	13
16	M	32.0	5.3	44	7
17	M	< 0.5	< 0.1	74	10
18	M	< 0.5	< 0.1	100	12
19	M	< 0.5	< 0.1	100	23
20	M	15.6	3.7	100	24

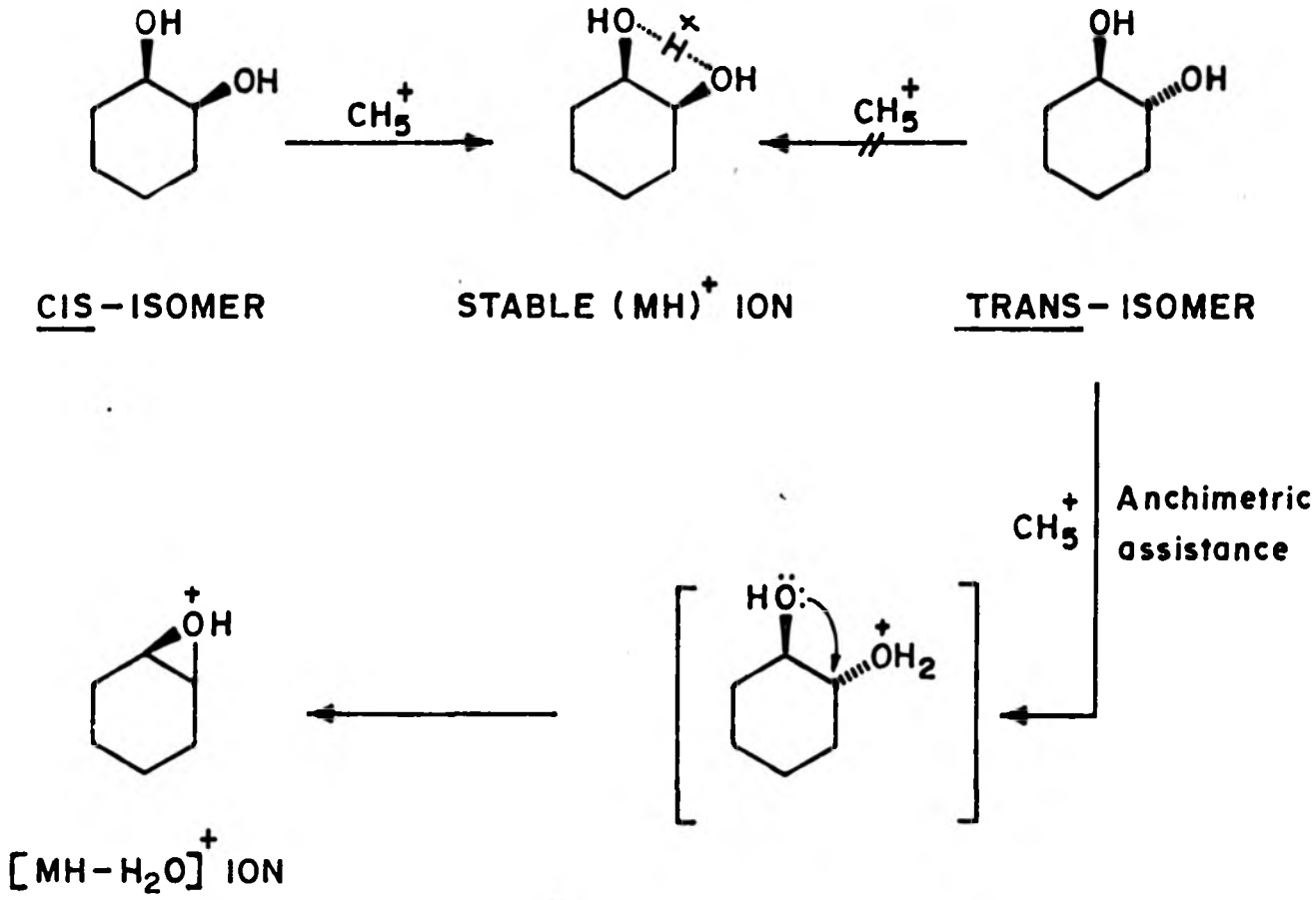
a: Refer to scheme 1 for the structures corresponding to the compound number here. The aryl groups are designated by R_1, R_2 and R_3.

b: I = Isobutane; M = Methane.

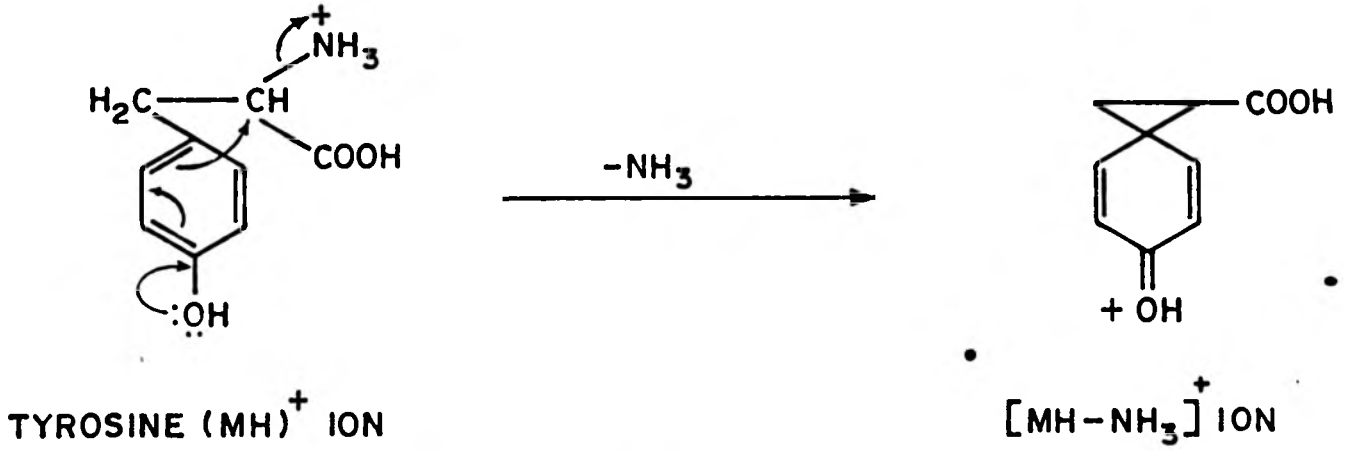
of the nitro group being the most probable sites for protonation. This assumption is supported by the observation on the further fragmentation of the $(MH)^+$ ion in these compounds. A facile loss of nitrous acid (HNO_2) can arise only if the nitro group is preferentially protonated. This elimination reaction seems to be favoured by neighbouring group participation[52] by adjacent aryl groups. A gas phase S_Ni type reaction is probably involved.

The relatively more stable $(MH)^+$ ions in 2, 13, 14, 16 and 20 may be due to the preferential protonation of alternate sites and proton bridging. Based on known proton affinity values[12,53], it can be assumed that the oxygen atom of the furyl group in 13 and 14 may have proton affinity of the same order of magnitude as the nitro group. Protonation on the oxygen atom of the furyl group can give stable $(MH)^+$ ions.

Schwarz and co-workers[43,44] differentiated epimeric cyclic diols by the stability of their $(MH)^+$ ions under CI conditions. The stability of $(MH)^+$ ions of cis-cyclohexane 1,2-diol was explained as due to proton bridging (Scheme 4) which is not possible in the other trans isomer. Similarly the stability of $(MH)^+$ ions in isomeric pairs 1,2 and 13,14 is subject to proton bridging. In compound 2, the C_4-nitro and C_3-phenyl groups are cis to each other. A proton bridging between the nitro group and the π electron system of the C_3-phenyl group is possible. Proton bridging is not possible in 1, since the nitro and adjacent phenyl groups have trans configuration.



SCHEME 4.



SCHEME 5.

Hence, less stable $(MH)^+$ ions are observed in this compound. The aryl group on C_5-position is invariably trans to the nitro group in all the compounds 1-20, which probably may trigger the loss of HNO_2 rather than the formation of a proton bridge. Significant differences in the relative intensity of the protonated molecular ions were observed in the spectra of compounds 13 and 14, in which 2-furyl group is present on the C_5-position.

(ii) Mechanism of elimination of HNO_2 from $(MH)^+$ ions:

In general, the fragmentation processes of mono-functional molecules under CI conditions proceed through protonation of the functional group by the reagent ion. It is followed by the energy transfer related to the proton affinity values of the respective conjugate bases[2]. Further fragmentation takes place if the transferred energy is enough to supply the required activation energy for the fragmentation process that results in the formation of stable ionic products[48].

It has been pointed out in the preceding section that protonation of nitro group results in the expulsion of HNO_2 to give $(MH-HNO_2)^+$ ions. The relative abundances of these ions are given in Table I for compounds 1-20. In compounds 1, 2, 5, 6, 9-11, 14 and 18-20, it is the base peak. In the

other compounds also these ions are abundant (%Σ_{90}, 7 to 21). Thus it is a favoured fragmentation process in these compounds. These ions can arise from the $(MH)^+$ ions by the elimination of nitrous acid by a simple heterolytic cleavage. The effect of stereochemistry on this fragmentation process appears to be less significant. However, the isomeric pairs 1,2, 7,8 and 11,12 show some minor differences on this elimination process. p-Substituents on the C_5-aryl group have some influence on these elimination reactions.

The preferential protonation of the nitro group leads to the cleavage of the -C-N bond. It is very interesting to observe that this heterolytic cleavage of -C-N bond is operating under CI conditions. In electron ionization mass spectrometry a similar type of cleavage is rare[55]. The loss of $-NO_2$ and $-NH_2$ groups are not observed to any significant extent in the EI spectra of tri-aryl substituted nitro cyclohexenes and their amino analogues[21,22].

Jardine and Fenselau[54] have investigated the mechanism of the expulsion of water from $(MH)^+$ ions of d_{11}-cyclohexanol. They have shown that both H_2O and HDO are lost from the $(MH)^+$ ions of d_{11}-cyclohexanol (equation 3), indicating the exchange between the hydroxy, the reagent gas,

$$[\text{Cyclo-}\ C_6D_{11}OH_2]^+ \longrightarrow \begin{cases} [C_6D_{11}]^+ + H_2O \\ [C_6D_{10}H]^+ + HDO \end{cases} \qquad (3)$$

and ring protons prior to the elimination of water from the $(MH)^+$ ions. Further, the stereospecificity of this exchange with ring protons in the cyclohexyl system was studied in more detail by the same workers[56]. However, the results obtained by Schwarz and his co-workers[43,57], in the elimination of water from $(MH)^+$ ions of 1,2- and 1,3-hexane diols are in sharp contrast to the observations made by Jardine and Fenselau. Several specifically labelled deuterated analogs of cis and trans 1,2- and 1,3-cyclohexane diols were studied under CI conditions. No exchange was observed between the hydroxy, reagent and ring protons to any considerable extent prior to the loss of first water molecule from the $(MH)^+$ ions. They have thus, concluded that the expulsion of the first molecule of water is a simple cleavage which is similar to E_1 type elimination since there was no exchange observed with the ring protons. However, the elimination of a second water molecule from $(MH-H_2O)^+$ ion, essentially involves ring deuterium atoms since it is a cis elimination process. The observation of relatively less stable $(MH)^+$ ions and more abundant $(MH-H_2O)^+$ ion in case of trans 1,2-cyclohexane diols was attributed to the absence of proton bridge and neighbouring group participation of the free hydroxyl group which involves a gas phase S_Ni type reaction (Scheme 4).

It is obvious that the present system is similar to trans 1,2-hexane diol examined by Schwarz et.al.,[43,57] in the

following respects - trans di-substitution and anchimeric assistance. Hence, it can be concluded that there is no exchange between the reagent and ring protons. The proton that is transferred from the reagent gas is involved in the elimination of HNO_2. No attempt was made to prove this aspect by examining the deuterated analogs labelled at specific positions.

The phenomenon of anchimeric assistance is well known in solution chemistry and has been reviewed by Capon[58]. The fundamental requirement for this assistance is the presence of a neighbouring group in such a position that it can act in an internal S_N2 reaction by donating an electron pair to assist the rear side expulsion of another adjacent group. In cyclic systems, the leaving and assisting groups must be anti co-planar[59] so that the intramolecular displacement (S_N2i) occurs from back side.

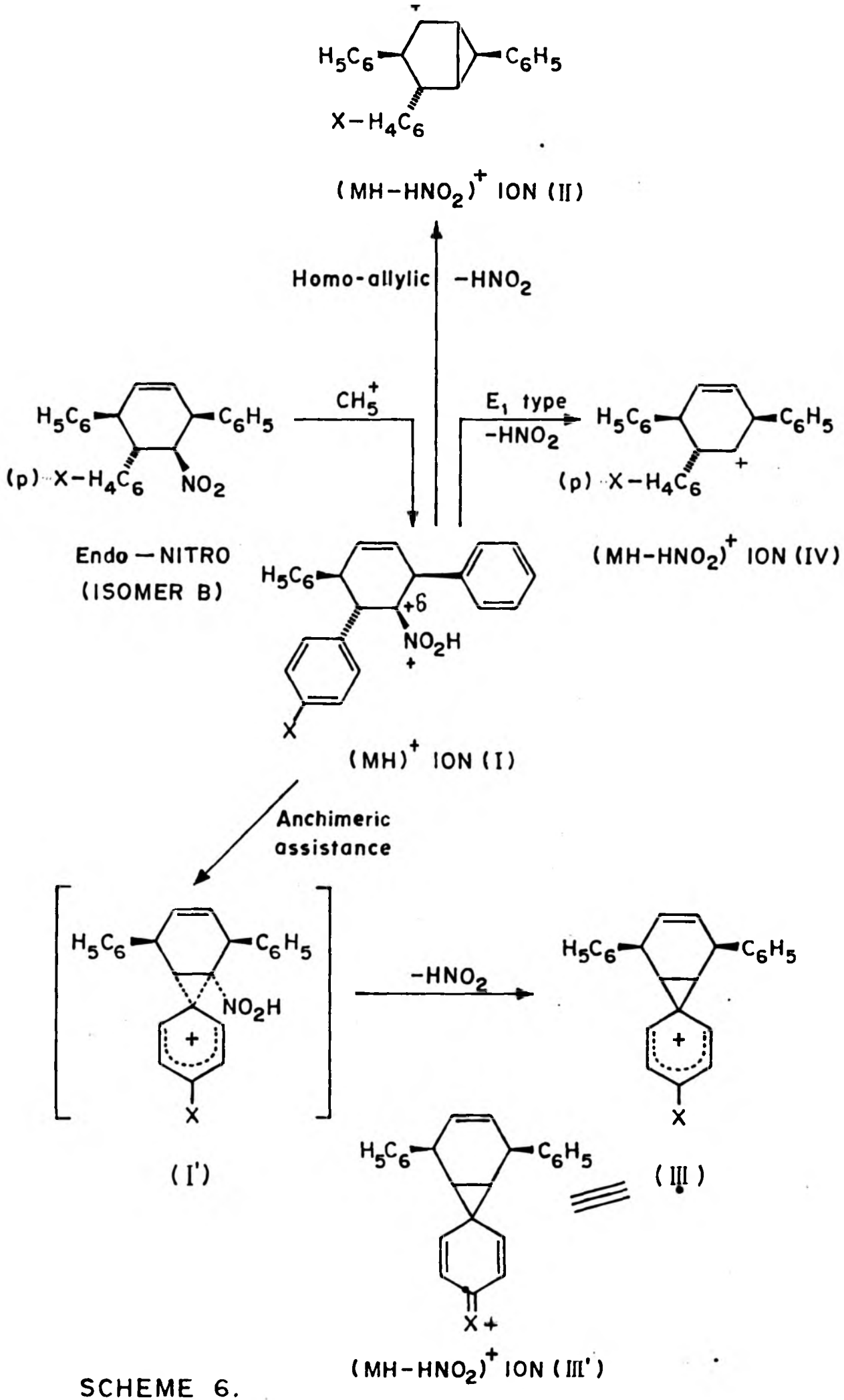
Though Djerassi et.al.,[60] have encountered this type of neighbouring group participation in the EI mass spectra of some substituted trimethyl silyl benzyl ethers, Shapiro and Jenkins[52] were the first to recognize this effect by phenyl group in the expulsion of bromine radical from the $M^{+\cdot}$ ions of β-phenyl ethyl bromide under EI conditions. The evidence for this was provided by labelling data, substituent effect and quasi-equilibrium theory[52]. Similar observations in favour of this phenomenon have been reported by Richter and Vetter[55] in the EI spectra of some substituted 2-aryl propyl amines.

There are some examples[61-65] in the literature where this effect has been reported under CI conditions in a few systems. Fales et.al.,[61] gave direct evidence for the anchimeric assistance in the CI mass spectra of some amino acids. One of the double bonds of the phenyl ring was shown to participate in the rear side S_Ni attack in the case of tyrosine and thereby facilitating the expulsion of ammonia from $(MH)^+$ ions (Scheme 5). Caserio and his associates[66] in their study on β-substituted alcohols, obtained results which were consistent with anchimeric assistance in the fragmentation pathways following protonation of molecules. Recently Van de Sande et.al.,[67-70] have reported this phenomenon in their CI studies on some bifunctional cyclopentane and cyclohexane molecules.

Anchimeric assistance is thus a known phenomenon in gas phase chemistry. In the present system also it may be playing an important role since the nitro and C_5-aryl groups have trans configuration and are anti co-planar[59] to each other. Additional evidence for achimeric assistance by neighbouring group was obtained from the substituent effect data on the HNO_2 elimination process. An electron donating group on C_5-aryl group was found to enhance the elimination reaction, while an electron withdrawing substituent inhibits the process.

Based on the above rationalizations, an attempt has been made to propose a satisfactory mechanism for the elimination of nitrous acid from $(MH)^+$ ions in the present system. As stated in the previous sections the preferential protonation on the nitro group results in the weakening of C-N bond. Consequently the carbon atom (C_4-) bearing nitro group acquires +δ charge, which is followed by the loss of nitrous acid. The heterolytic cleavage can be assisted by the neighbouring aryl group and homoallylic participation of the double bond. A stepwise[68,70] E_1 type elimination has also to be considered.

In all the compounds examined in the present study, the C_4-nitro group and C_5-aryl group or heterocyclic group as the case may be have a trans configuration. The trans stereochemistry of the C_5-aryl group helps in the anchimeric assistance. One of the double bonds of the aryl groups can attack the electron deficient C_4- carbon atom from the rear side (shown in Scheme 6) to give a stable cyclopropane intermediate. This results in the formation of a stable phenonium ion (III, Scheme 6) which is well known in solution chemistry[71]. The phenonium ion intermediates have been also invoked by several workers in the gas phase[52,62]. The C_3-aryl group can also particpate in the elimination of nitrous acid. The participation by the adjacent aryl groups and the rupture of C-N bond may be taking place in a concerted manner[72]. Some minor stereochemical differences are observed on this


H_5C_6
C_6H_5
$X-H_4C_6$
$(MH-HNO_2)^+$ ION (II)
Homo-allylic
$-HNO_2$
CH_5^+
E_1 type
$-HNO_2$
H_5C_6
C_6H_5
(p) $X-H_4C_6$
NO_2
Endo — NITRO
(ISOMER B)
$(MH-HNO_2)^+$ ION (IV)
H_5C_6
+δ
NO_2H
X
$(MH)^+$ ION (I)
Anchimeric
assistance
H_5C_6
C_6H_5
NO_2H
X
$-HNO_2$
H_5C_6
C_6H_5
X
(I')
(III)
H_5C_6
C_6H_5
X+
$(MH-HNO_2)^+$ ION (III')

SCHEME 6.

fragmentation mode in isomeric pairs 1,2; 7,8 and 11,12. As expected in the pairs 7,8 and 11,12 the endo phenyl isomers (7 and 11) exhibit relatively more $(MH-HNO_2)^+$ ions, since they have two adjacent aryl groups for anchimeric assistance. However, consistent stereochemical differences are not observed in the other pairs of isomers. This clearly indicates that some other mechanism is also operating in the elimination reaction. For example the double bond of cyclohexene ring can also assist in the elimination of HNO_2 molecule by a homoallylic participation, which is well known in solution chemistry[73,74]. Homoallylic participation in the present system can lead to the formation of a substituted 2-bicyclo-(3,1,0)hexyl cation (II, Scheme 6). In addition to this, an E_1 type of elimination is likely to operate. This type of elimination is reported in cis disubstituted cyclic compounds[43,67-70]. In the endo phenyl compounds (isomer A), this elimination mechanism may not operate, since the nitro group has two trans aryl groups adjacent to it. This should favour anchimeric assistance. On the other hand, when the C_3-aryl group is cis and C_5-aryl group is trans to the nitro group an E_1 type elimination process can operate. The degree of contribution from anchimeric assistance, homoallylic participation and E_1 type elimination, need not be the same. This provides a rationale for the observed lack of consistent stereochemical differences in the HNO_2 elimination reaction in the isomers A and B. The possible mechanisms for this

elimination process are indicated for the endo nitro compound in Scheme 6. Hence, it is reasonable to believe that anchimeric assistance plays a major role in this elimination process, with minor contributions from the homoallylic participation and E_1 type elimination.

(iii) Retro Diels-Alder reaction:

The retro Diels-Alder reaction (RDA) is one of the important fragmentation modes under electron ionization[75]. This fragmentation process has been shown to depend on the stereochemistry in some molecules[76,77]. In several compounds it is not stereospecific[78,79]. Some polycyclic dienones[80] have been reported to exhibit stereoselective RDA fragmentation under CI conditions. Biros et al.[77] were successful in establishing the molecular configuration of some polychlorinated insecticides and their metabolites from the stereospecific RDA fragments observed under CI conditions. The mechanism of RDA reaction in the gas phase resembles the thermal retrodiene reaction.

RDA is a major fragmentation mode under electron ionization of these compounds[21,22], while it is less significant under CI. The molecular ion undergoes this reaction under EI conditions while the protonated molecular ions exhibit this fragmentation in CI mode. The relative intensities of the diene and protonated diene ions are shown in Table II. The dienophile ions are not observed in these compounds. Minor stereochemical effects were noticed in this fragmentation reaction.

Table II

Abundances of $[(MH-HNO_2)-(RH)]^+$ and RDA fragment ions in the CI spectra of nitro cyclohexenes[a] 1-20. (as % base peak and % Σ_{90}).

Compd. No.	$[(MH-HNO_2)$ - $(R_1H)]^+$ ion		$(R_2H)]^+$ ion		$(R_3H)]^+$ ion		Retro Diels-Alder Reaction: Diene ion		Protonated diene ion	
	% base peak	% Σ_{90}	% base peak	% Σ_{90}	% base peak	% Σ_{90}	% base peak	% Σ_{90}	% base peak	% Σ_{90}
1	< 5	< 2.0[b]	-	-	-	-	-	-	-	-
2	< 5	< 1.4[b]	-	-	-	-	-	-	-	-
3	42	13.0[c]	-	-	-	-	< 5	< 1.2	< 5	< 0.4
4	100	27.0[c]	-	-	-	-	13	3.5	9	2.4
5	9	2.7[b]	21	6.2	-	-	8	2.3	< 5	< 0.7
6	< 5	< 1.2[b]	87	26.0	-	-	13	3.9	9	2.7
7	17	3.2[b]	74	14.0	-	-	10	2.0	< 5	< 0.7
8	5	1.4[b]	100	27.0	-	-	16	4.2	16	4.2
9	28	4.2[b]	37	5.4	-	-	24	3.5	11	1.6
10	14	3.0[b]	38	8.0	-	-	22	4.7	14	3.0
11	14	1.9[b]	33	4.4	-	-	39	5.2	14	1.9
12	16	2.1[b]	36	4.6	-	-	100	13.0	36	4.6
13	< 5	< 0.6[b]	14	2.2	-	-	28	4.5	8	1.2

contd...

Table II (contd.)

Compd. No.	[(MH-HNO_2) -						Retro Diels-Alder Reaction			
	$(R_1H)]^+$ ion		$(R_2H)]^+$ ion		$(R_3H)]^+$ ion		Diene ion		Protonated diene io	
	% base peak	$\%\Sigma_{90}$	% base peak	$\%\Sigma_{90}$	% base peak	$\%\Sigma_{90}$	% base peak	$\%\Sigma_{90}$	% base peak	$\%\Sigma_{90}$
14	< 2	< 0.5[b]	68	9.6	-	-	31	4.4	31	4.4
15	< 2	< 0.5[b]	42	8.5	-	-	42	8.5	15	3.1
16	10	1.7[b]	6	1.0	-	-	12	2.0	< 5	< 0.6
17	28	3.8	28[d]	3.8	-	-	6	0.8	< 5	< 0.7
18	22	2.6	11	1.3	9	1.0	18	2.1	15	1.7
19	20	4.4	20	4.4	< 5	< 0.7	< 5	< 0.9	< 5	0.6
20	< 5	< 1.2	15	3.7	< 5	< 0.9	13	3.1	< 5	< 0.9

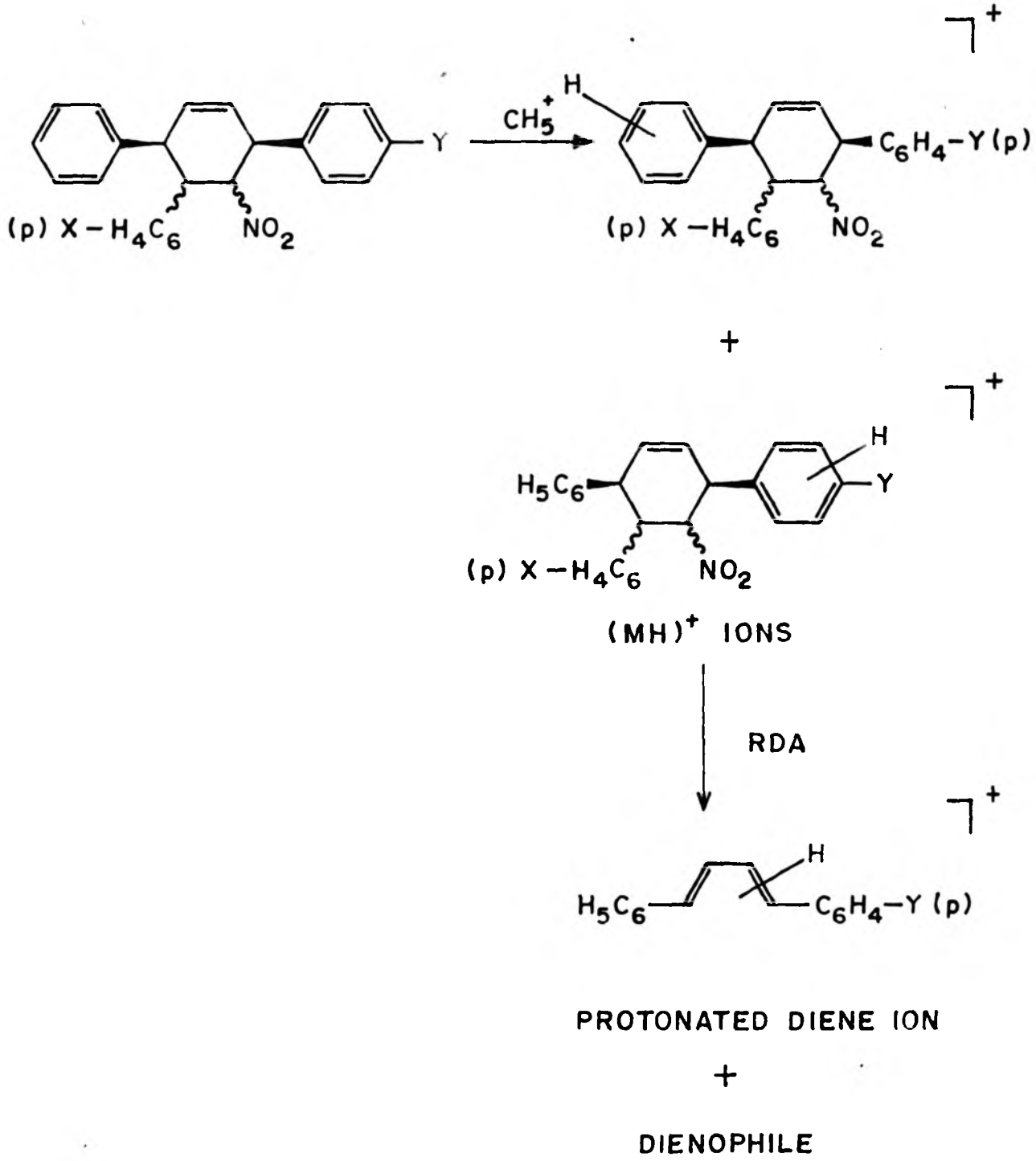
a: Refer to scheme 1, b: Refers to a sum of the exact percentage of R_1H and R_3H loses,

c: Refers to a sum of the exact percentage of R_1H, R_2H and R_3H ($R_1=R_2=R_3=Ph$) loses.

d: Refers to a sum of the exact percentage of R_2H and R_3H loses.

In the present system this fragmentation process in the CI mode appears to be similar to that observed under electron ionization. The presence of protonated diene ions in the CI spectra clearly indicates that the double bond[46], C_3- and C_6-aryl groups[47,48] as alternative sites for protonation. The protonation of the double bond may be ruled out since the resulting ion will lose its olefinic character and inhibit the RDA process[80]. Due to the presence of charge destabilizing nitro group, the dienophile and protonated dienophile ions are not observed in the CI spectra. The corresponding amino compound (22) shows both protonated diene and dienophile ions which arise from different $(MH)^+$ ions. The probable structure of the diene ion is shown in Scheme 7. The ionic signals corresponding to unprotonated diene ions were also observed which can arise from RDA reaction under electron ionization[22].

It is favoured in endo nitro compounds. The observed stereochemical difference on this fragmentation mode, even-though it is minor lents support to a concerted process. Concerted mechanisms have been proposed based on stereochemical effects[80] on RDA, on the charge distribution and low ionization potentials[81].


CH5+
H
Y
(p) X – H4C6
NO2
C6H4–Y(p)
+
H5C6
(MH)+ IONS
RDA
PROTONATED DIENE ION
+
DIENOPHILE

SCHEME 7.

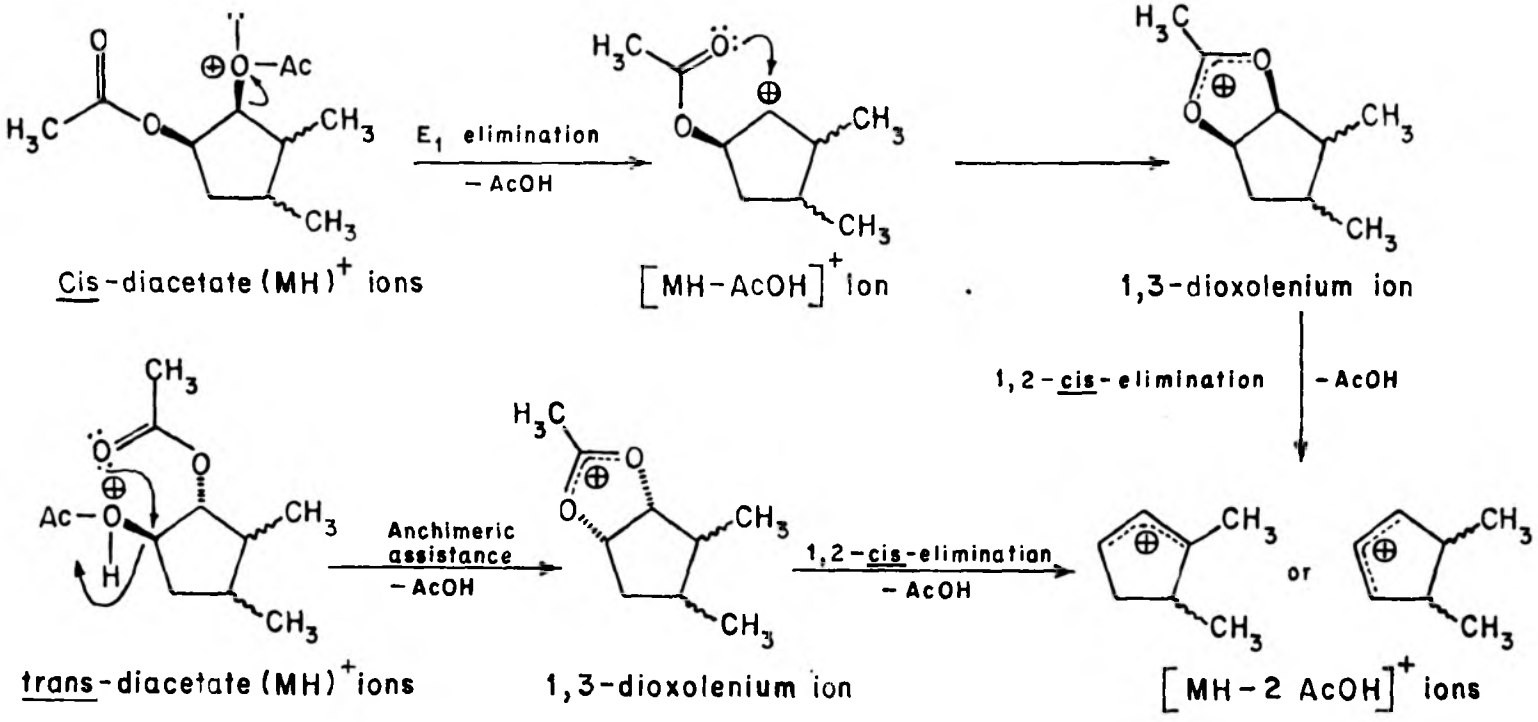
(iv) Elimination reaction of $(MH-HNO_2)^+$ ions:

The $(MH-HNO_2)^+$ ions decompose by two competing modes in the CI source. (i) An elimination reaction involving the loss of an arene molecule and (ii) isomerization followed by skeletal rearrangement. The latter fragmentation process will be discussed in the next section. The $(M-HNO_2)^{+\cdot}$ ions formed from the $M^{+\cdot}$ ions under electron ionization do not undergo this elimination reaction. The mass analyzed ion kinetic energy (MIKE) and collisional activation (CA) spectra of the $(M-HNO_2)^{+\cdot}$ ions generated from compounds 3 and 4 revealed that these ions can lose phenyl radicals to give an ion at m/z 231.

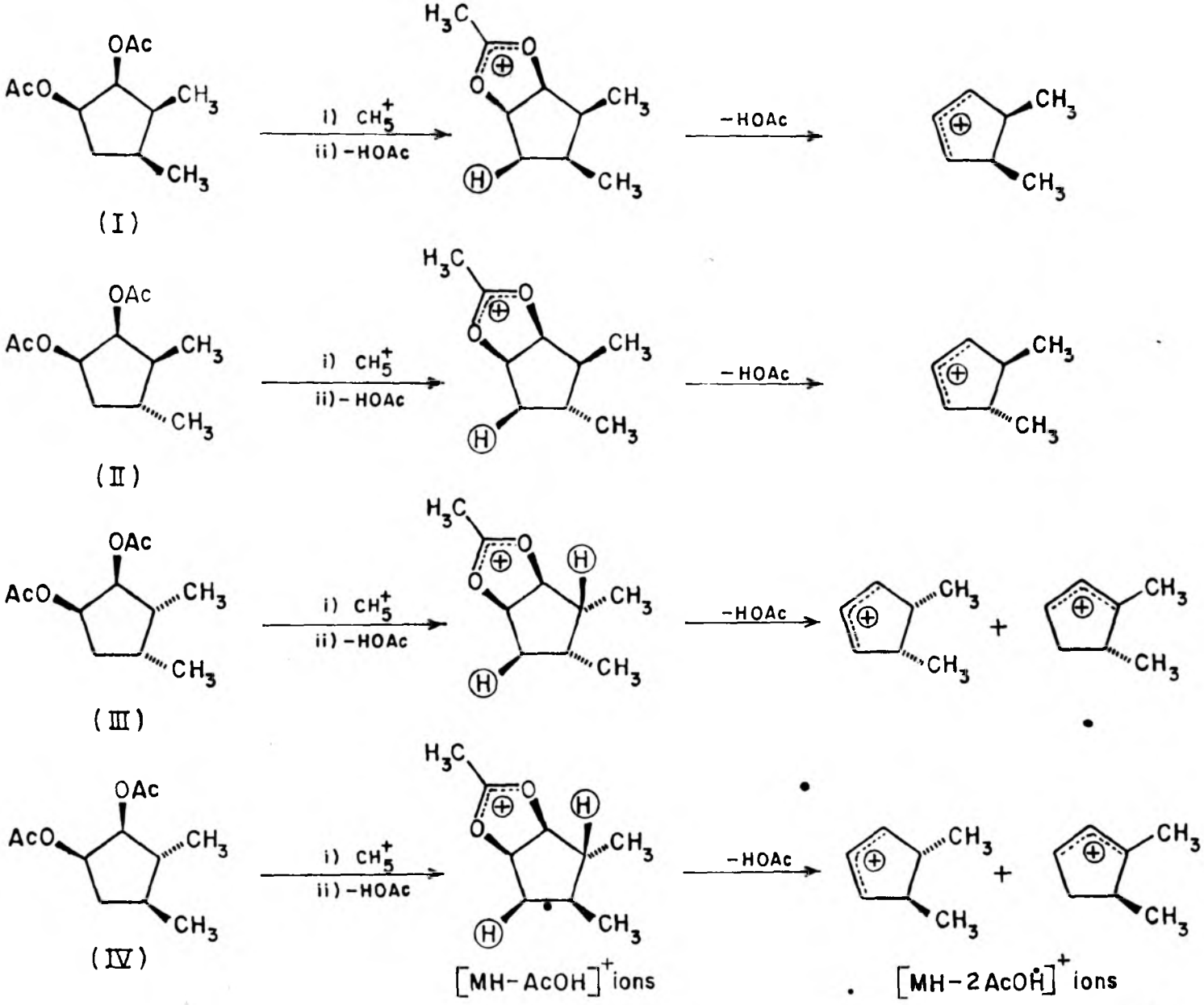
The elimination reaction leading to the formation of $[(MH-HNO_2)-(RH)]^+$ ions is observed under chemical ionization. A comparative study of the relative intensities of these ions (Table II) indicates that it mainly involves a stereoselective elimination of the C_5-aryl group. From the table it is evident that when the aryl group and the vicinal hydrogen atom are cis to each other in the precursor ion, this fragmentation mode is preferred. This is a good example of a cis elimination in the gas phase[67,68]. It is in contrast to the preferred trans elimination known in solution[82]. The elimination reaction is minor in the diphenyl compounds 1 and 2. Hence, the contributions from C_3- and C_6-aryl groups are not significant. Only R_1H and R_2H are lost significantly from $(MH-HNO_2)^+$ ions when all the aryl groups are different as in 18-20. The expulsion

of R_3H appears to be less significant.

Van de Sande and his co-workers[67] have studied the successive loss of two molecules of acetic acid from the $(MH)^+$ ions of many 3,4-dimethyl-1,2-cyclopentane diol acetates in which the acetate groups have cis and trans stereochemistry. They have postulated that an E_1 type mechanism is involved in the elimination of the first molecule of acetic acid from the $(MH)^+$ ions in the cis isomers. In the trans compounds the elimination has been shown to be assisted by the participation of second (neighbouring) acetate group which is trans to the leaving group (Scheme 8). This leads to the formation of stable 1,3-dioxolenium ions. Further studies on the CI spectra of four cis di-acetates I-IV in which the C_3- and C_4-methyl groups have different stereochemistry (Scheme 9) were carried out[67]. The relative intensities of the $(MH-AcOH)^+$ and $(MH-2AcOH)$ ions are given in Table III. In all these cases the first molecule of acetic acid has been shown to be lost by an E_1 type mechanism. This is followed by the formation of a 1,3-dioxolenium ion. The expulsion of a second molecule of acetic acid showed significant stereochemical differences. It appears to be analogous to a 1,2 thermal cis elimination. In the case of diacetates I and II (Scheme 9) only one cis hydrogen is available for this elimination. But in compounds III and IV two cis hydrogen atoms are present for abstraction in the elimination of a second acetic acid molecule. Hence



SCHEME–8



SCHEME–9

Table III

Partial isobutane CI spectra of I to IV[a]
(as % Σ_{70}).

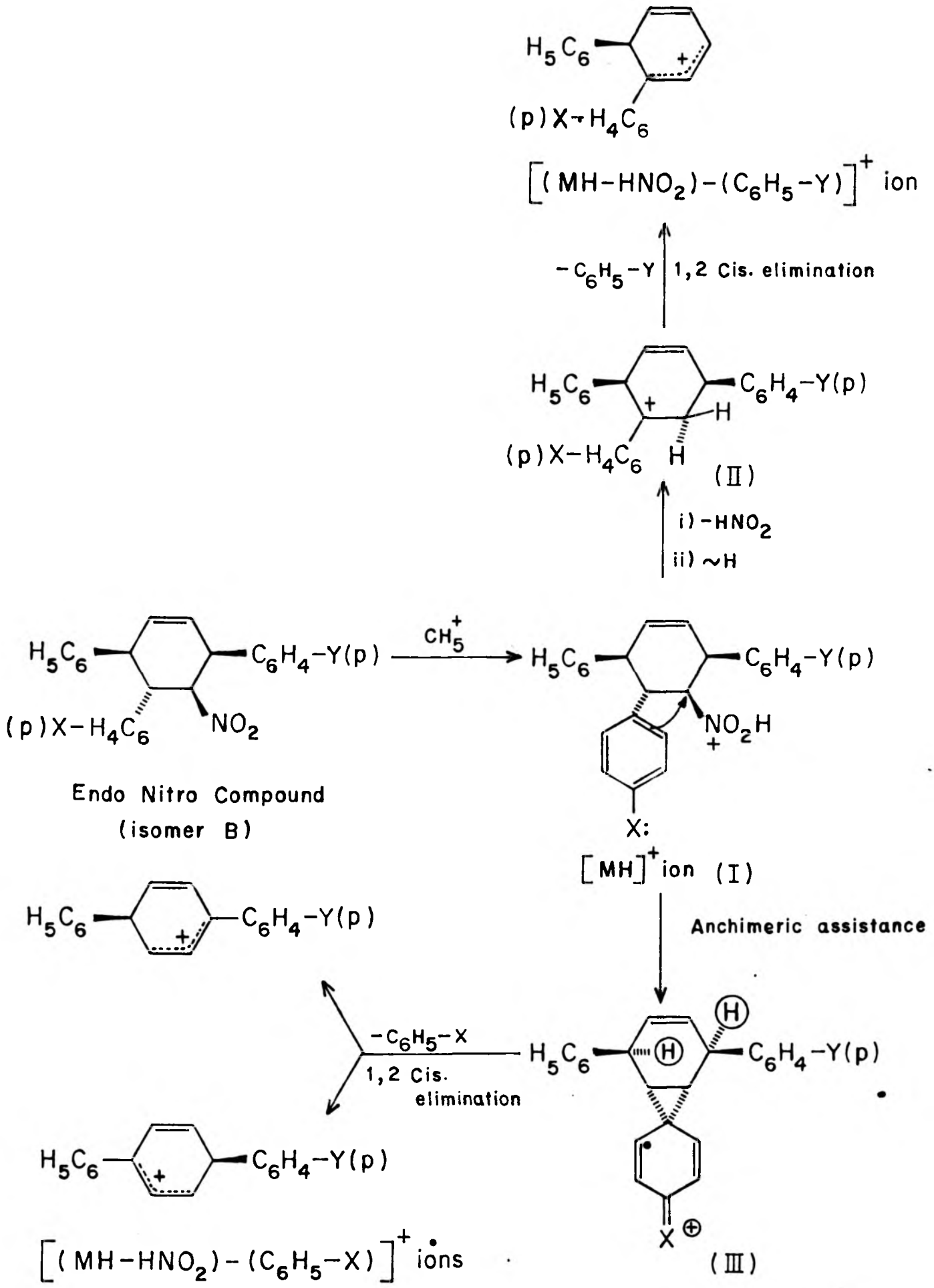
Compd. No.	$(MH)^+$ ions	$(MH-ACOH)^+$ ions	$(MH-2ACOH)^+$ ions
I	52.9	26.1	21.0
II	56.6	30.5	12.9
III	51.6	23.9	24.5
IV	48.0	22.8	29.2

a : Refer to scheme 9

compounds III and IV show relatively more abundant ions corresponding to $(MH-2AcOH)^+$ in their CI spectra (Table III).

In the present system the loss of HNO_2 from the protonated molecular ions appear to be a more complicated process. It can not be compared to the elimination of the first molecule of acetic acid from the $(MH)^+$ ion of trans 1,2-cyclopentane diol acetates reported by Van de Sande and co-workers[67,70]. On the other hand the elimination of arene molecule from the $(MH-HNO_2)^+$ ions appears to be similar to the loss of a second molecule of acetic acid from the $(MH-AcOH)^+$ ions of cyclopentane diacetate. In both cases, the elimination is controlled by the stereochemistry of the precursor ions. As expected the endo nitro compounds show more abundant $[(MH-HNO_2)-(RH)]^+$ ions in their CI spectra. In these compounds two cis hydrogen atoms are available for the cis elimination of an arene molecule from $(MH-HNO_2)^+$ ions. On the contrary, the endo phenyl compounds do not have cis hydrogen atoms for abstraction. Hence this fragmentation mode is less. A mechanism for this elimination process is shown in Scheme 10.

Electron donating groups on C_5-aryl group enhance this reaction in the endo nitro compounds. The driving force for this reaction could be the ease of formation of the ion (III, Scheme 10), and the availability of two cis hydrogen atoms for the elimination process. On the other hand the electron withdrawing group retards this fragmentation mode. In the


H5C6
(p)X-H4C6
[(MH-HNO2)-(C6H5-Y)]+ ion
-C6H5-Y
1,2 Cis. elimination
H5C6
C6H4-Y(p)
H
(p)X-H4C6
H
(II)
i) -HNO2
ii) ~H
H5C6
C6H4-Y(p)
(p)X-H4C6
NO2
CH5+
Endo Nitro Compound
(isomer B)
H5C6
C6H4-Y(p)
NO2H
X:
[MH]+ ion (I)
Anchimeric assistance
H5C6
C6H4-Y(p)
-C6H5-X
1,2 Cis.
elimination
H5C6
C6H4-Y(p)
H5C6
C6H4-Y(p)
[(MH-HNO2)-(C6H5-X)]+ ions
X⊕
(III)

SCHEME 10

3,6-diphenyl-5-aryl nitrocyclohexenes (5-16), the loss of benzene is also observed. This can arise by the elimination of either C_3- or C_6-phenyl groups. But, the striking observation is that in compounds 18-20, which have different aryl groups, only C_3- and C_5-aryl groups are lost in the elimination reactions. On the other hand the expulsion of C_6-phenyl group is less significant. The preferred elimination of C_3-phenyl over C_6-phenyl can be satisfactorily explained by invoking a hydride shift in ion (I) to form ion II, (Scheme 10). This ion has a cis hydrogen available for the loss of C_3-phenyl group as a molecule of benzene. The driving force for such a hydride shift may be the stability of the resulting benzylic carbonium ion (II).

In conclusion, it could be stated that cis elimination is predominant in endo nitro compounds. The hydride transfer followed by elimination is a competing process in the endo phenyl compounds. The driving force for this reaction may be the formation and stability of the substituted cyclohexadienyl ions. Hence the precursor ions may have a cyclohexenyl structure and the daughter ions could be represented as cyclohexadienyl cations.

(v) Skeletal rearrangements:

In general, the skeletal rearrangement processes are comparatively less common than hydrogen rearrangements in the gas phase and are low energy processes. They are the pit falls

in the application of mass spectrometry as a structural tool. These processes which are known under electron ionization[83-87] are rare in chemical ionization mass spectrometry. One reason for this differential behaviour is the driving force pushing the radical cations formed by electron ionization to fragment so as to separate the radical from the charge. Thus, prior rearrangement within the molecular cation radical will be revealed when it falls apart. This driving force is absent in the even electron ions formed under CI.

The CI spectra of the nitro cyclohexenes, 1-20, show the presence of abundant skeletal rearranged ions (m/z 167 and its analogs). The relative abundances of these ions are shown in Table IV. It is obvious from the table that they are one of the major ions formed. They form the base peak in the spectra of compounds 3, 7, 9, 15 and 17 and are very abundant in the spectra of the other compounds. In compounds 3 and 4 the rearrangement ions at m/z 167 are only observed. These ions can be assigned the diphenyl methyl cationic structure and they can arise by 1,2; 1,3 and/or 1,4 phenyl migrations. In the spectra of compounds 5-16, where an aryl/heterocyclic group is present at C_5-position of the cyclohexene ring, two types of skeletal rearrangement ions are observed. They are the $(CHR_1R_3)^+$ and $(CHR_1R_2)^+$ ions ($R_1 = R_3$). In these compounds the ions $(CHR_1R_3)^+$ can arise only by 1,4 phenyl migrations. On the other hand, the $(CHR_1R_2)^+$ ions can result by 1,2 and/or

Table IV

Relative intensities of skeletal rearrangement ions in the CI spectra of nitrocyclohexenes[a] 1-20. (as % base peak and $\%\Sigma_{90}$).

Compd. No.	$(CHR_1R_2)^+$		$(CHR_2R_3)^+$		$(CHR_1R_3)^+$	
	% base peak	$\%\Sigma_{90}$	% base peak	$\%\Sigma_{90}$	% base peak	$\%\Sigma_{90}$
1	-	-	-	-	10	5.4
2	-	-	-	-	9	3.4
3	100	30[b]	-	-	-	-
4	62	17[b]	-	-	-	-
5	86	25[b]	-	-	7	1.9
6	35	10.5[b]	-	-	< 5	< 0.78
7	100	20[b]	-	-	25	4.8
8	31	8.4[b]	-	-	7	1.8
9	100	15[b]	-	-	30	4.5
10	66	14[b]	-	-	14	3.0
11	92	12[b]	-	-	22	3.0
12	52	6.7[b]	-	-	12	1.5
13	72	11.4[b]	-	-	8	1.2
14	65	9.2[b]	-	-	< 5	< 0.5
15	100	21[b]	-	-	9	1.8
16	32	5.3[b]	-	-	8	1.3
17	-	-	100	13.3	77[c]	10.3
18	18	2.1	50	6.0	14	1.7
19	29	6.5	41	9.3	18	4.1
20	34	8.1	38	9.0	< 5	< 1.0

a : Refer to scheme 1

b : Refers to a sum of the exact percentage of $(CHR_1R_2)^+$ and $(CHR_2R_3)^+$

c : Refer to a sum of the exact percentage of $(CHR_1R_3)^+$ and $(CHR_2R_3)^+$.

1,3-aryl migrations. They are more abundant. An examination of the spectra of 18-20 in which R_1, R_2 and R_3 are different, clearly showed that all the three different rearrangement ions which can arise by 1,2; 1,3 and 1,4 aryl migrations are formed. The relative intensities of the ions formed by 1,2 and 1,3 migrations are more or less the same, while the abundance of the ions formed by 1,4 migration is relatively low.

The formation of the diaryl methyl cations is less under the EI mode. The data obtained from metastable ion dofucusing[21], MIKE and CA spectra on compounds 3 and 4 under electron impact conditions indicated that these rearrangement ions are formed from $(M-NO)^+$, $(M-NO_2)^+$ and $(M-HNO_2)^{+\cdot}$ ions. The mechanism of formation of the diaryl methyl cations may be different under EI and CI conditions.

As indicated earlier, the $(MH-HNO_2)^+$ ion formed in the spectra of the nitro cyclohexenes under study, exhibit two fragmentation processes. An elimination reaction which was discussed in the earlier section, and a multistep rearrangement process leading to the formation of the diaryl methyl cations. The skeletal rearrangement processes are relatively more in isomer A. The elimination process takes precedence over the skeletal rearrangements in isomer B. This clearly illustrates that they are two competing reactions of the $(MH-HNO_2)^+$ ions.

Although there are several studies on hydrogen transfer rearrangements in CI mass spectrometry, the studies on skeletal

rearrangements are few. Field has invoked several structural rearrangements in some cycloalkanes[38], cycloalkenes[40] and bicyclo(2,2,2)alkanes[88] to explain their CI behaviour. McCloskey and Liehr[89] have reported skeletal rearrangements in allyl phenyl acetate and allyl phenoxy acetate. The rearranged ions were reported to be 40 to 50% of the total ionization. No analogy was observed with the EI fragmentation. They have proposed a mechanism involving an intramolecular substitution of the phenyl ring by the allyl group. The protonated benzoic acid esters and their analogs[90] under CI conditions were shown to lose water and carbon dioxide molecules. This elimination reaction involves the migration of alkyl or aryl group to the aromatic ring.

Very recently Schwarz and his associates[43] have invoked a skeletal rearrangement involving a ring contraction in the formation of $(MH-2H_2O)^+$ ions in the CI spectra of both cis and trans 1,2-cyclohexanediol. Further it was shown[57] that these ions have the structure of protonated cyclopentane carboxaldehyde. The evidence was obtained from CI/CA data. There are a few other examples where alkyl migrations[91-94] and other skeletal rearrangements[95] are invoked to rationalize CI fragmentation processes.

The key and striking observation in the compounds examined in the present study is the abundance of $(CHR_1R_2)^+$, $(CHR_2R_3)^+$ and $(CHR_1R_3)^+$ ions ($\%\Sigma_{90}$ 5.3 to 30.0). It is

difficult to understand the formation of these diaryl methyl cations directly from a substituted cyclohexenyl structure. However, it is certainly safe to conclude that extensive rearrangements have taken place. As outlined below, a reasonable solution to this apparent conundrum may be found in the literature of cyclohexenyl cations encountered in solution.

Deno and Houser[96] first reported on the basis of NMR spectral data the opening of bicyclic alcohols to cyclohexenyl cations which then undergo ring contraction to yield cyclopentenyl cations. They have also examined the effect of structural changes on the ring contraction of cyclohexenyl to the methyl cyclopentenyl cation in strong acid medium[97]. It was shown that an alkyl substituent in the allylic position of the cationic centre would facilitate this rearrangement. Sorensen et al.,[98,99] have reported that cyclopropyl allyl cations cyclize to give a variety of cyclohexenyl cations which in turn isomerise to the corresponding methyl cyclopentenyl cations. They have further shown that this carbocation system undergoes a series of degenerative rearrangements which scramble the ring positions[100]. Olah and co-workers[101,102] in their studies of carbocations in super acid systems have observed that many substituted cyclohexenyl cations undergo ring contraction to form substituted cyclopentenyl cations. The cyclohexenyl cations are formed from a number of precursors directly without rearrangement when the leaving group is α- to the double bond. When the

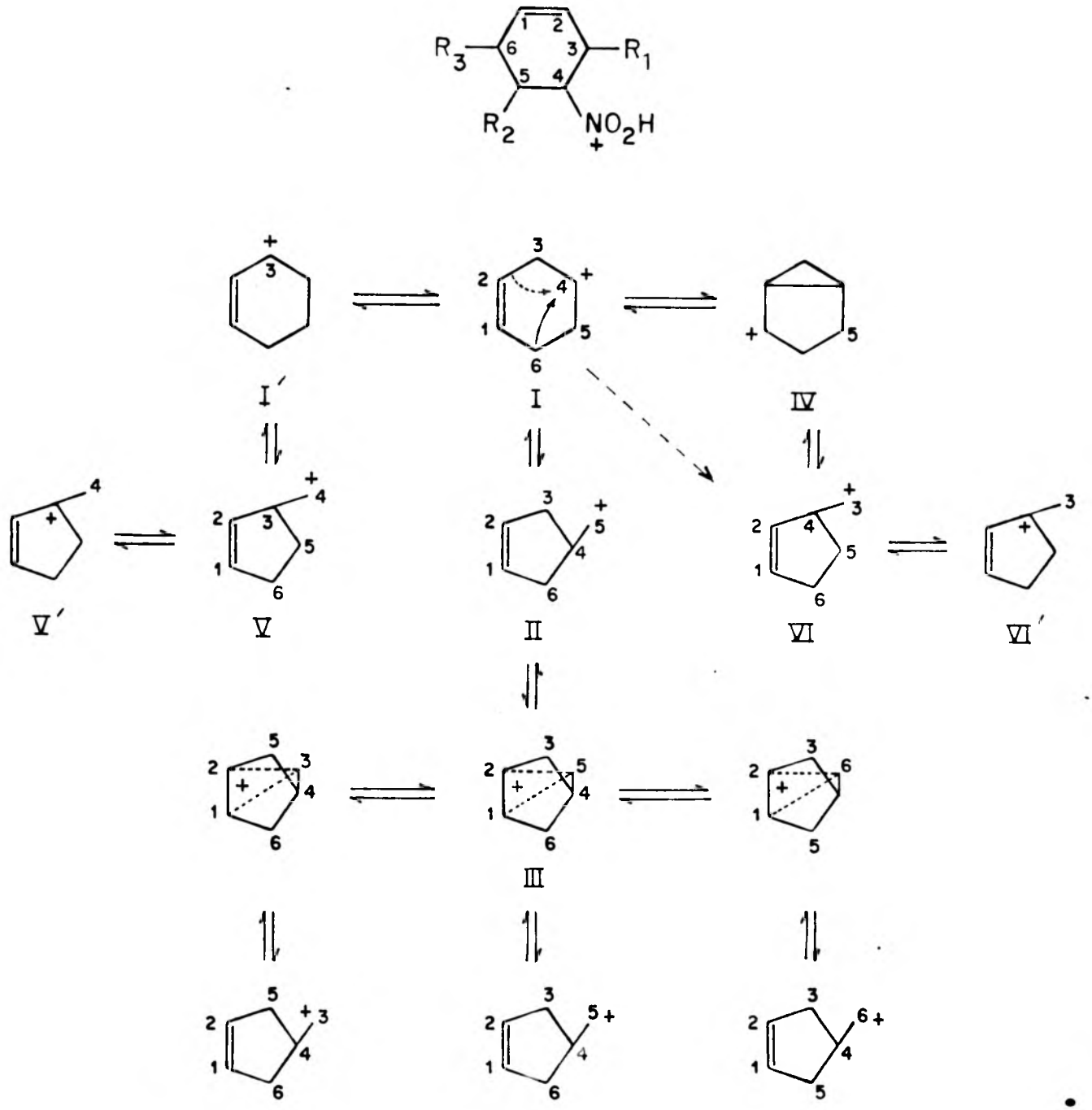
leaving group is in the homoallylic position, ring contraction or other rearrangement processes would result. Generation of methyl cyclopentenyl cation[101] from hex-3-enol in super acid medium provides the key intermediate for the present system which can undergo a series of hydride shifts and phenyl migrations. In a related work when 2-phenyl cyclohexyl amine[103] and 2,3-dimethyl-6-phenyl-cyclohexylamine[104] were treated with nitrous acid the corresponding ring contracted alcohols have been obtained in good yields. Further work in this area has led to details of the scrambling mechanisms in these ions[105,106].

The work mentioned above suggests the possibility of ring contraction in the $(MH-HNO_2)^+$ ion produced in the CI spectra of compounds 1-20. Further evidence to support this ring contraction (isomerization) in gaseous phase was obtained from CI/CA studies. Treatment of 3,5,6-triphenyl-4-amino-Δ^1-cyclohexene with nitrous acid (deamination) gave a ring contracted 2,5-diphenyl-cyclopent-3-en-1-yl benzyl alcohol (21) in ~ 75% yield. This compound was used in the CA studies as an authentic sample. The corresponding 3,5,6-triphenyl-4-hydroxy-Δ^1-cyclohexene was also prepared by Diels-Alder reaction of 1,4-diphenyl butadiene and styryl acetate, followed by the hydrolysis. The CI/CA spectra of $(MH-H_2O)^+$ generated from the $(MH)^+$ ions of the above two alcohols were measured. Similarity in the spectra indicated that the $(MH-H_2O)^+$ ions generated from these two compounds equilibrate in the gas phase or isomerise to a common intermediate. (This phenomenon of isomerization in the gas and

its analogy with condensed phase behaviour will be discussed in detail in the next Chapter). Based on the NMR studies[96,98-102,105,106], some of the possible directions that the substituted cyclohexenyl cation would take are outlined in Scheme 11.

The interconversions shown in Scheme 11 constitute an extremely complex kinetic system which was studied in part by many workers and in which the individual rates and equilibria are strongly dependent on the substitution pattern of the cyclohexenyl cation precursor. These studies have for the most part been carried out in strong acid media at low temperatures, e.g. $< -50^{\circ}$. Although temperature has a strong effect on these rearrangements, the ring contraction is observed at the highest temperatures reported[105,106]. There is no reason to doubt that the rearrangements outlined in Scheme 11 would be easily accessible to the cyclohexenyl cation formed by the elimination of HNO_2 from the $(MH)^+$ ions.

Thus, ring contraction of initially produced cyclohexenyl cation would result in the ion (I), (Scheme 11). This precursor can only push out either C_5-(II) or C_3-(VI). This might very well explain the observed fact that the expelled group in all cases overwhelmingly contains R_2. Nevertheless either *via* intermediate (III) (Scheme 11) and/or by double bond participation to (IV), C_3- and C_6-carbons may occupy the expelled



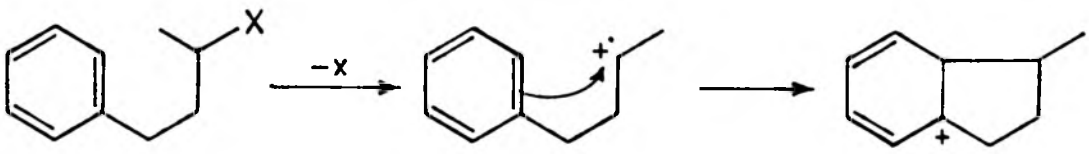
SCHEME -11

Known Intermediates from Cyclohexenyl cations (Only Carbon Skeleton is shown)

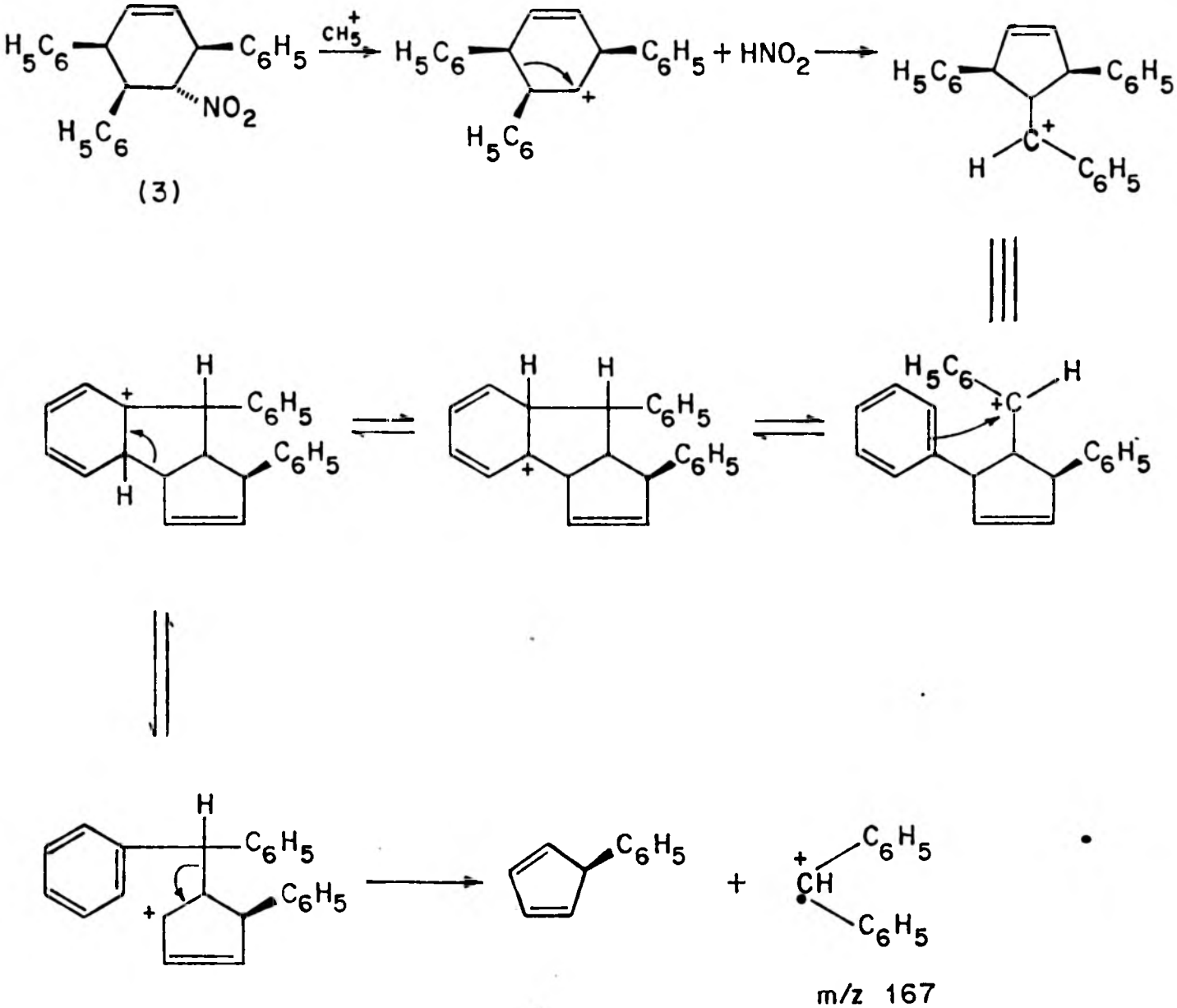
position. This longer route places R_1 and R_3 on the carbon to be ejected. Hence, the rearranged ions corresponding to $\overset{+}{C}HR_1R_3$ form in relatively low abundance. The CI results are thus not contradicted by expectations based on the known NMR intermediates in solution. The occurrence of this type of rearrangement processes involving multiple bond forming steps, hydride transfers and aryl migrations within a few micro seconds in the ion source (CI) is not unexpected[107]. Ions of low internal energy typically undergo complex bond reorganization sequence in fragmenting by low activation energy pathways.

In the NMR studies discussed above, it was found that the ring contracted ion e.g. (V, Scheme 11) rapidly transfers hydride from C_3- to C_4- so as to place the charge within the ring. A large body of evidence on intramolecular Friedal Crafts alkylations and acylations[108] indicates that the process shown in Scheme 12 is rapid. Carbocations located so as to close the five membered ring are favourable. This is precisely the situation in the molecules discussed in the present study and moreover such an intervention hypothesis could reasonably lead to the rearranged ions. This hypothesis leads to an overall mechanism which is outlined for compound 3 in Scheme 13.

The proposal in Scheme 13 is supported by the following observations: (i) Analogy to known solution carbocation chemistry in ring contraction or isomerization process, (ii) similar CI/CA spectra of $(MH-HNO_2)^+$ ions generated from the $(MH)^+$ ions of



SCHEME - 12



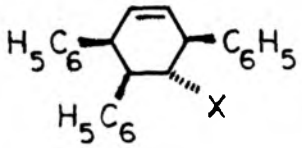
SCHEME - 13

Mechanistic Hypothesis

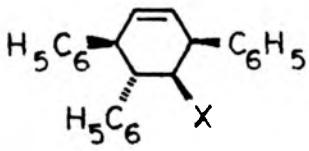
3,5,6-tripheryl-4-hydroxy-Δ^1-cyclohexene and 2,5-diphenyl-cyclopent-3-en-1-yl-benzyl alcohol, (iii) the extrusion of diaryl methyl cations predominently containing R_2 aryl groups of widely varying structure and (iv) a strong stereochemical dependence. The latter two observations would be difficult to understand if more random and extensive rearrangements were occurring prior to fragmentation.

2. The effect of C_4-substituent on the fragmentation of triphenyl cyclohexenes in the CI source.

In the preceding section of this Chapter some aspects of the chemistry of gaseous carbonium ions generated from triaryl substituted nitrocyclohexenes were discussed. In order to study the effect of different C_4-functional groups on the fragmentation under CI conditions, the following C_4-substituted 3,5,6-triphenyl cyclohexenes were examined.



Isomer A



Isomer B.

22	:	X = NH_2	Isomer A
23	:	X = OAc	Isomer B
24	:	X = OH	Isomer B
25	:	X = CHO	Isomer A
26	:	X = COOH	Isomer A
27	:	X = COOMe	Isomer A
28	:	X = COOMe	Isomer B
29	:	X = CN	Isomer A
30	:	X = CN	Isomer B.

These compounds were prepared by Diels-Alder reaction between 1,4-diphenyl butadiene and the appropriate dienophiles. The pure compounds were obtained by column chromatography. The CI spectra of these compounds were recorded using either isobutane (3, 25-27) or methane (22-24, 29) as reagent gas. The corresponding EI spectra of these compounds were recorded, and compared.

The chemical ionization spectra of compounds 22-27 and 29 are given in figures 6 and 7. The relative abundances of the major fragment ions formed in the CI spectra of these compounds are shown in Table V. The CI spectrum of compound 3 (Scheme 1) is given in the table for comparison. The protonated molecular ions are stable in all these compounds except in 23 and 24. It forms the base peak in the compound 22, which has an amino function. Loss of 'HX' from the protonated molecular ions was observed in compounds 22-24. Loss of benzene from $(MH-HX)^+$ ions and skeletal rearrangement ions (m/z 167) are also observed in these compounds. Elimination of HX from the $(MH)^+$ ions is a minor process in compounds 25-27 and 29. Protonated molecular ions of compounds (22, 25, 27 and 29) expel benzene to give $(MH-C_6H_6)^+$ ions (7 to 44%). Retro Diels-Alder (RDA) reaction is a general fragmentation mode of these molecules. Protonated diene and dienophile ions are formed. The dienophile ions form base peak in the spectrum of 3,5,6-triphenyl-Δ^1-cyclohexene-4-carboxaldehyde (25). The peak corresponding to

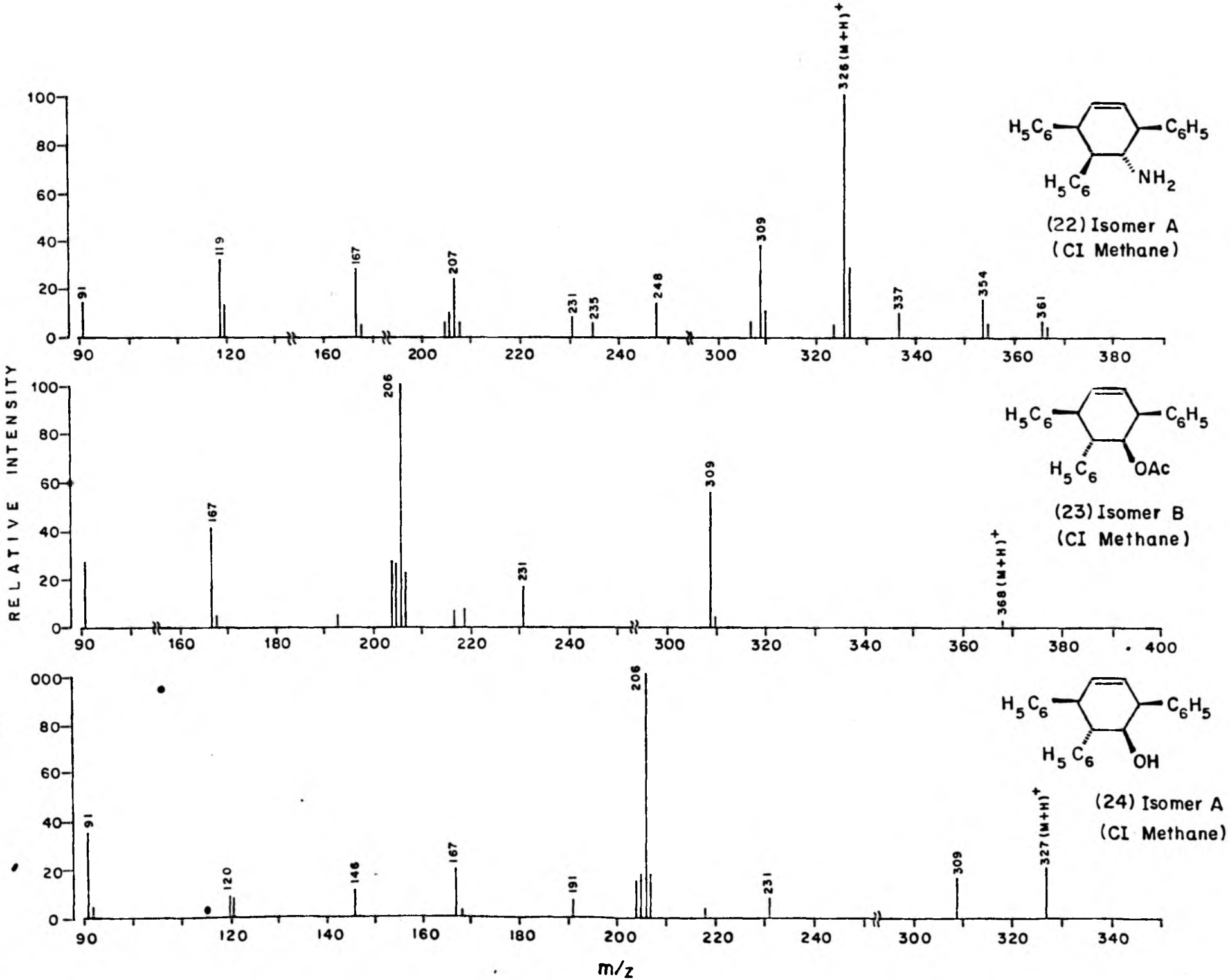

RELATIVE INTENSITY
m/z
326(M+H)+
309
207
248
235
231
167
119
91
337
354
361
206
309
231
167
368(M+H)+
206
91
120
146
167
191
231
309
327(M+H)+
H5C6
C6H5
NH2
OAc
OH
(22) Isomer A
(CI Methane)
(23) Isomer B
(CI Methane)
(24) Isomer A
(CI Methane)

FIGURE 6

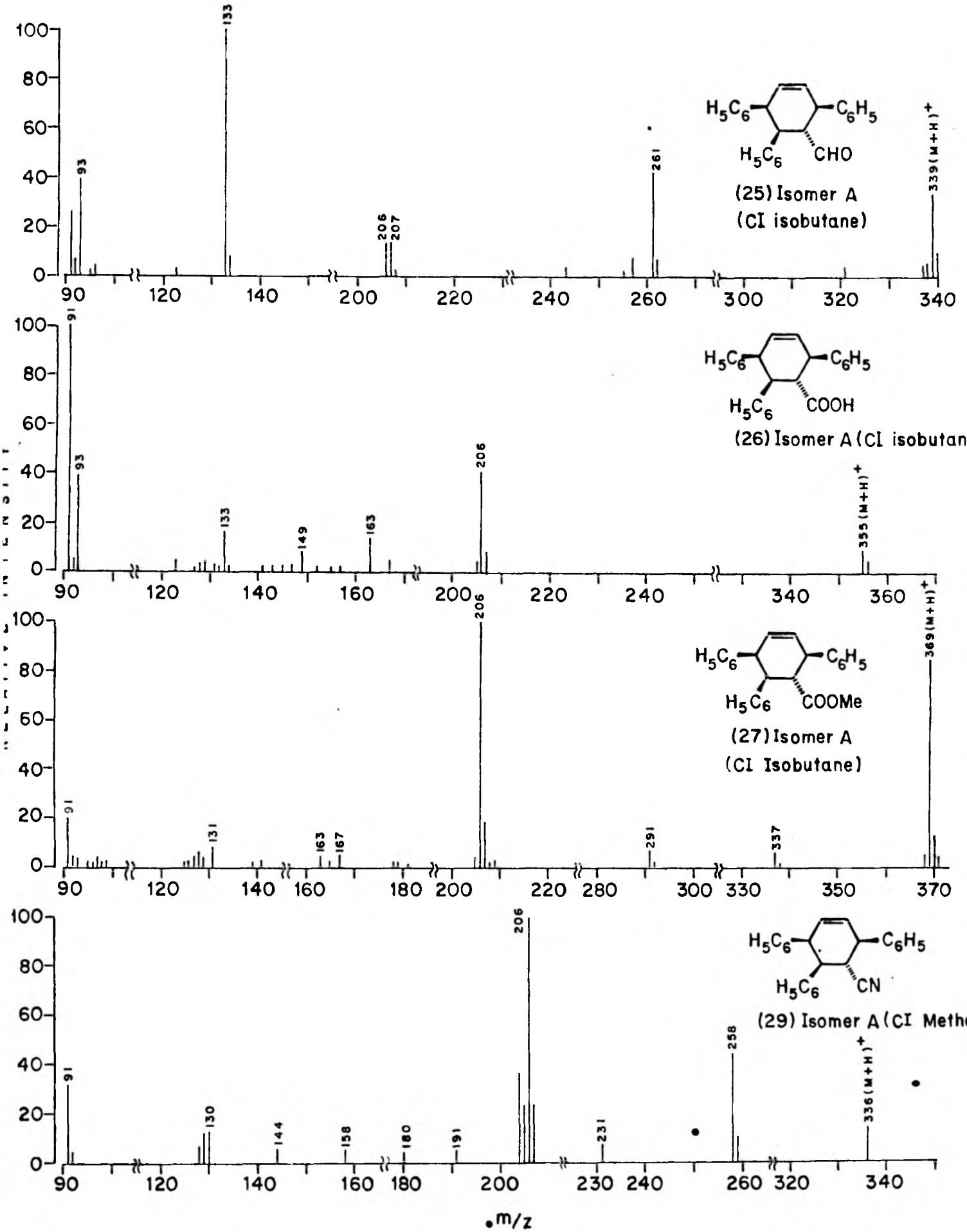

100
80
60
40
20
0
90
120
140
200
220
240
260
300
320
340
133
93
206
207
261
339(M+H)+
H5C6
C6H5
H5C6
CHO
(25) Isomer A
(CI isobutane)
91
93
133
149
163
206
355(M+H)+
H5C6
C6H5
H5C6
COOH
(26) Isomer A (CI isobutane)
206
369(M+H)+
91
131
163
167
291
337
H5C6
C6H5
H5C6
COOMe
(27) Isomer A
(CI Isobutane)
206
91
130
144
158
180
191
231
258
336(M+H)+
H5C6
C6H5
H5C6
CN
(29) Isomer A (CI Methane)
m/z

FIGURE 7

Table V

CI spectra of 3,5,6-triphenyl-4-substituted-Δ^1-cyclohexenes 3, 22-27 and 29 (as % base peak).

Compd. No.	X	$(MH)^+$ ions	$(MH-HX)^+$ ions m/z 309	$(MH-C_6H_6)^+$ ions	$[(MH-HX)-(C_6H_6)]^+$ ions m/z 231	$^+CH\emptyset\emptyset$ ions m/z 167	Retro-Diels Alder Reaction				Tropylium cations m/z 9
							Diene ions		Dienophile ions		
							Unprotonated m/z 206	Protonated m/z 207	Unprotonated	Protonated	
3[a]	$-NO_2$	< 2.0	69.0	-	42.0	100.0	4.0	2.0	-	-	-
22[b]	$-NH_2$	100.0	38.0	13.0	8.0	28.0	10.0	24.0	32.0	13.0	13.0
23[b]	-OAc	< 2.0	56.0	-	16.0	40.0	100.0	23.0	-	-	27.0
24[b]	-OH	< 2.0	18.0	-	8.0	20.0	100.0	18.0	8.0	8.0	35.0
25[a]	-CHO	33.0	-	43.0	-	2.0	14.0	14.0	-	100.0	26.0
26[a]	-COOH	9.0	-	-	-	2.0	40.0	9.0	7.0	-	100.0
27[a]	-COOMe	86.0	-	7.0	-	3.0	100.0	18.0	-	4.0	21.0
29[b]	-CN	14.0	-	44.0	-	-	100.0	24.0	13.0	13.0	33.0

a : Reagent gas used isobutane

b : Reagent gas used methane.

tropylium cations (m/z 91) is significant in the CI spectra of all these compounds.

A common fragmentation mode of monofunctional molecules under CI conditions involves the elimination of

$$RX \xrightarrow{CH_5^+} (RXH)^+ \longrightarrow R^+ + HX \qquad (4)$$

a functional group 'X' as the stable neutral molecule HX from the protonated molecular ion $(RXH)^+$ (equation 4). Field[109] has predicted that the extent to which the above reaction occurs should be inversely proportional to the proton affinity of the neutral HX molecule expelled. There are a few systematic investigations[54,110,111] on this aspect. The work of Jardine and Fenselau[54] on the CI behaviour of a number of cyclohexenyl derivatives provides direct support to this prediction. Although these workers have observed the general inverse trend on the extent of reaction 4 with the proton affinity of HX, some anomalous results were also obtained. Some of these could possibly be due to competing dissociations of the $(MH)^+$ ions. Thus, they have concluded that the inverse correlation with proton affinity may only be valid when other fragmentation processes are negligible, the departing X group is small and the initial site of protonation is the substituent X.

Very recently Harrison and Onuska[110] have also checked the validity of Field's prediction. They have studied the CI

mass spectra of some 5,6-dihydro-2-methyl-1,4-oxathiins and the corresponding sulfoxides and sulfones. The reagent gases, hydrogen, methane and isobutane were employed. The elimination of HX from the protonated molecular ion $(RCOXH)^+$ was observed as a major fragmentation process in these compounds. For the sulfides and sulfones, with X ranging from -OH to $-N(CH_3)C_6H_5$, it was observed that the elimination reaction is inversely correlated with the proton affinity of the departing HX molecule in both the H_2 and CH_4 CI spectra. No consistent correlation was observed for sulfoxides which could be attributed to the competing fragmentation reactions. In the isobutane CI spectra, only $(RCOXH)^+$ ions were observed for most of the compounds. It was also suggested that the departing neutral HX need not be a small molecule.

More recently Leung and Harrison[111] have demonstrated the specific substituent effects in the elimination of HX (X = halogen) from the halo-benzene derivatives under CI conditions. The HX elimination from $(MH)^+$ ions of several substituted halo-benzenes, was shown to occur only when a substituent is meta to the leaving group (halogen). These workers have concluded that substituents can alter the carbon-halogen (C-X) bond dipole.

In the present study the elimination of HX was observed in compounds 22-24, whose CI spectra were recorded using methane as reagent gas. It is a general observation that the H_2 and CH_4 chemical ionization mass spectra show extensive fragmentation

processes with less abundant or no protonated molecular ions. The corresponding isobutane CI spectra exhibit very abundant $(MH)^+$ ions and are relatively less complicated. In H_2 and CH_4 CI spectra the fragmentation reactions precede with relatively more exothermicity.

The ions formed by HX elimination further fragment by the following modes. (i) The elimination of neutral benzene molecule and (ii) rearrangement to form diphenyl methyl cations. The mechanism of formation of these ions in compounds 22-24, may be similar to that proposed for the corresponding nitro compound (3).

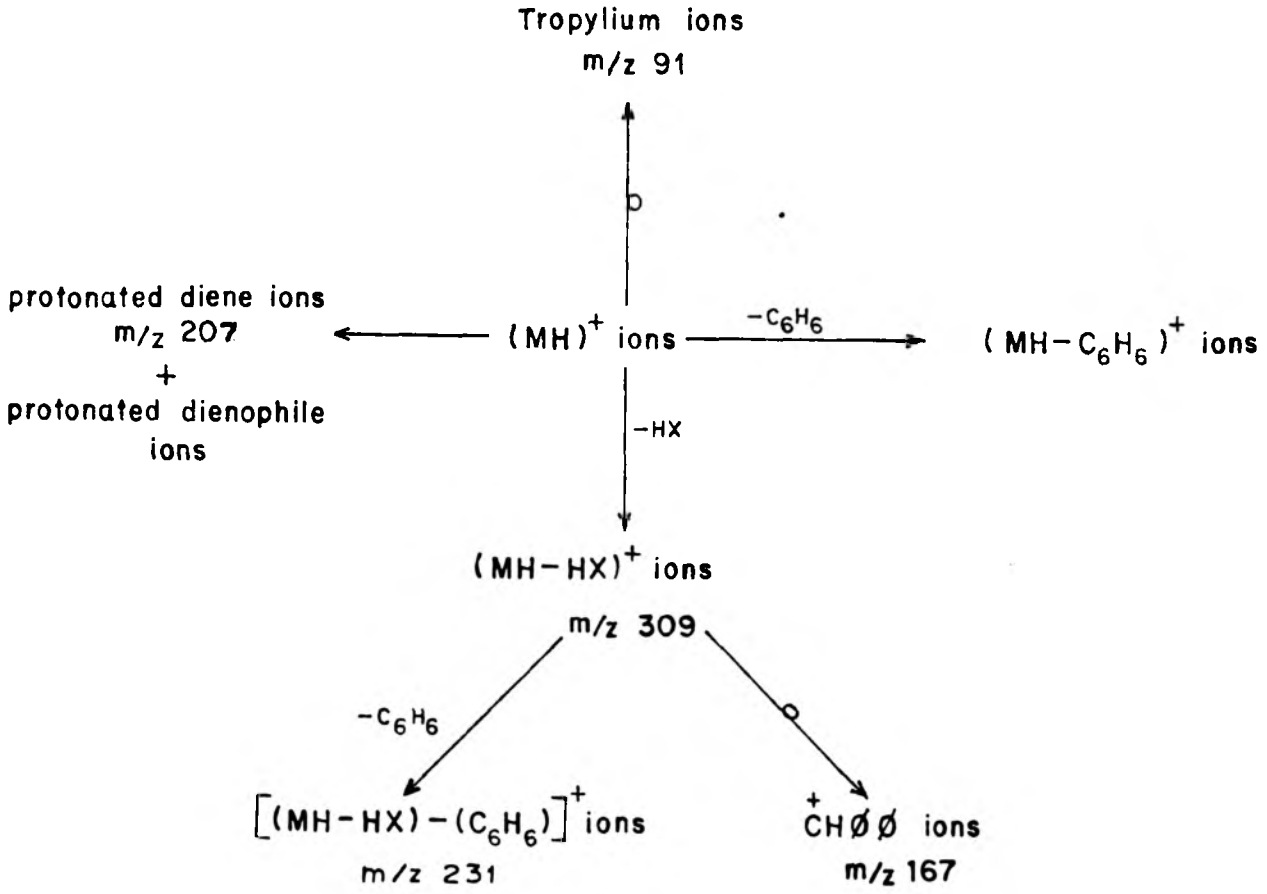
Compounds 25-27 and 29 do not readily lose HX from their protonated molecules. Their protonated molecular ions fragment by the elimination of a neutral benzene molecule. This fragmentation mode is relatively insignificant in the other compounds. The formation of $(MH-C_6H_6)^+$ ions in the above compounds indicates the initial protonation on one of the phenyl groups followed by a simple cleavage reaction. The $(MH)^+$ ions of ester analog lose methanol[112] [m/z 337 (5.0), Fig.7]. In compound 26, no loss of water was observed from the MH^+ ions. The protonated molecular ions of 22 lose tropylium radicals to give an ion at m/z 235 (6,0, Fig.6). The 3,5,6-triphenyl-Δ^1-cyclohexene-4-carboxaldehyde (25) shows the loss of molecule of water. Aldehydes and ketones under CI conditions[113,114] are known to lose water.

The Retro Diels-Alder reaction results in the formation of protonated diene and dienophile ions in these compounds. Protonated dienophile ions are observed in compounds with $-NH_2$, -OH, -CHO, -COOMe and -CN substituents. It is the base peak in the spectrum of compound 25. The formation of tropylium cations (m/z 91) is observed in the CI spectra of all the compounds. The general fragmentation processes observed in these compounds are shown in Scheme 14.

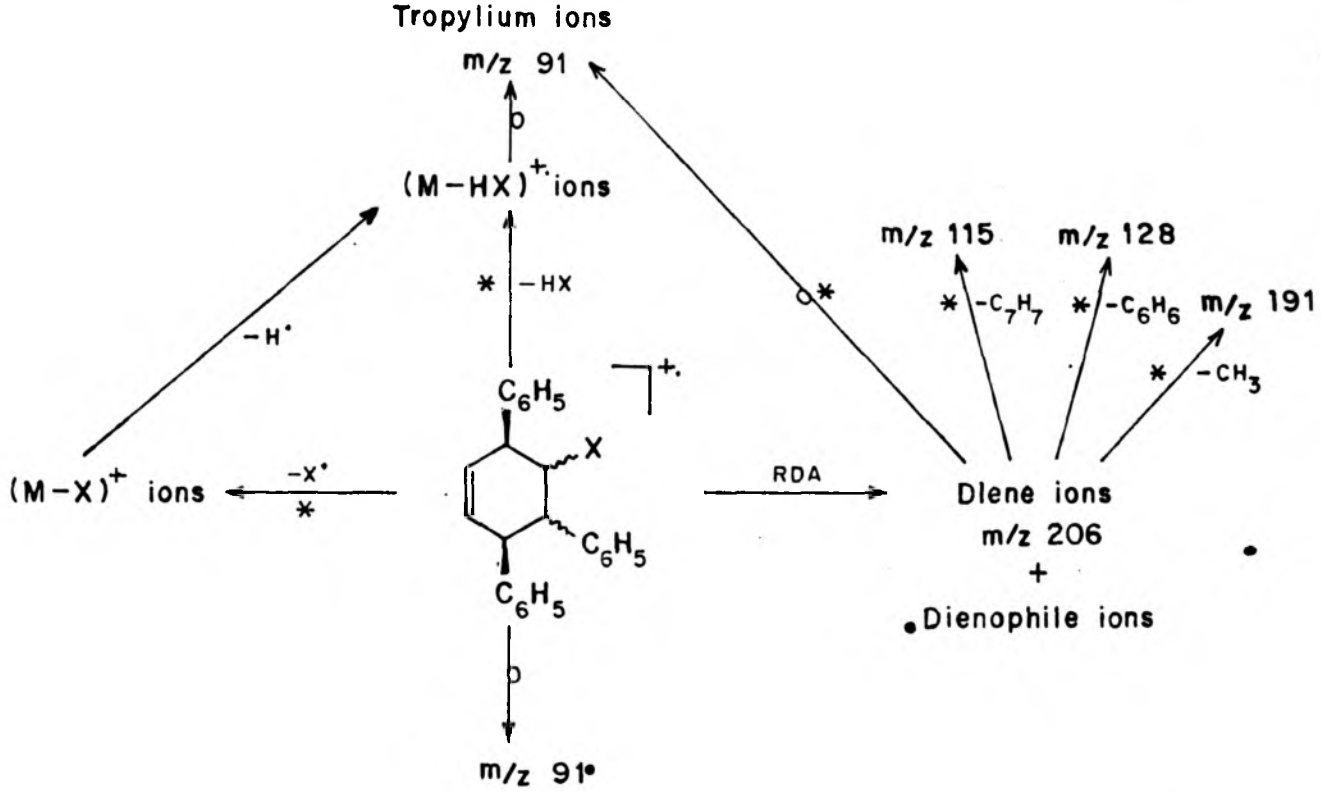
The EI spectra of these compounds were examined. The major fragments are shown in Table VI. All these molecules except 22, fragment by RDA reaction, which gives rise to the base peak in their spectra. Dienophile ion forms the base peak in 22. Molecular ions are insignificant except in compound 26. The $M^{+\cdot}$ ions lose X and HX. The ion at m/z 91 is abundant. The general fragmentation modes observed in the EI spectra are shown in Scheme 15.

3. MIKE data on $(M-NO)^+$ and $(M-HNO_2)^{+\cdot}$ ions and CA spectra of $(M-NO)^+$ ions generated from compounds 3 and 4 under EI conditions.

In the electron impact spectra of the 3,5,6-triphenyl-4-nitro-Δ^1-cyclohexenes (3 and 4, Scheme 1) the ions corresponding to $(M-NO)^+$ and $(M-HNO_2)^{+\cdot}$ are abundant. The elimination of nitric oxide (NO) from the molecular ions is a characteristic fragmentation mode observed in the EI spectra of aromatic nitro compounds. The elimination of nitric oxide is followed by the expulsion of



SCHEME-14



SCHEME-15

(* metastable ions observed in normal 70 eV

Table VI

Partial EI spectra[a] of compounds 23-30[b]

Compd.No.	$M^{+\cdot}$	$(M-X)^{+}$	$(M-HX)^{+\cdot}$	Diene ion m/z 206	Dienophile ion	Rearrangement ion m/z 167	Tropylium ion
22	-	-	-	25.0	100.0	-	18.0
23	2.0	6.0	25.0	100.0	-	3.0	35.0
24	0.8	-	0.5	100.0	5.0	-	30.0
25	1.8	1.8	-	100.0	-	3.0	75.0
26	13.0	3.0	4.0	100.0	-	3.0	45.0
27	2.6	3.0	1.3	100.0	-	2.0	20.0
28	0.5	1.1	1.0	100.0	-	3.0	26.0
29	0.3	-	-	100.0	22.0	-	40.0
30	0.2	-	0.2	100.0	19.0	2.0	40.0

a : The relative intensity expressed % to the base peak and recorded at 70 eV.

carbon monoxide[75,115]. In the present system the loss of NO is followed by the expulsion of $OH^{\cdot}$ and water molecule. The loss of carbon monoxide was not observed from the $(M-NO)^+$ ions. As mentioned earlier the $(M-NO)^+$ and $(M-HNO_2)^{+\cdot}$ ions are the precursors of the diphenyl methyl cations under electron ionization. A study of the mass analyzed ion kinetic energy (MIKE) spectra[116] of the $(M-NO)^+$ and $(M-HNO_2)^{+\cdot}$ ions was undertaken to understand the fragmentation reactions of these ions. In the absence of model compounds from which ions of known structure could be generated for comparison, no attempt was made to obtain evidence on the structure of $(M-NO)^+$ and $(M-HNO_2)^{+\cdot}$ ions.

All the metastable ions decomposing in the first field free region of a conventional double focusing mass spectrometer can be focused by scanning the voltage of the electrostatic analyser (ESA). This gives the ion kinetic energy (IKE) spectrum. If the ion is preselected by the magnetic sector, its decomposition can be studied by the MIKE technique. Modern instruments with reverse geometry are ideally suited for such measurements.[117,11]

The MIKE spectra* of $(M-NO)^+$ and $(M-HNO_2)^{+\cdot}$ ions generated from 3,5,6-triphenyl-4-nitro-Δ^1-cyclohexene (3) were recorded

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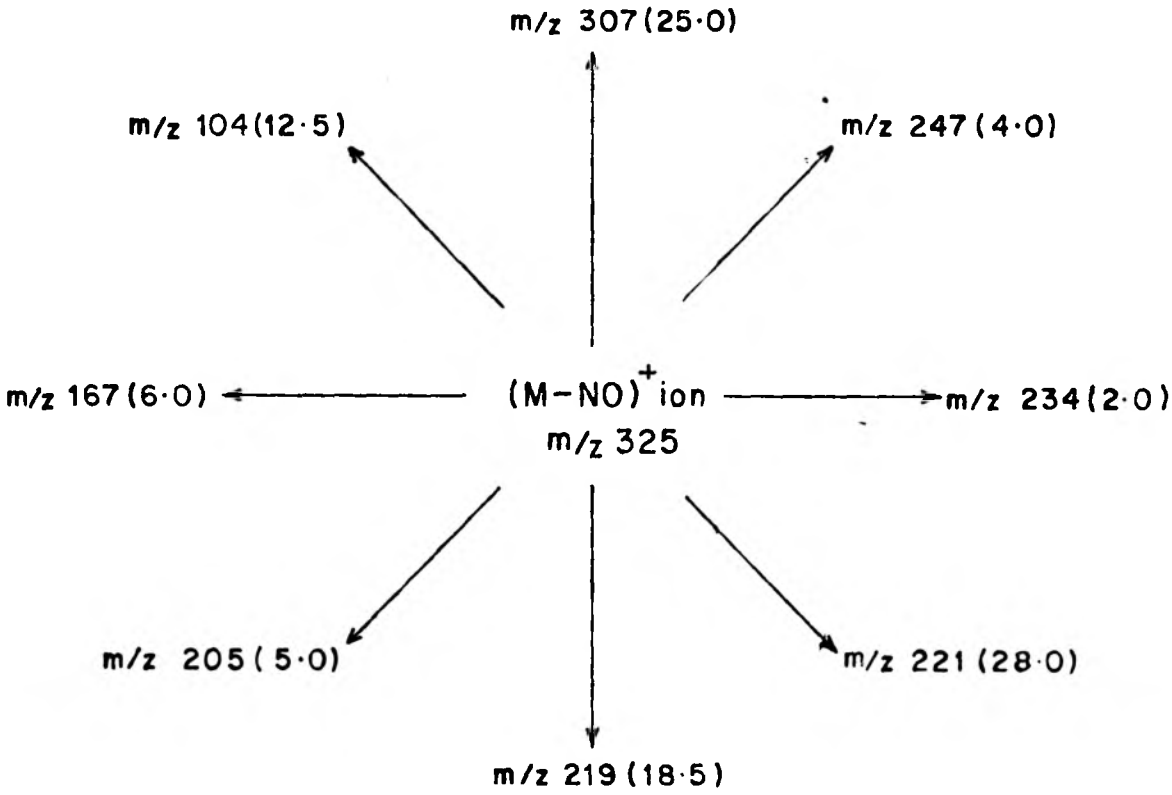
* The author is grateful to Dr. B. Schladach, Universitat Bielfeld, Bielfeld, West Germany.

by high voltage scan method and are shown in Scheme 16 and 17. The MIKE spectrum of $(M-NO)^+$ ion from compound 3 showed that eight competing decomposition pathways are operating. Elimination of molecules of water and benzene and tropylium radicals was observed from these ions. An ion at m/z 205 is presumably formed by a RDA reaction preceding a hydride shift. The transition for the formation of the skeletal rearrangement ion corresponding to diphenyl methyl cation was observed. An abundant ion was also observed at m/z 219 which can arise by the loss of benzaldehyde from the $(M-NO)^+$ ions. The expulsion of styrene molecule results in the formation of an ion at m/z 221. This reaction appears to be a simple cleavage reaction which may precede hydride transfer rearrangement. The ion corresponding to styrene (m/z 104) was observed in the spectrum.

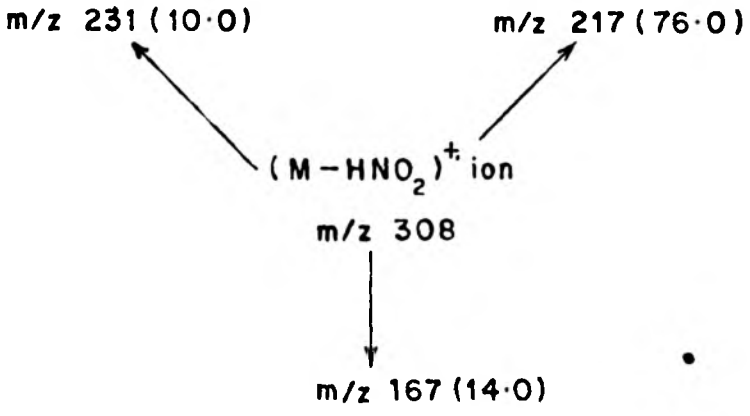
The MIKE spectrum of $(M-HNO_2)^{+\cdot}$ ion of compound 3 is relatively simple and has shown only three competing fragmentation modes (Scheme 17). Elimination of phenyl and tropylium radicals and formation of skeletal rearrangement ion give ionic signals at m/z 231, 217 and 167.

The collisional activation[34] (CA) is a technique to obtain evidence on the structure of non-decomposing ions in the gaseous phase. The CA spectrum of the ion under



SCHEME-16

(Figures in parantheses refer to the relative intensities of the ions expressed as a sum of total ionization)



SCHEME-17

study is compared with that of an ion of known structure formed either by direct ionization or fragmentation.

Any ion formed in the source is selected by means of magnetic sector. It is then introduced into the collision chamber where it collides with the neutral collision gas. As a result of this the ions acquire high internal energy, which promote further unimolecular ion decompositions[119] to give a CA or CID (collision induced dissociation) spectrum of the ion under investigation. The spectrum often resembles 70 eV mass spectrum.

The CA spectra* of $(M-NO)^+$ ions generated from isomeric 3,5,6-triphenyl-4-nitro-Δ^1-cyclohexene (3 and 4) were measured using nitrogen as collision gas. The fragment ions formed are shown in Table VII. The major decomposition pathways of $(M-NO)^+$ ion from compound 3 are indicated in Scheme 18.

The CA spectrum of $(M-NO)^+$ ion from compound 3 is complex and exhibit nineteen competing fragmentation pathways. All the dissociation processes which are observed in the MIKE spectrum are also observed in the corresponding CA spectrum.

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* The author is indebted to Prof. K. Levsen, Institute fur Physikalische, Universitat Bonn, West Germany.

Table VII

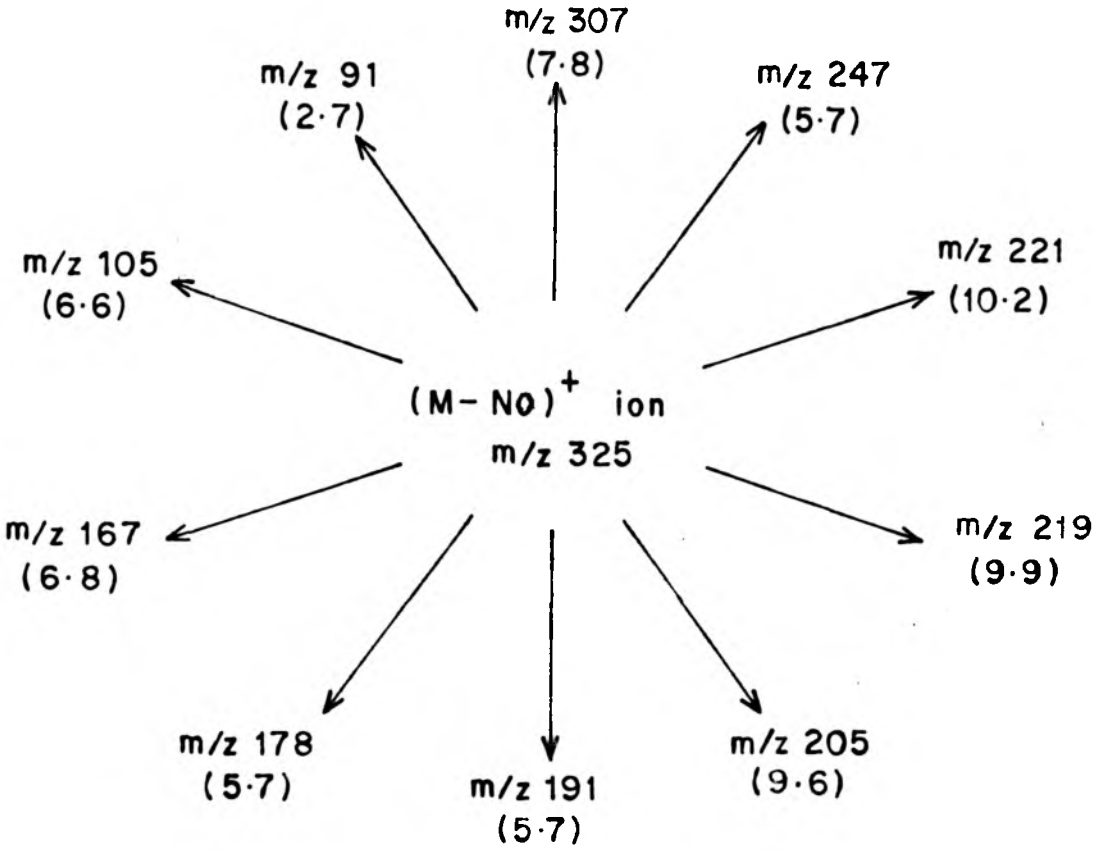
CA spectra[a] of $(M-NO)^+$ ions (m/z 325) from 3 and 4[b]

m/z	c		m/z	c	
	3	4		3	4
307	7.8	14.0	180	-	4.3
290	2.7	-	179	-	4.8
288	-	4.8	178	5.7	-
247	5.7	6.7	177	-	4.3
234	3.3	7.2	167	6.8	8.9
232	-	6.4	152	2.7	-
221	10.2	20.4	142	1.8	-
219	9.9	-	128	2.1	-
205	9.6	8.4	115	2.7	-
203	-	10.8	105	6.6	4.0
202	7.5	-	91	2.7	2.8
191	5.7	6.0	77	1.2	2.4
189	5.4	-			

a : The spectra recorded at 70 eV using nitrogen as collision gas.

b : Refer to Scheme 1

c : Ion abundances are given as percent of total ionization.



SCHEME 18

(Figures in parantheses refer to the relative abundances expressed as a sum of total ionization)

Conclusion

From the studies on the CI spectra of a series of triphenyl nitrocyclohexenes, the following conclusions have been drawn:

(i) The relatively less intensity of $(MH)^+$ ion is due to the elimination of a molecule of nitrous acid which is facilitated by anchimeric assistance, homoallylic participation and an E_1 type elimination.

(ii) The $(MH-HNO_2)^+$ ion undergoes fragmentation with and without rearrangement. The cis elimination of arene molecule takes place from the unrearranged ion. The rearranged ions undergo skeletal rearrangements which are very rare under CI conditions.

(iii) When the C_4-substituents 'X' is protonated, it is lost as HX. The resulting carbonium ion undergoes skeletal rearrangement. If the initial protonation takes place on alternate sites retro Diels-Alder fragmentation mode is favoured.

D. EXPERIMENTAL

The electron impact spectra were recorded on Dupont CEC-21-110B double focusing mass spectrometer at 70 eV. The samples were introduced through the direct inlet system and vaporised at temperatures ranging from 120-220°C. The beam monitor was steady during recording. All the spectra were checked for reproducibility. The CI spectra of all the compounds were recorded on a Finnigan Mass Spectrometer 3200, using methane and isobutane as reagent gases. The pressure was maintained at 1 torr. The temperature of the ionization chamber was between 140-214°C.

All the substituted cyclohexene derivatives were prepared by known procedures. Purity of all the compounds was checked by TLC in two different solvent systems. They were unequivocally characterized by spectral and analytical methods. The melting points were determined in electrically heated silicone oil melting point apparatus and are uncorrected. NMR spectra were recorded on a Varian T-60 spectrometer using CCl_4 and $CDCl_3$ as solvents and TMS as internal standard. IR spectra were recorded on a Perkin-Elmer Infracord spectrophotometer.

Trans- trans-1,4-Diphenyl-1,3-butadiene

86 g of phenyl acetic acid, 84 g of freshly distilled cinnamaldehyde, 70 g of powdered litharge and 89 ml of freshly distilled acetic anhydride were placed in a 500 ml round bottomed

flask fitted with a reflux condensor and a $CaCl_2$ guard tube. The reaction mixture was refluxed for 5 hours on an oil bath at 140-150°C. During the first half an hour the flask was heated gently and shaken several times. It was then poured into a 500 ml beaker while still hot and kept overnight. The contents were stirred and filtered. The solid was washed twice with 30 ml portions of cold ethanol. The solid was transferred to a beaker, stirred with 40 ml of ethanol, filtered, washed again with 30 ml of ethanol and dried in a vacuum desiccator. Light yellow flakes, 40 g. Decolourized by activated charcoal in benzene solution. The benzene filtrate after cooling was treated with 250 ml of hot ethanol, heated to boiling and cooled to 10°C with occasional shaking. Colourless flakes separated out, which were filtered and washed with 40 ml of cold ethanol. Yield, 32 g. MP, 153°. Lit.,[120] 152-153.5°.

Trans-trans-1-p-chlorophenyl-4-phenyl-1,3-butadiene

It was prepared by the Wittig reaction. Cinnamyl triphenyl phosphonium bromide was treated with p-chlorobenzaldehyde in the presence of lithium ethoxide in absolute ethanol. The cinnamyl triphenyl phosphonium bromide was prepared from cinnamyl bromide and triphenyl phosphine.

Cinnamyl bromide

Cinnamyl bromide was prepared according to a reported procedure[121]. 10 g of freshly distilled cinnamyl alcohol and 30 g of 48% hydrobromic acid were taken in a 100 ml round

bottomed flask and the contents were stirred by a mechanical stirrer at room temperature for 3 1/2 hours. A heavier liquid collected at the bottom. It was extracted with 50x2 ml of ether and washed with water to remove hydrobromic acid. The ethereal layer was dried over anhydrous magnesium sulfate for 10 mts. Removal of ether gave a brown residue. It was distilled under reduced pressure. A pale yellow liquid, 10.5 g; BP, 95°/5 mm.

Cinnamyl triphenyl phosphonium bromide

10 g of freshly distilled cinnamyl bromide, 18.2 g of triphenyl phosphine and 100 ml of benzene were taken in a 250 ml round bottomed flask fitted with a reflux condensor and a calcium chloride guard tube. The contents were refluxed on a water bath for 2 1/2 hours. A solid separated on cooling. It was filtered and washed several times with cold benzene. Colourless crystals, 26 g. MP, 247°. Lit.,[122] 249°.

Trans-trans-1-p-chlorophenyl-4-phenyl-1,3-butadiene

A procedure described by McDonald and Campbell[123] was followed. 24 g of triphenyl cinnamyl bromide and 8.4 g of p-chlorobenzaldehyde were dissolved in 75 ml of absolute ethanol. 280 ml of 0.2M lithium ethoxide in ethanol was added to the contents with continuous stirring. A light orange colour developed immediately which was followed by the formation of leaflets. The contents were allowed to stand at room temperature for half an hour. 280 ml of water was added and cooled to 15°C.

The colourless crystals separated were filtered, washed with 75 ml of 60% ethanol and dried in the vacuum. Colourless crystals, 16 g. MP, 158°. Lit.,[124] 161°.

Nitro ethylene

It was prepared from 2-nitroethanol by dehydration[125].

2-Nitroethanol

2-Nitroethanol was prepared according to a procedure reported by Hopff and Capaul[126]. 50 ml of freshly distilled nitromethane and 2.5 g of paraformaldehyde were taken in a 100 ml round bottomed flask and heated to boiling. 50 mg of potassium carbonate was added and the contents were refluxed for 3.5 hours on a water bath with occasional shaking. The reaction mixture was cooled, acidified with concentrated hydrochloric acid and filtered. The excess of nitromethane was distilled off on a water bath and the reddish brown residue obtained was distilled under reduced pressure. The fraction boiling at 82-85°/3 mm was collected. Yield, 4.6 g. Lit.,[127] BP, 102°/11 mm.

Nitroethylene

It was prepared by dehydration from 2-nitroethanol in the presence of phthalic anhydride[125]. 4.0 g of 2-nitroethanol and 7.0 g of phthalic anhydride were taken in a small 25 ml pear shaped flask to which a distillation condensor was attached. It was evacuated to 80 mm using a pump. The contents were then

heated on an oil bath at 140-150°. When the mixture became homogeneous, the bath temperature was raised slowly to 175° and held at that temperature until distillation ceased. Nitroethylene was dried over anhydrous $CaCl_2$ and redistilled. The fraction boiling at 40°/90 mm was collected. A light yellow liquid. Yield, 3.5 g. Lit.,[125] BP, 38-39°/80 mm.

Trans-β-nitrostyrene

10.6 g of benzaldehyde and 6.1 g of nitromethane were placed in a 100 ml three-necked flask fitted with a mechanical stirrer and a thermometer. The flask with the contents was kept in freezing mixture. 20 ml of methanol was added to the flask. When the temperature was below 5° a solution of 4.2 g of sodium hydroxide in 10 ml of water (cooled to 10°) was added in small quantities so that the temperature of the mixture was kept between 10 to 15°. After the addition was over, it was allowed to stand for 15 minutes. 60 ml of cold water containing some crushed ice was added and this solution was added to 20 ml cold concentrated hydrochloric acid diluted with 30 ml ice water. The precipitate formed was filtered, dried and crystallized from methanol. Yellow needles, 10.5 g. MP, 56-57°. Lit.,[128] 57-58°

3,6-Diphenyl-4-nitro-Δ^1-cyclohexenes (1 and 2)

2 g of 1,4-diphenyl-1,3-butadiene, 0.35 g of nitroethylene, 25 mg of hydroquinone and 2.5 ml of benzene were taken in a thick walled glass tube. It was sealed at -20°. The contents

were heated for 20 hours in an oven at 120°. The tube was cooled in liquid nitrogen and opened carefully. The reaction mixture showed the presence of two compounds as evidenced by TLC (in 1:1 benzene petroleum solvent system). The crude reaction mixture was chromatographed on 100 g of silica gel. Elution with petroleum ether gave 0.6 g of unreacted diene. Elution with 20% benzene in petroleum ether gave the two isomers of 3,6-diphenyl-4-nitro-Δ^1-cyclohexene.

Isomer A (1) was a pale yellow thick liquid.

Yield, 0.85 g. BP, 225°/5 mm. Lit.,[22] 220°/5 mm.

MW (mass spectrum), 279.

IR (CCl_4) 1560, 1370 (C-NO_2).

NMR (CCl_4) 2.88 (m, 10H, aromatic protons), 4.13 (s, 2H, H-1 and H-2), 5.6 (m, 1H, H-4), 5.9 (d, 1H, H-3), 7.5 (m, 2H, H_2-5), 6.4 (m, 1H, 6-H).

Isomer B (2) was crystallized from benzene-petroleum ether, colourless crystals, 0.45 g. MP, 121°. MP, 121° Lit.,[22] 122°.

MW (mass spectrum), 279.

IR (CCl_4) 1560, 1370 (C-NO_2).

NMR (CCl_4) 2.7 (m, 10H, aromatic protons), 4.03 (s, 2H, H-1 and H-2), 5.1 (m, 1H, H-4), 5.17 (m, 1H, H-3), 7.81 (m, 2H, H_2-5), 6.45 (m, 1H, H-6).

3,5,6-Triphenyl-4-nitro-Δ^1-cyclohexenes (3,4) and 3,6-diphenyl-5-aryl-4-nitro-Δ^1-cyclohexenes (5-16) were prepared by Diels-Alder reaction between 1,4-diphenyl-1,3-

butadiene and substituted β-nitroethylenes. The procedure for the preparation of 3 and 4 is described in detail. This procedure was adopted to prepare the other compound 5-16.

3,5,6-Triphenyl-4-nitro-Δ^1-cyclohexenes (3 and 4)

6 g of trans- trans-1,4-diphenyl-1,3-butadiene, 4 g of trans-β-nitrostyrene[128], 20 ml of o-dichlorobenzene and 25 mg of hydroquinone were placed in a 100 ml round bottomed flask fitted with a reflux condensor and a $CaCl_2$ guard tube. The contents were refluxed on an oil bath for 12 hours at 190-195°. The o-dichlorobenzene was removed under reduced pressure. The residue was chromatographed on 400 g of silica gel. Elution with petroleum ether gave 0.5 g of unreacted diene. Elution with 20% benzene-petroleum ether followed by 25% benzene-petroleum ether gave the isomeric compounds 3 and 4.

Isomer A (3), 2.7 g, was recrystallized from benzene-petroleum ether. Colourless crystals, 2.5 g. MP, 157°. Lit.,[129] 159°.

MW (mass spectrum), 355.

IR (nujol) 1560, 1360 (C-NO_2).

NMR ($CDCl_3$) 3.1 (m, 15H, aromatic protons), 4.02 (s, 2H, H-1 and H-2), 4.9 (dd, 1H, H-4), 5.77 (d, 1H, H-3), 5.98 (q, 1H, H-5), 6.2 (bs, 1H, H-6).

Isomer B, 2.3 g, was recrystallized from benzene-petroleum ether, colourless crystals, 2.0 g. MP, 170°. Lit.,[129] 169°.

MW (mass spectrum), 355.

IR (nujol) 1550, 1360 (C-NO_2).

NMR ($CDCl_3$) 2.9 (m, 15H, aromatic protons), 4.0 (s, 2H, H-1 and H-2), 4.55 (q, 1H, H-4), 5.75 (q, 1H, H-3), 6.75 (t, 1H, H-5), 6.4 (d, 1H, H-6).

3,6-Diphenyl-5-(p-tolyl)-4-nitro-Δ^1-cyclohexenes (5 and 6)

2.4 g of 1,4-diphenyl butadiene, 1.6 g of p-methyl-β-nitrostyrene[130], 25 mg of hydroquinone and 10 ml of o-dichlorobenzene were refluxed for 12 hours. Similar reaction conditions and work-up procedure were followed as described above. The product was chromatographed on 200 g of silica gel. The unreacted diene (0.2 g) was obtained by elution with petroleum ether. Elution with 20% benzene in petroleum ether gave isomer A (5), while the other isomer (6) was eluted with 30% benzene-petroleum ether.

Isomer A, 1.3 g was recrystallized from benzene-petroleum ether, colourless crystals, 1.0 g. MP, 135°, Lit.,[22] 142°.

MW (mass spectrum), 369.

IR ($CHCl_3$) 1560, 1370 (C-NO_2).

NMR ($CDCl_3$) 3.2 (m, 14H, aromatic protons), 4.1 (s, 2H, H-1 and H-2), 5.05 (dd, 1H, H-4), 5.83 (d, 1H, H-3), 6.05 (q, 1H, H-5), 6.3 (bs, 1H, H-6).

Isomer B, 0.8 g was recrystallized from benzene-petroleum ether, colourless crystals, 0.71 g, MP, 130°, Lit.,[22] 135°.

MW (mass spectrum), 369.

IR ($CHCl_3$) 1560, 1365 (C-NO_2).

NMR ($CDCl_3$) 2.96 (m, 14H, aromatic protons), 4.1 (s, 2H, H-1 and H-2), 4.67 (q, 1H, H-4), 5.84 (q, 1H, H-3), 6.92 (t, 1H, H-5), 6.55 (d, 1H, H-6).

3,6-Diphenyl-5-(p-chlorophenyl)-4-nitro-Δ^1-cyclohexene (7 and 8)

2.4 g of 1,4-diphenyl butadiene, 1.8 g of p-chloro-β-nitrostyrene[130], 10 ml of o-dichlorobenzene and 25 mg of hydroquinone were refluxed for 12 hours. The solvent was removed from the reaction flask in vacuo and the residue was chromatographed on 200 g of silica gel. The unreacted diene (0.2 g) was obtained by eluting with petroleum ether. Elution with 20% benzene-petroleum ether gave pure isomers A and B. Isomer A (7), 1.8 g was recrystallized from benzene-petroleum ether, colourless crystals, 1.6 g. MP, 170°, Lit.,[22] 171.5°.

MW (mass spectrum), 389.

IR ($CHCl_3$) 1560, 1365 (C-NO_2), 760 (C-Cl).

NMR ($CDCl_3$) 3.06 (m, 14H, aromatic protons), 4.0 (s, 2H, H-1 and H-2), 5.11 (dd, 1H, H-4), 5.84 (d, 1H, H-3), 6.1 (q, 1H, H-5), 6.3 (bs, 1H, H-6).

Isomer B (8), 0.8 g was recrystallized from benzene-petroleum ether, colourless crystals, 0.6 g. MP, 194°. Lit.,[22] 196°.

MW (mass spectrum), 389.

IR ($CHCl_3$) 1560, 1370 (C-NO_2), 780 (C-Cl).

NMR ($CHCl_3$) 2.9 (m, 14H, aromatic protons), 4.02 (s, 2H, H-1 and H-2), 4.6 (q, 1H, H-4), 5.75 (q, 1H, H-3), 6.8 (t, 1H, H-5), 6.44 (d, 1H, H-6).

3,6-Diphenyl-5-(p-fluorophenyl)-4-nitro-Δ^1-cyclohexene (9 and 10)

2.5 g of 1,4-diphenyl butadiene, 1.68 g of p-fluoro-β-nitrostyrene[131], 25 mg of hydroquinone and 8 ml of o-dichlorobenzene were refluxed for 12 hours. After removing the solvent under reduced pressure the residue was chromatographed on 200 g of silica gel. Elution with petroleum ether gave unreacted diene (0.13 g). Isomer A was obtained by eluting with 15% benzene in petroleum ether, while isomer B was obtained with 20% benzene in petroleum ether. Isomer A (9), 1.5 g was recrystallized from ethyl acetate - petroleum ether, 1.1 g, MP, 155°. Lit.,[132] 154°.

MW (mass spectrum), 379.

IR (CCl_4) 1560, 1370 (C-NO_2), 1350 (C-F).

NMR (CCl_4) 3.1 (m, 14H, aromatic protons), 4.03 (s, 2H, H-1 and H-2), 5.1 (dd, 1H, H-4), 5.73 (d, 1H, H-3), 5.96 (q, 1H, H-5), 6.2 (bs, 1H, H-6).

Isomer B (10), 0.6 g. It was recrystallized from ethyl acetate - petroleum ether, 0.5 g. MP, 167°.

MW (mass spectrum), 379.

IR (CCl_4) 1560, 1365 (C-NO_2) 1360 (C-F).

NMR (CCl_4) 2.9 (m, 14H, aromatic protons), 4.C (s, 2H, H-1 and H-2), 4.53 (q, 1H, H-4), 5.7 (q, 1H, H-3), 6.73 (t, 1H, H-5), 6.43 (d, 1H, H-6).

3,6-Diphenyl-5-(p-bromophenyl)-4-nitro-Δ^1-cyclohexene (11 and 12)

p-Bromo-β-nitrostyrene[130] (2.3 g), 1,4-diphenyl butadiene (2.4 g), hydroquinone (25 mg) and o-dichlorobenzene (10 ml) were refluxed for 12 hours. The o-dichlorobenzene was removed by distillation under vacuum. The residue was chromatographed on 200 g silica gel. Elution with petroleum ether gave 0.16 g of diene. The two isomers were obtained in pure form by eluting with 20% benzene-petroleum ether.

Isomer A (11), 1.72 g was recrystallized from ethyl acetate-petroleum ether, colourless crystals, 1.5 g. MP, 164°.

MW (mass spectrum), 433.

IR (nujol) 1560, 1370 (C-NO_2), 560 (C-Br).

NMR (CCl_4) 2.96 (m, 14H, aromatic protons), 4.1 (s, 2H, H-1 and H-2), 5.1 (dd, 1H, H-4), 5.8 (d, 1H, H-3), 6.05 (q, 1H, H-5), 6.3 (bs, 1H, H-6).

Isomer B (12), 0.56 g was recrystallized from ethylacetate-petroleum ether, colourless crystals, 0.4 g. MP, 218°.

MW (mass spectrum), 433.

IR (nujol) 1560, 1370 (C-NO_2), 560 (C-Br).

NMR (CCl_4) 2.84 (m, 14H, aromatic protons), 4.0 (s, 2H, H-1 and H-2), 4.6 (q, 1H, H-4), 5.75 (q, 1H, H-3), 6.82 (t, 1H, H-5), 6.55 (d, 1H, H-6).

3,6-Diphenyl-5-(2-furyl)-4-nitro-Δ^1-cyclohexene (13 and 14)

2.5 g of 1-(2-furyl)-2-nitroethylene[133], 2.5 g of 1,4-diphenyl butadiene, 25 mg of hydroquinone and 10 ml of o-dichlorobenzene were refluxed for 12 hours. The solvent was removed under diminished pressure and the residue was chromatographed on 200 g of silica gel. Elution with petroleum ether yielded 0.2 g of unreacted diene. The pure isomers were eluted with 30% benzene-petroleum ether.

Isomer A (13) was crystallized from ether, colourless crystals, 1.2 g. MP, 134°.

MW (mass spectrum), 345.

IR (CCl_4) 1560, 1370 (C-NO_2).

NMR ($CDCl_3$) 3.2 (m, 13H, aromatic protons), 4.04 (s, 2H, H-1 and H-2), 5.44 (dd, 1H, H-4), 5.82 (d, 1H, H-3), 5.9 (q, 1H, H-5), 6.02 (bs, 1H, H-6).

Isomer B (14) was recrystallized from ether, colourless crystals, 1.0 g. MP, 165-166°.

MW (mass spectrum), 345.

IR (CCl_4) 1560, 1365 (C-NO_2).

NMR ($CDCl_3$) 2.96 (m, 13H, aromatic protons), 3.95 (s, 2H, H-1 and H-2), 4.6 (q, 1H, H-4), 5.76 (q, 1H, H-3), 6.6 (t, 1H, H-5), 6.25 (d, 1H, H-6).

3,6-Diphenyl-5-(2-thienyl)-4-nitro-Δ^1-cyclohexene (15)

2.5 g of 1-(2-thienyl)-2-nitroethylene[133], 2.5 g of 1,4-diphenyl butadiene, 25 mg of hydroquinone and 10 ml of o-dichlorobenzene were refluxed for 12 hours. After removing the solvent under vacuum, the residue was chromatographed on 200 g of silica gel. The unreacted diene (0.25g) was obtained by eluting with petroleum ether. The pure isomers were eluted with 40% benzene-petroleum ether.

Isomer A (15), was recrystallized from benzene-petroleum ether, colourless crystals, 1.3 g. MP, 183°.
MW (mass spectrum), 361.
IR (CCl_4) 1550, 1360 (C-NO_2).
NMR ($CDCl_3$) 2.83 (m, 10H, aromatic protons), 3.2 (m, 3H, thienylic protons), 4.08 (s, 2H, H-1 and H-2), 5.07 (dd, 1H, H-4), 5.64 (d, 1H, H-3), 5.8 (q, 1H, H-5), 6.1 (bs, 1H, H-6).

Isomer B was recrystallized from benzene-petroleum ether, colourless crystals, MP, 214°.

3,6-Diphenyl-5-(p-cyanophenyl)-4-nitro-Δ^1-cyclohexene (16)

A mixture of 2.4 g of 1,4-diphenyl butadiene, 1.75 g of p-cyano-β-nitrostyrene[134], 10 ml of o-dichlorobenzene and 25 mg of hydroquinone was refluxed for 12 hours. The solvent was removed in vacuo and the residue was chromatographed on 180 g of silica gel. Elution with petroleum ether gave 0.08 g of unreacted diene. Elution with 30% benzene-petroleum ether gave isomer A (16). Isomer B was

eluted with 1:1 benzene-petroleum ether.

Isomer A (16) was recrystallised from benzene-petroleum ether, colourless crystals, 2.1 g. MP, 175°. Lit.,[132] 177°.

MW (mass spectrum), 380.

IR ($CHCl_3$) 1560, 1370 (C-NO_2), 2215 (CN).

NMR ($CDCl_3$) 2.93 (m, 14H, aromatic protons), 4.0 (s, 2H, H-1 and H-2), 5.1 (dd, 1H, H-4), 3.82 (d, 1H, H-3), 6.05 (q, 1H, H-5), 6.3 (bs, 1H, H-6).

Isomer B was recrystallized from benzene-petroleum ether, colourless crystals, 1.0 g. MP, 211°.

3-p-Chlorophenyl-5,6-diphenyl-4-nitro-Δ^1-cyclohexene (17)

1.3 g of trans-trans-1-p-chlorophenyl-4-phenyl-1,3-butadiene, 0.7 g of trans-β-nitrostyrene[128], 25 mg of hydroquinone and 5 ml of o-dichlorobenzene were placed in a 20 ml round bottomed flask fitted with a reflux condensor and a $CaCl_2$ guard tube. The contents were refluxed on an oil bath for 24 hours at 200°. The o-dichlorobenzene was removed from the reaction flask by distillation under reduced pressure. TLC showed the presence of four new spots. The residue was chromatographed on 80 g of silica gel. Elution with petroleum ether gave 0.3 g of unreacted diene. The mixture of adducts were then eluted from the column with benzene. Yield, 1.3 g. TLC of this mixture in 1:1 benzene-petroleum ether showed the presence of 4 isomers.

It was again chromatographed on 50 g of silica gel. Elution with 10% benzene-petroleum ether gave Isomer A, 0.21 g. The other 3 isomers (isomers B, C and D) were not isolated in pure form. Only isomer A from this mixture was isolated in pure state. It was recrystallized from benzene-petroleum ether, colourless crystals, 0.19 g. MP, 229°.

MW (mass spectrum), 389.

IR (nujol) 1560, 1370 (C-NO_2).

NMR (CCl_4) 2.8 (m, 14H, aromatic protons), 3.96 (s, 2H, H-1 and H-2), 5.1 (dd, 1H, H-4), 5.63 (d, 1H, H-3) and 6.06 (m, 2H, H-5 and H-6).

Analysis calculated for $C_{24}H_{20}ClNO_2$; N, 3.6; Cl, 9.3.

Found: N, 3.7; Cl, 9.38%.

3-p-Chlorophenyl-5-p-cyanophenyl-6-phenyl-4-nitro-Δ^1-cyclohexene (18).

1.3 g of trans-trans-1-p-chlorophenyl-4-phenyl butadiene, 0.85 g of p-cyano-β-nitrostyrene[134] and 25 mg of hydroquinone were taken in a 20 ml round bottomed flask attached with a reflux condensor. 6 ml of o-dichlorobenzene was added to the flask and contents were refluxed for 24 hours at 200-205°. The o-dichlorobenzene was removed from the flask by distillation under reduced pressure. TLC of the residue showed the presence of 4 compounds. It was chromatographed on 90 g of silica gel. Elution with petroleum ether gave 0.15 g of unreacted diene. The isomeric mixture

was eluted from the column with benzene. Yield, 1.54 g. It was again chromatographed on 60 g of silica gel. Elution with 15% benzene-petroleum ether mixture gave isomer A. 0.32 g. The other isomers were not isolated in pure state.

The isomer A was crystallized from benzene-petroleum ether, colourless needles, 0.28 g. MP, 211°.
MW (mass spectrum), 414.
IR (CCl_4) 1560, 1365 (C-NO_2), 2220 (-CN).
NMR ($CDCl_3$) 2.96 (m, 13H, aromatic protons), 3.96 (s, 2H, H-1 and H-2), 4.93 (dd, 1H, 4H), 5.8 (d, 1H, H-3), 5.9 (q, 1H, not resolved, H-5), 6.16 (bs, 1H, overlaped with 5H proton, H-6).
Analysis calculated for $C_{25}H_{19}ClN_2O_2$; N, 6.7; Cl, 8.4.
Found: N, 6.5; Cl, 8.7%.

3-p-Chlorophenyl-5-p-fluorophenyl-6-phenyl-4-nitro-Δ^1-cyclohexene (19).

A mixture of 0.8 g of trans-p-fluoro-β-nitrostyrene[131], 1.3 g of trans,trans-1-p-chlorophenyl-4-phenyl-1,3-butadiene, 25 mg of hydroquinone and 6 ml of o-dichlorobenzene were refluxed for 24 hours at 200°. The solvent was removed by distilling under reduced pressure. The TLC of the residue (in 6:4 benzene-petroleum ether) showed the presence of 4 isomers. It was chromatographed on 80 g of silica gel. The unreacted diene (0.2 g) obtained on the elution with petroleum ether. The mixture of adducts was obtained by eluting the

column with benzene. Yield, 1.35 g. This was rechromatographed on 50 g of silica gel. Elution with 10% benzene-petroleum ether yielded isomer A, 0.24 g. The other three isomers were not isolated. The isomer A was recrystallized from ethyl acetate-petroleum ether, 0.20 g, colourless needles, MP, 198°. MW (mass spectrum), 407.

IR ($CHCl_3$) 1570, 1360 (C-NO_2).

NMR ($CDCl_3$) 3.0 (m, 13H, aromatic protons), 4.0 (s, 2H, H-1 and H-2), 5.03 (dd, 1H, H-4), 5.76 (d, 1H, H-3), 5.93 (q, 1H, merged with 6-H, H-5), 6.13 (bs, 1H, H-6).

Analysis calculated for $C_{24}H_{19}ClFNO_2$; N, 3.44; Cl, 8.86; F, 3.7. Found: N, 3.2; Cl, 8.6; F, 3.9%.

3-p-Chlorophenyl-5-(2-thienyl)-6-phenyl-4-nitro-Δ^1-cyclohexene (20).

0.78 g of 1-(2-thienyl)-2-nitroethylene [133], 1.3 g of trans,trans-1-p-chlorophenyl-4-phenyl butadiene, 25 mg of hydroquinone and 5 ml of o-dichlorobenzene were taken in a 20 ml round bottomed flask. The contents were heated on oil bath at 200°C for 24 hours. The o-dichlorobenzene was removed from the reaction flask by distilling it under suction. The TLC of the residue (in 7:3 benzene:petroleum ether solvent system) showed the presence of 4 isomers. It was chromatographed on 80 g of silica gel. The elution with petroleum ether afforded unreacted diene (0.18 g). Elution with benzene gave the mixture of adducts, 1.26 g. It was rechromatographed

on 50 g of silica gel. Elution with 15% benzene-petroleum ether gave isomer A, 0.19 g. No attempt was made to separate the other three isomers. Isomer A was recrystallized from ethyl acetate-petroleum ether, 0.16 g, colourless crystals, MP, 241°.

MW (mass spectrum), 395.

IR ($CHCl_3$) 1560, 1370 (C-NO_2).

NMR ($CDCl_3$) 2.87 (m, 9H, aromatic protons), 3.3 (m, 2H, thienylic protons), 3.96 (d, 1H, β-proton of thienyl group), 4.01 (s, 2H, H-1 and H-2), 5.06 (dd, 1H, H-4), 5.6 (d, 1H, H-3), 6.0 (m, 2H, H-5 and H-6).

Analysis calculated for $C_{22}H_{18}ClSNO_2$; N, 3.54; Cl, 8.86; S, 8.1. Found: N, 3.45; Cl, 8.9; S, 8.3%.

The procedures for compounds 21, 22 to 24 are given in Chapter III of this volume.

3,5,6-Triphenyl-Δ^1-cyclohexene-4-carboxaldehyde (25).

It was prepared by a Diels-Alder reaction between 1,4-diphenyl-butadiene and cinnamaldehyde. 2.0 g of trans-trans-1,4-diphenyl-butadiene, 1.2 g of freshly distilled cinnamaldehyde, 25 mg of hydroquinone and 7.5 ml of xylene were taken in a hard glass tube. It was sealed with the help of an oxygen torch. The contents were heated at 180° (oven temp.) for 24 hours. After cooling in ice bath the tube was opened and the solvent was removed by distillation under suction. The TLC of the residue showed the presence of a new compound. It was chromatographed on 120 g of silica

gel. Elution with petroleum ether gave 0.8 g of unreacted diene. The DA adduct was obtained from the column by the elution with 10% benzene-petroleum ether. Yield, 0.558 g. TLC of this compound in benzene-petroleum ether (4:6) solvent system showed a single spot. It is isomer A. It was recrystallized from petroleum ether, 0.5 g, colourless crystals. MP, 113°.

MW (mass spectrum), 338.

IR (nujol) 1715 (-CHO), 2650 (C-H of -CHO group).

NMR (CCl_4) 3.2 (m, 15H, aromatic protons), 4.1 (s, 2H, H-1 and H-2), 6.1 (m, 4H, H-3, H-4, H-5 and H-6), 0.8 (d, 1H, -CHO, J = 3 Hz).

Analysis calculated for $C_{25}H_{22}O$; C, 88.76; H, 6.509.

Found: C, 88.5; H, 6.7%.

3,5,6-Triphenyl-Δ^1-cyclohexene-4-carboxylic acid (26)

It was prepared from the corresponding aldehyde (25) by oxidation using silver oxide. A method described by Clarke et al.[135] was followed. A solution of 0.5 g of silver nitrate in 1 ml of water was taken in a 20 ml round bottomed flask. 0.25 g of sodium hydroxide dissolved in 1 ml of water was added to the flask with vigorous stirring. After the addition the mixture was stirred for additional 5 minutes. Suspension of silver oxide in solution was obtained. It was cooled in ice bath and then 0.34 g of 3,5,6-triphenyl-Δ^1-cyclohexene-4-carboxaldehyde was added to the reaction flask

in portions with stirring. The addition was completed in 15 minutes. The black silver suspension was removed by filtration. It was washed several times with hot water. The cold combined filtrate was acidified with 1:1 dilute hydrochloric acid. A white precipitate obtained. It was filtered and dried, 0.18 g. Recrystallized from aqueous ethanol, 0.15 g, colourless crystals. MP, 228°.

MW (mass spectrum), 354.

IR (nujol) 1700 (-CO), 2560 (-OH).

NMR (CCl_4) 3.2 (m, 15H, aromatic protons), 4.1 (s, 2H, H-1 and H-2), 6.8 (m, 4H, H-3, H-4, H-5 and H-6), 0.6 (bs, 1H, -COOH).

Analysis calculated for $C_{25}H_{22}O_2$; C, 84.74; H, 6.216.

Found: C, 84.9; H, 6.1%.

3,5,6-Triphenyl-4-carbomethoxy-Δ^1-cyclohexene (27 and 28)

Prepared by Diels-Alder reaction between trans-trans-1,4-diphenyl butadiene and methyl cinnamate. 1.0 g of 1,4-diphenyl-1,3-butadiene, 0.8 g of methyl cinnamate, 25 mg of hydroquinone and 5 ml of benzene were taken in a hard glass tube. It was sealed and the contents were heated at 160° for 48 hours. The tube was cooled and opened. The solvent was removed by distillation. The TLC of the residue (in benzene solvent system) showed the presence of two isomers. It was chromatographed on 75 g of silica gel. Elution with petroleum ether provided 0.35 g of unreacted diene. The mixture of adducts was obtained from the column by elution with benzene.

A pale yellow solid, 0.61 g. It was rechromotographed on 30 g of silica gel. Elution with 15% benzene-petroleum ether gave isomer A. Isomer B was obtained by eluting the column with 20% benzene-petroleum ether.

Isomer A (27), 0.46 g was recrystallized from benzene-petroleum ether, colourless needles, 0.4 g. MP, 148°.

MW (mass spectrum), 368.

IR (CCl_4) 1725 (-CO).

NMR (CCl_4) 3.06 (m, 15H, aromatic protons), 4.03 (s, 2H, H-1 and H-2), 6.43 (m, 4H, H-3, H-4, H-5 and H-6), 6.96 (s, 3H, -OMe).

Analysis calculated for $C_{26}H_{24}O_2$; C, 84.8; H, 6.52.

Found: C, 84.9; H, 6.5%.

Isomer B (28), 0.12 g was crystallized from methylene chloride - petroleum ether, colourless needles, 0.1 g. MP, 105°.

MW (mass spectrum), 368.

IR (CCl_4) 1720 (-CO).

NMR (CCl_4) 3.0 (m, 15H, aromatic protons), 4.1 (s, 2H, H-1 and H-2), 6.06 (q, 1H, H-4), 6.6 (m, 3H, H-3, H-5 and H-6), 7.06 (s, 3H, -OMe).

Analysis calculated for $C_{26}H_{24}O_2$; C, 84.8; H, 6.52.

Found: C, 84.7; H, 6.7%.

3,5,6-Triphenyl-4-cyano-Δ^1-cyclohexene (29 and 30)

The Diels-Alder reaction of trans-trans-1,4-diphenyl butadiene and cinnamonitrile yielded these isomeric compounds. 1.2 g of 1,4-diphenyl butadiene, 0.7 g of freshly distilled

cinnamonitrile and 25 mg of hydroquinone were placed in a 10 ml round bottomed flask attached with a reflux condensor and a guard tube. The contents were heated at 190-200° for 24 hours in an oil bath. TLC of the reaction mixture in benzene solvent system showed the presence of two compounds. It was chromotographed on 80 g of silica gel. The unreacted diene was removed by eluting the column with petroleum ether (0.3 g). Elution with benzene gave isomeric mixture, 0.75 g. The mixture of these isomers was rechromotographed on 30 g of silica gel. Elution with 20% benzene-petroleum ether gave isomer A (29) 25% benzene-petroleum ether was used as eluent to get isomer B (30).

Isomer A (29), 0.45 g. It was recrystallized from methylene chloride-petroleum ether, 0.4 g, colourless needles, MP, 174°.
MW (mass spectrum), 335.
IR (nujol) 2205 (-CN).
NMR ($CDCl_3$) 3.0 (m, 15H, aromatic protons), 4.0 (s, 2H, H-1 and H-2), 6.5 (m, 4H, H-3, H-4, H-5 and H-6).
Analysis calculated for $C_{25}H_{21}N$; N, 4.179. Found: N, 4.3%.

Isomer B (30), 0.35 g. It was recrystallized from methylene chloride-petroleum ether, 0.3 g, colourless needles. MP, 157°.
MW (mass spectrum), 335.
IR (nujol) 2210 (-CN).
NMR ($CDCl_3$) 2.8 (m, 15H, aromatic protons), 4.06 (s, 2H, H-1 and H-2), 6.1 (q, 1H, 4H), 6.4 (m, 2H, H-3 and H-6), 7.1 (t, 1H, H-5).
Analysis calculated for $C_{25}H_{21}N$; N, 4.179. Found: N, 4.1%.

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CHAPTER III : ISOMERIZATION OF TRIPHENYL CYCLOHEXENYL CARBONIUM IONS TO DIPHENYL CYCLOPENTENYL BENZYL CARBONIUM IONS

A. INTRODUCTION

It is a common practice to rationalize mass spectral reactions with the help of known carbonium ion chemistry in solution. Several workers[1-5] have drawn analogy between reactions in the isolated and condensed phases. Structural and mechanistic aspects in mass spectrometry are however, more complicated than in solution chemistry even though there are no solvent effects in the gas phase.

In the preceding Chapter the skeletal rearrangement observed in tri-aryl nitrocyclohexenes in the gas phase was explained by assuming that substituted cyclohexenyl cation first undergoes ring contraction (isomerisation) to a substituted cyclopentenyl benzyl cation which is followed by aryl migrations. Evidence in support of this phenomenon was sought from the further studies in the gas phase and in solution. Studies on the action of nitrous acid on the corresponding tri-aryl amino cyclohexenes showed that the same rearrangement takes place in solution. The analogy between the gas phase and solution reaction was thus observed.

As early as in 1907 Demjanov[6] has reported that both cyclobutyl amine and cyclopropyl carbinyl amine when subjected to nitrous acid deamination gave mixtures of cyclobutanol and cyclopropyl carbinol (equation 1). Roberts and co-workers[7] have reported that the reaction of cyclobutyl, cyclopropyl carbinyl and allyl carbinyl derivatives proceed through a common bicyclobutonium ion intermediate.

In literature there are a number of examples of rearrangements accompanying deamination and solvolysis[8-14]. Many n-alkyl amines[15-17] on treatment with nitrous acid give rearranged alcohols. Solvolysis of the corresponding tosylates[16] and brosylates[17] may or may not lead to rearrangement products. This difference was explained on the basis of 'hot' or 'poorly solvated' carbonium ion formation from the initially produced diazonium ions[17].

B. PREVIOUS WORK

1. Rearrangements of cyclohexyl and cyclohexenyl carbonium ions accompanying nitrous acid deamination.

(a) Cyclohexyl carbonium ion rearrangements:

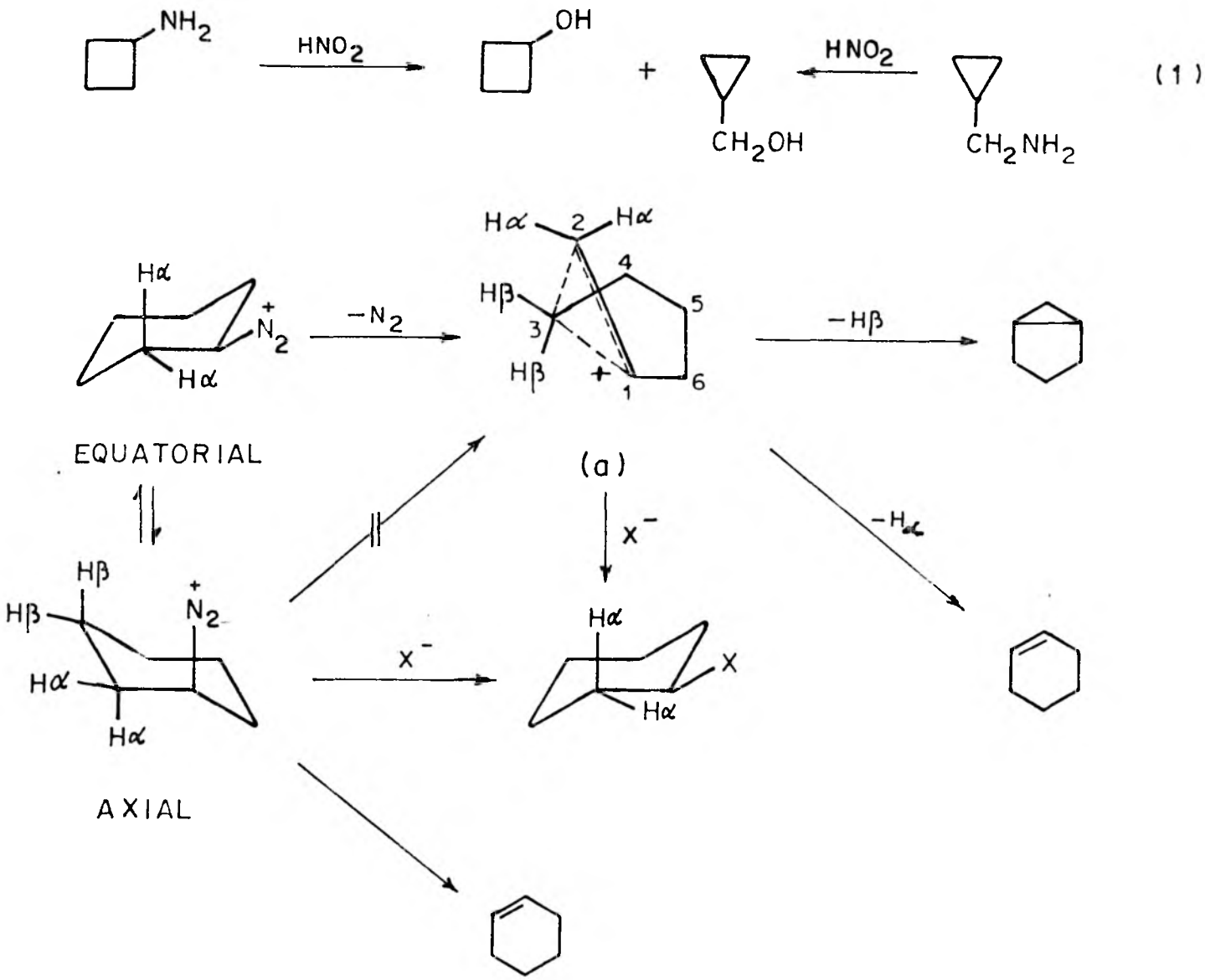
A comparative study on the nitrous acid deamination of several cycloalkyl amines[10] (C_5-C_{10}) revealed that product fall out is dependent upon reaction conditions, substituents and ring size 1,3-Transannular bond formation leading to cyclopropane derivatives was observed in the case of cyclohexyl and cycloheptyl systems. Considerable amount of information is available on the deamination reactions of acyclic and cyclic systems[10,12-14]. Comparatively less amount of data is available on the cycloalkenyl systems.

In unsubstituted cyclohexyl amine, the amino group can be either axial or equatorial. Aqueous deamination of cyclohexyl amine with equatorial amino group affords mainly the equatorial alcohol (82%) with retention of configuration. The olefin (16%)

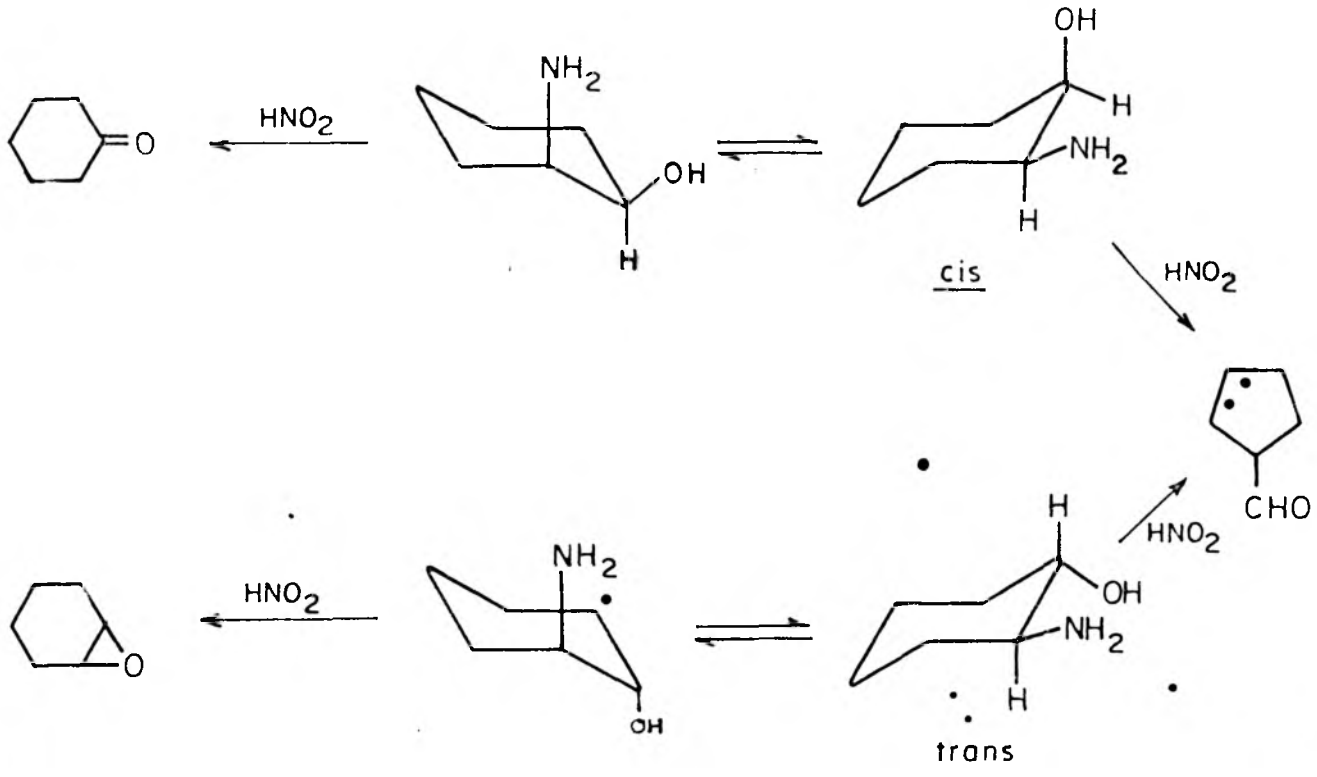
and a bicyclic product (~ 1-2%)[14,18] are also formed. Elimination product is less due to the absence of hydrogens trans to the equatorial leaving group. The corresponding amine with the amino function in the axial position predominantly yields the olefin with small amounts of both axial and equatorial alcohols. An explanation was offered by postulating an intermediate ion (a) (Scheme 1). Thus the equatorial diazonium ion loses nitrogen to give bridged intermediate carbonium ion (a) which can either form cyclohexene or bicyclo(3,1,0)hexane by deprotonation at α- or β-positions. It may also give substitution products by nucleophilic attack. The formation of the intermediate ion (a) from the axial diazonium ion has to proceed via the equatorial conformation.

The stereochemical differences which are observed in deamination reaction are not significant in the corresponding solvolytic reactions. Thus, the solvolysis of axial and equatorial cyclohexyl arene sulfonates in aqueous acetic acid gives mainly elimination product. Some minor substitution product with inversion of configuration is also formed. The deamination and solvolysis of simple cyclohexyl derivatives do not proceed via rearrangements.

Mills[19] has reported that cyclohexyl amines with simple alkyl substituents when treated with nitrous acid behave more or less in a similar fashion as the corresponding unsubstituted cyclohexyl amines. 2-Methyl-5-isopropyl-cyclohexyl amine


NH2
HNO2
OH
+
HNO2
CH2OH
CH2NH2
(1)
Hα
+
N2
Hα
−N2
Hα
2
Hα
4
Hβ
5
3
Hβ
+
1
6
−Hβ
EQUATORIAL
(a)
X−
−Hα
Hβ
Hβ
+
N2
Hα
Hα
X−
Hα
X
Hα
AXIAL

SCHEME – 1


O
HNO2
NH2
OH
H
OH
H
NH2
H
cis
HNO2
CHO
O
HNO2
NH2
OH
H
OH
NH2
H
HNO2
trans

(carvomenthyl amine) and 2-isopropyl-5-methyl-cyclohexyl amine (menthyl amine) with the amino group in equatorial conformation give the corresponding alcohols on deamination[19,20]. The corresponding epimers with axial amino group, undergo elimination reaction. The alcohol with inverted configuration is also formed. There was no indication of any rearrangement or the formation of bicyclic compounds. Bicyclic compounds were isolated in some conformationally rigid molecules[18]. The trans (equatorial)-4-t-butyl-cyclohexyl amine, on nitrous acid treatment in aqueous acetic acid gave the corresponding acetate (55%), cyclohexene (13%) and bicyclohexane (~ 2%). Small amounts of acetate (7%) with inversion of configuration was also isolated. The axial epimer on the other hand mainly gave elimination product together with cis and trans acetates under similar conditions. The formation of the substitution and elimination products was explained with the help of the intermediate ion (a)[18] as shown in Scheme 1. Huckel and Thomas[21] have isolated the corresponding ring contracted alcohol (10% yield) along with the trans-2-methylcyclohexanol (86%) and the corresponding cis alcohol (4%) in the deamination of trans 2-methyl cyclohexyl amine. A Wagner-Meerwein type mechanism was considered to explain the formation of the rearranged alcohol.

Nightingale and associates[22,23] have isolated ring contracted alcohols in good yield (~ 60-80%) from trans 2-phenyl cyclohexyl amine and 2,3-dimethyl-6-phenyl hexyl amine

on treatment with sodium nitrite in aqueous acetic acid. The trans form of 4-phenyl, 4-cyclohexyl, 4-t-butyl and 4-methyl cyclohexyl amines gave the corresponding unrearranged trans alcohols under similar reaction conditions. Based on these results, it was shown that a phenyl group α- to the amino function in the cyclohexyl ring is necessary for rearrangement. The reported ring contraction in 2-methyl cyclohexyl amine[21] has demonstrated that the presence of phenyl group α- to the leaving group is not essential.

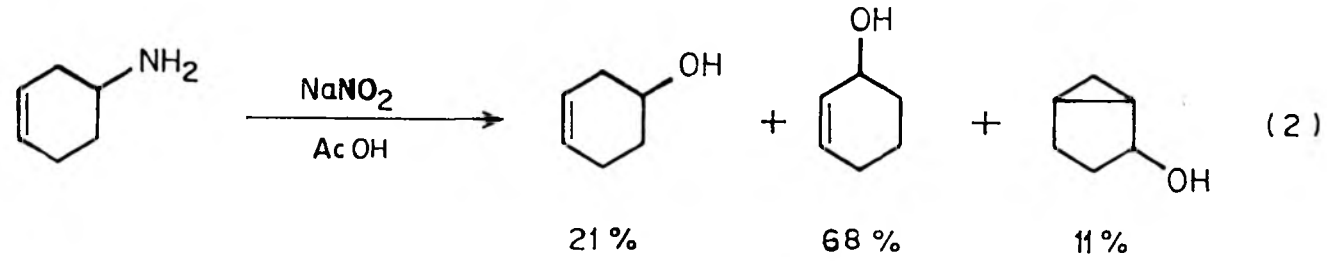
Nitrous acid deamination of axial and equatorial trans -2-decalylamines in mixed solvents, e.g. water, dioxane and sulfolane containing increasing concentrations of acetic acid was studied by Cohen and co-workers[24-26]. The nitrosation conditions were found to destory substantial proportions of the elimination and substitution products. It was shown that the stereochemical effects and the product distribution (alcohol/acetate) are nearly identical for two epimers in non-hydroxylic solvents containing low concentration of acetic acid. The substitution products with retention of configuration (30-32% alcohol and 30-32% acetate) was shown to be formed by collapse of an ion pair containing the carbocation, an acetate ion and a water molecule formed in the reaction. The inverted acetate was shown to arise by collapse of an inverted ion pair[24]. The stereochemical differences observed for the epimeric amines were found to diverge as the nonhydroxylic solvents become richer in acetic acid concentration. This was attributed to

unpairing of ion pairs. The study has thrown light on the effect of solvent and acidity on nitrous acid deamination reaction.

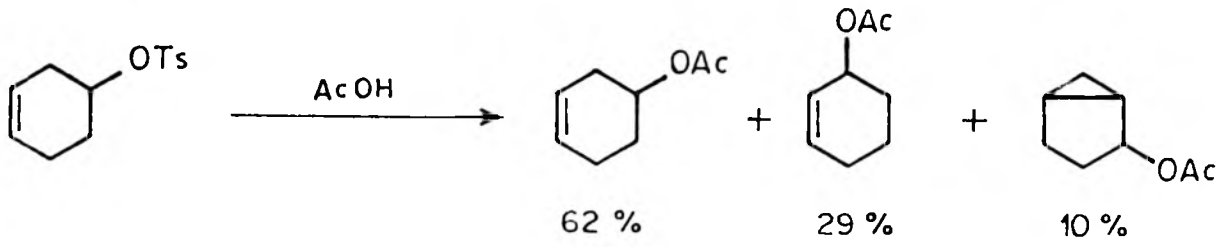
Bifunctional and conformationally mobile cyclohexyl derivatives such as 2-aminocyclohexanol exhibit rearrangements on treatment with nitrous acid. Similar to parent cyclohexyl amines, stereochemical effects were observed in bifunctional compounds. The cis-2-aminocyclohexanol[27,28] on deamination affords ring contracted aldehyde and cyclohexanone in the ratio 53:47. The cyclohexanone is formed by hydrogen migration. Migration of C-C bond occurs when the leaving group is equatorial. This leads to the formation of a ring contracted aldehyde (Scheme 2). In the corresponding trans epimer ring contraction has been reported since ring carbon 5 is trans coplanar to equatorial diazonium ion. When the diazonium ion is axial neither ring carbon nor hydrogen is in a favourable position for migration. This leads to the formation of cis epoxide (Scheme 2). Similar rearrangement processes have been reported in the deamination of conformationally 'rigid' 4-t-butyl-2-aminocyclohexanols[27,29].

(b) Cyclohexenyl carbonium ion rearrangements

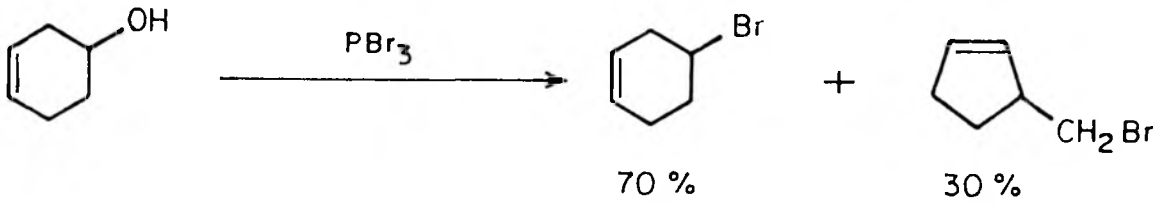
Deamination of 4-amino cyclohexene[30] in aqueous acetic acid was shown to give allylic, homoallylic and bicyclo(3,1,0)-hexyl alcohols (equation 2). A non-classical tris-homocyclopropenyl cation intermediate was proposed to explain the formation of



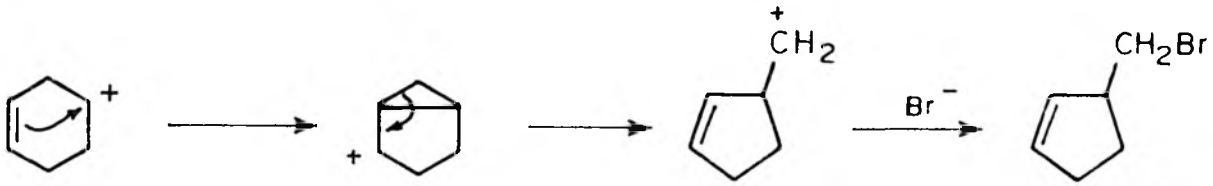
(2)



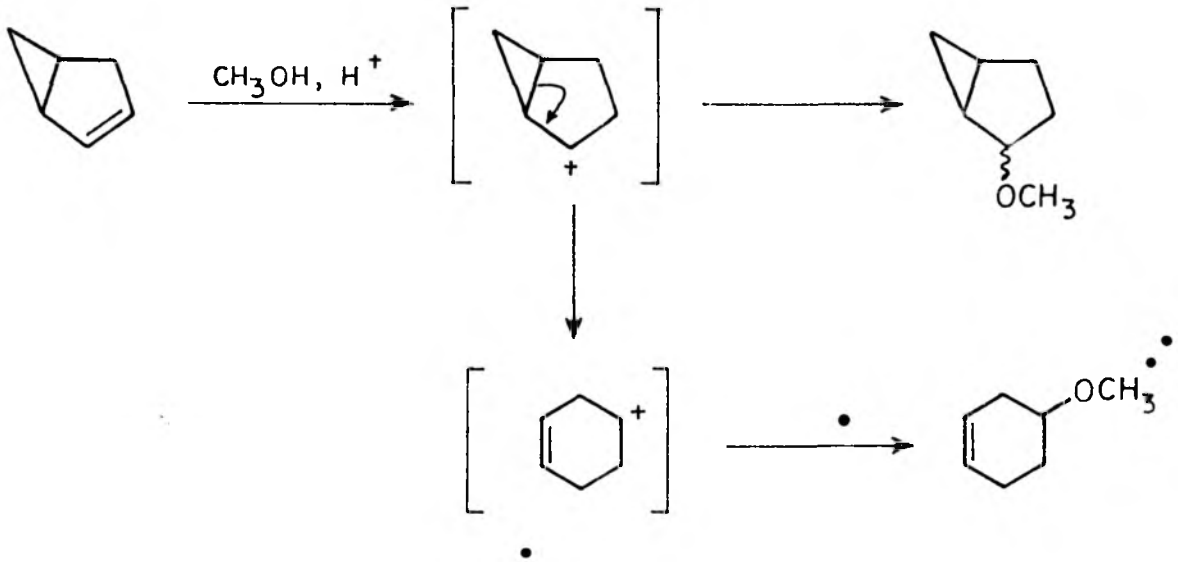
(3)



(4)



(5)



SCHEME – 3 .

the substitution products formed. Similarly, the acetolysis of 3-cyclohexenyl tosylate[31,32] gave the corresponding allylic, homoallylic and bicyclic acetates, but in a different ratio (equation 3). Formation of allylic product is favoured under deamination, while the simple substitution without rearrangement is a major process under solvolytic conditions. It is well known that homoallylic cations rearrange to more stable allylic cations by a 1,2 hydride shift. Lambert and Featherman[33] have reinvestigated the solvolysis of 3-cyclohexenyl tosylate in different solvents. Two competitive pathways were suggested for the solvolysis of this compound. A simple solvent displacement takes place in highly nucleophilic aqueous 1,4-dioxane which leads to an inverted product. Poor nucleophilic solvents e.g. hexafluoro 2-propanol, on the other hand favour a homoallylic participation which leads to a product with retention of configuration.

A literature survey has shown that there are no examples of nitrous acid deamination of substituted cyclohexenyl systems. The 4-hydroxy cyclohexene when treated with PBr_3 gave ring contracted cyclopentenyl methyl bromide (30%) along with the unrearranged 4-bromocyclohexene (70%)[34] (equation 4). The formation of the rearranged alcohol was explained by homoallylic participation, followed by the attck of bromide on the primary carbonium ion (equation 5).

Stable cyclohexenyl derivatives have been obtained

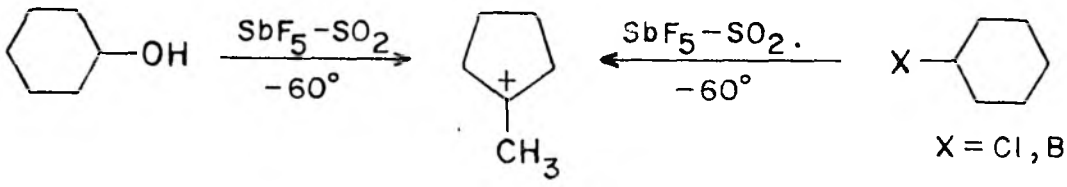
from bicyclic systems under different conditions. Freemann and co-workers[35] have reported the acid catalyzed methanolysis of 2-bicyclo(3,1,0)hexane and found that 4-substituted cyclohexene to be a major product. A possible mechanism was proposed. They have concluded that the 2-bicyclo(3,1,0)hexyl cation is more stable than the corresponding 3-cation (Scheme 3). Friedrich and Saleh[36] treated epimeric 2-bicyclo(3,1,0)hexyl-3,5-dinitrobenzoates with 80% aqueous acetone at 100° and obtained the unrearranged and rearranged alcohols. Both the epimers gave identical product distribution and followed a good first order kinetics.

2. Rearrangements of cyclohexyl and cyclohexenyl cations under stabl ion conditions.

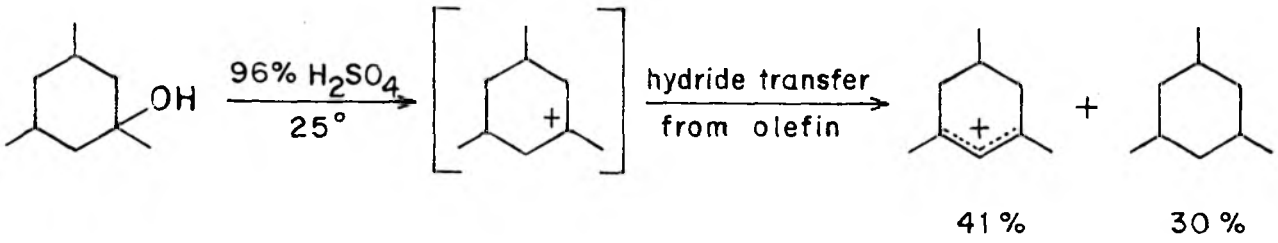
(a) Rearrangements of cyclohexyl carbonium ions

The stability of many substituted allylic and homoallylic, cyclic and acyclic carbocations in strong acidic media has provided the opportunity to study various rearrangement processes of these ions. These rearrangements often depend upon time and temperature. The effect of substituents and the acidity of the medium on these rearrangements is known. These investigations are carried out by low temperature proton or ^{13}C n.m.r. techniques.

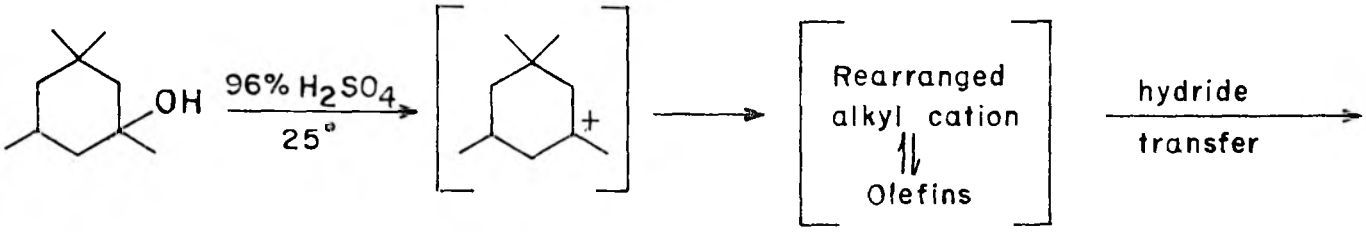
Olah and co-workers[37,38], based on their NMR studies have shown that cyclohexanol and the corresponding halides when dissolved in a super acid e.g. SbF_5-SO_2 at -60° give a stable solution of the 1-methyl-cyclopentyl cation (equation 6).

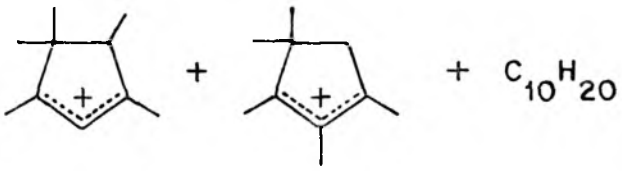

OH
SbF5-SO2
-60°
CH3
SbF5-SO2.
-60°
X
X = Cl, Br

(6)

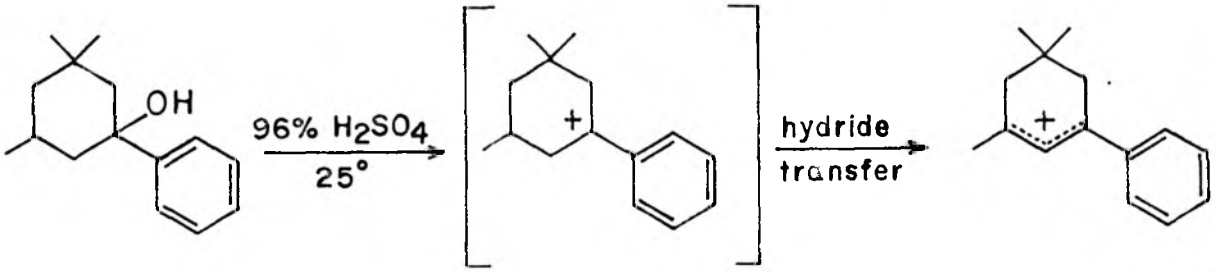

OH
96% H2SO4
25°
hydride transfer
from olefin
41 %
30 %

(7)


OH
96% H2SO4
25°
Rearranged
alkyl cation
Olefins
hydride
transfer


+ C10H20
8 %
12 %
28 %

(8)


OH
96% H2SO4
25°
hydride
transfer

(9)

There was no evidence for the formation of the corresponding unrearranged cyclohexyl cation. Thus, the initially formed cyclohexyl cation spontaneously isomerises to methyl cyclopentyl cation. The formation of this ion is due to its higher thermodynamic stability. This involves a rearrangement of secondary to tertiary carbonium ion. A mechanism was proposed invoking a protonated cyclopropane (bicyclo(3,1,0)hexane) intermediate. Cyclohexane and cyclohexene also gave rearranged methyl cyclopentyl cation under similar conditions. The cyclohexyl cation in these cases is formed by the proton abstraction and addition. Similar observations were made by Arnett and Petro[39]. They calculated the heats of formation of several cycloalkyl cations in solution.

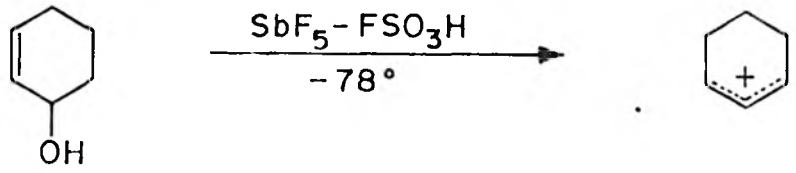
Very little work has been reported on substituted cycloalkyl cations. Aliphatic alcohols and their corresponding olefins are known to disproportionate to produce cycloalkenyl cations and saturated hydrocarbons in acid medium (80-100% H_2SO_4). The oxidation reduction nature of this reaction has been studied by Deno and co-workers[40-41]. The degree to which these processes occur is dependent on the structure of the alcohol. Cyclic aliphatic alcohols were shown to form the corresponding unrearranged cations which can abstract hydride ion from the corresponding olefin. Thus, 1,3,5-trimethyl-cyclohexan-1-ol[41] in 96% H_2SO_4 at 25° produces the corresponding hydrocarbon and cycloalkenyl cation as shown in equation 7.

In the case of 1,3,5,5-tetramethyl-cyclohexan-1-ol, isomerization takes place under similar conditions (equation 8). This demonstrates the effect of alkyl substituent on ring contraction. Surprisingly, this rearrangement was not observed when a phenyl group is introduced at C_1-position in the above system. A stable cyclohexenyl cation was observed (equation 9).

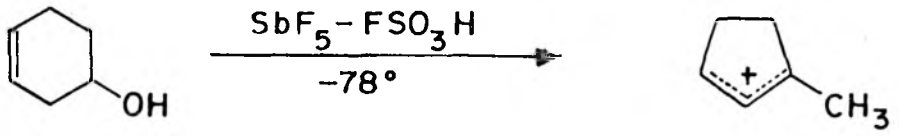
(b) Rearrangements of cyclohexenyl carbonium ions:

The pioneering work of Deno[43-46], Sorensen[47-52] and Olah[53-56] on cyclic and acyclic alkenyl carbocations in super acid solutions has thrown light on the stabilities and rearrangements of these ions. The cyclization of linear alkenyl cations to cyclopentenyl and hexenyl ions, alkyl migrations within the cyclopentenyl and cyclohexenyl ions, and isomerization of cyclohexenyl to the corresponding ring contracted methyl cyclopentenyl ions are some of the important rearrangements observed in these systems.

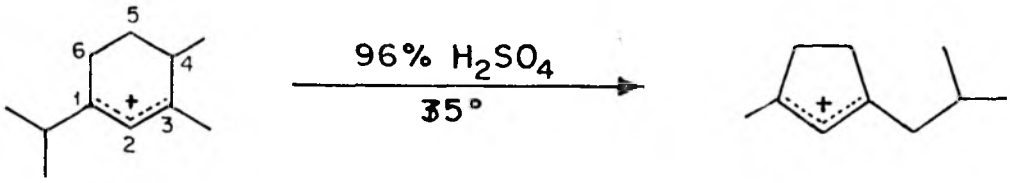
Olah and co-workers[53] generated unsubstituted allylic and homoallylic cyclohexenyl cations from the corresponding alcohols by ionization under stable ion conditions. 3-Hydroxy-Δ^1-cyclohexene in SbF_5-FSO_3H at -78^o gave the corresponding unrearranged cyclohexenyl cation (equation 10). The corresponding homoallylic alcohol (4-hydroxy-Δ^1-cyclohexene) under similar conditions gave methyl cyclopentenyl cation. Both the cations were characerized from their NMR spectral data. They have postulated that in the cyclohexenyl systems



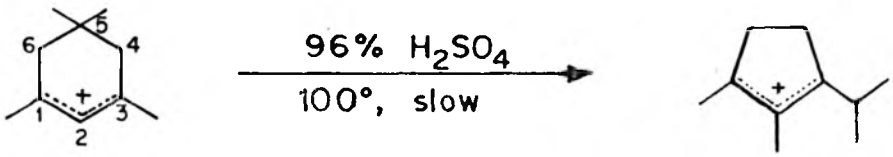
(10)



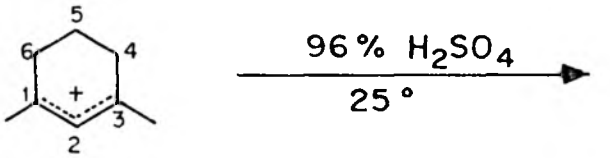
(11)



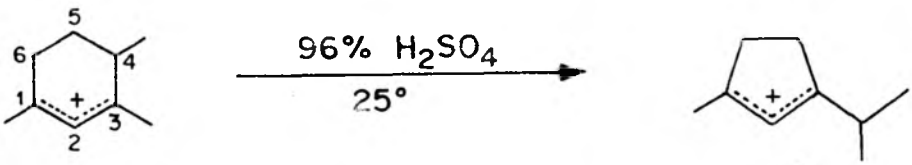
(b) (c) (12)



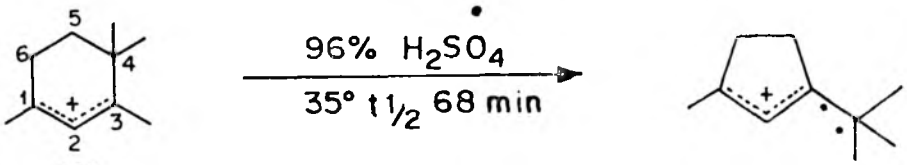
(d) (e) (13)



(14)



(15)



(16)

when the leaving group i.e., hydroxyl is in the allylic position the resulting cation is produced without rearrangement. When the leaving group is attached to the carbon which is homoallylic to the double bond, ring contraction or other rearrangements take place. The phenomenon of ring contraction was also observed in cyclohexadiene and 3-hydroxy(3,1,0)hexane. These compounds in FSO_3H gave only methyl cyclopentenyl cation. It was suggested that ring contraction occurs prior to intramolecular hydride shifts. Farcasiu[57] and Whittaker et al.[58] have also reported that 3- and 4-cyclohexenyl derivatives undergo ring contraction to give methyl cyclopentyl and methyl cyclopentenyl cations in FSO_3H-SbF_5 solution. Initial ionization of the double bond followed by ring contraction results in the formation of substituted cyclopentyl ion.

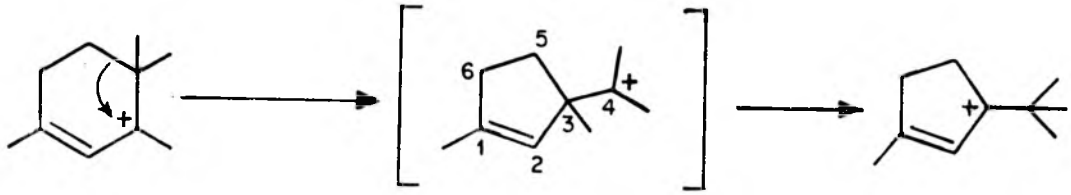
Deno and Lastomirsky[45] have examined the effect of alkyl substituents on the ring contraction of cyclohexenyl to methyl cyclopentenyl cation under stable ion conditions. They have carried out the investigations at room temperature and at higher temperatures. It was found that (b) rearranges to (c) (equation 12) in 96% H_2SO_4 solution whereas (d) is stable at 35° though it slowly rearranges to (e) (equation 13) at 100°. The difference in the rates of reactions (12) and (13) revealed that alkyl groups present at C_4-position of cyclohexenyl cation would facilitate isomerization to the corresponding five membered cation. This was further supported by the studies on the following cations (equations 14-16). The

intermediate cation formed has the positive charge on C-4 and is stabilized by increasing the number of alkyl groups on C-4 (hyperconjugation). Ion (f) (equation 16) undergoes a fast isomerization to the corresponding substituted pentenyl ion since it has two methyl group on C_4-position. Based on these results a mechanism involving a Wagner-Meerwein type rearrangement was proposed (equation 17).

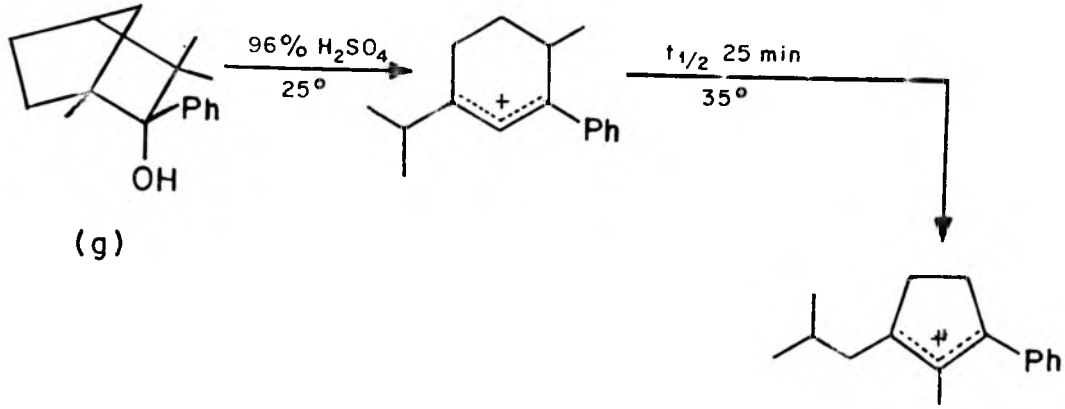
The cation (b) (equation 12) was also shown to be formed from bicyclic alcohols such as 2-methyl fenchol and 2-methyl borneol[42] in 96% H_2SO_4. The ion (b) further undergoes isomerization to form a stable ion (c) (equation 12). Similarly 2-phenyl fenchol (g) and 2-phenyl borneol (h) have also been shown to give the substituted cyclohexenyl cations which further isomerize to the corresponding cyclopentenyl ions (i). All these time dependent transformation were studied by NMR technique.

Masamune and co-workers[59] reported the formation of a non-classical tris-homocyclopropenyl cation from cis-bicyclo(3,1,0)hex-3-yl chloride in FSO_3H-SbF_5 at -78° (equation 19). The previous failure[53,60] was attributed to the proton initiated opening of the cyclopropyl ring of the bicyclic alcohol prior to ionization[56]. This is consistent with Sorensen's observations[52] that bicyclic alcohols tend to form methyl cyclopentenyl cations in protic media.

The substituent effects of alkyl and aryl groups in



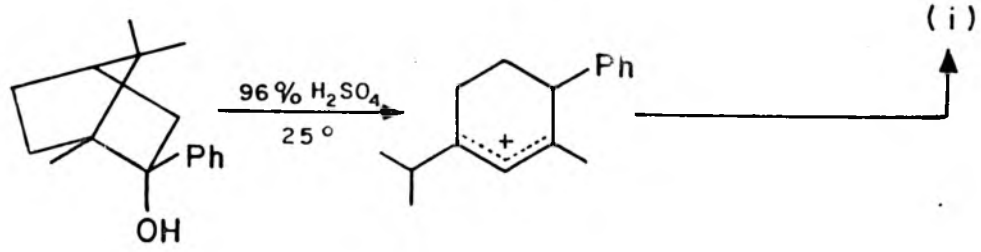
(17)



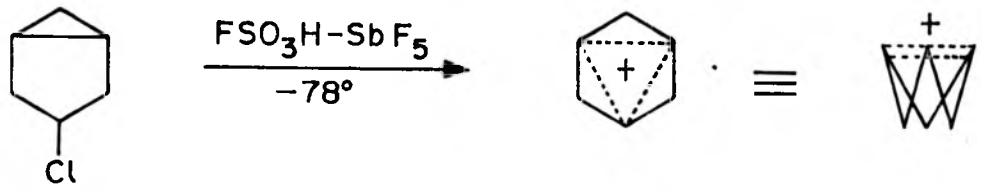
(g)

(18)

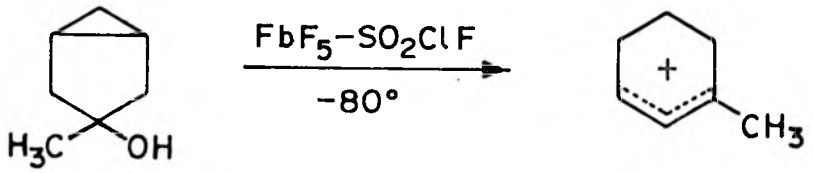
(i)



(h)

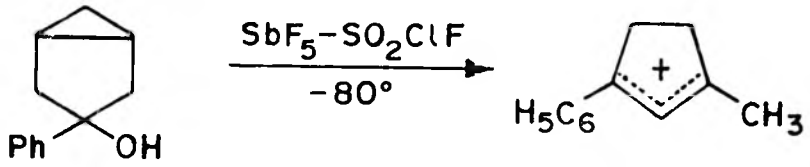


(19)



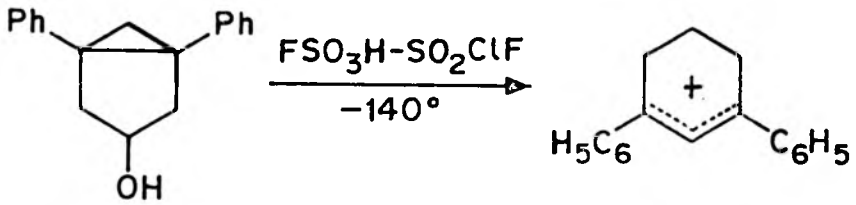
(j) (k)

(20)



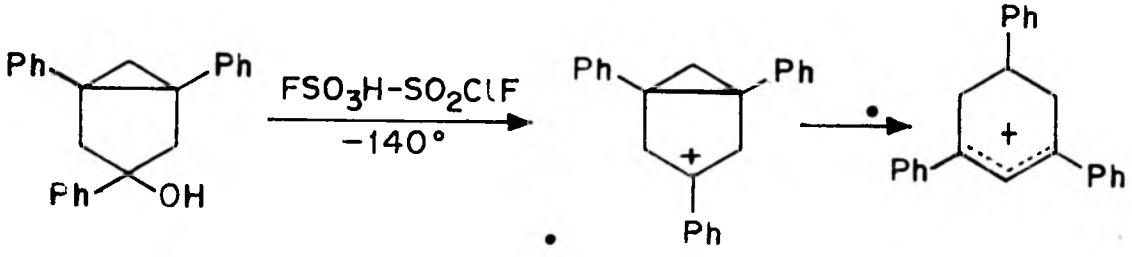
(l) (m)

(21)



(n) (o)

(22)



(p) (q) (r)

(23)

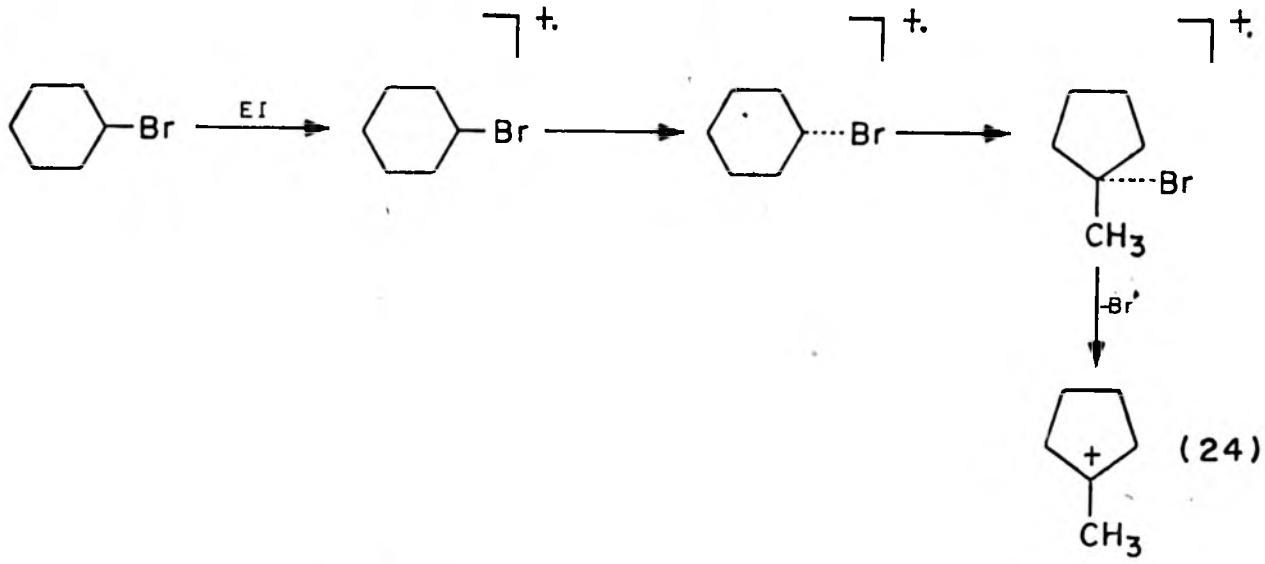
the 3-bicyclo(3,1,0)hexyl system has been reported[56]. Ionization of 3-methyl cis-bicyclo(3,1,0)hexan-3-ol (j) in super acid was shown to yield 3-methylcyclohexenyl cation (k) (equation 20). No evidence for the formation of either classical or non-classical ion was obtained. The corresponding phenyl substituted alcohol (l) gave ring contracted methyl phenyl cyclopentenyl cation (m) (equation 21). 1,5-Diphenyl-cis-bicylo(3,1,0)hexan-3-ol (n), on the other hand when ionized in FSO_3H/SO_2ClF solution at -140° gave diphenyl cyclohexenyl cation (o) (equation 22). It was found to be stable up to -70°. The corresponding 1,3,5-triphenyl alcohol (p) produced a classical ion (q) under similar conditions. On further warming the ion (q) was converted to triphenyl cyclohexenyl cation (r) (equation 23). Again there was no evidence for the formation of non-classical ion in these aryl substituted bicyclic compounds. Jorgensen's theoretical calculations[61] are in agreement with the spectral data obtained by Olah et al.[56] The non-classical ions do not result in alkyl and aryl substituted bicyclic systems due to the hindrance in the change of the boat to the chair conformation.

3. Rearrangements of cyclohexyl carbonium ions in gaseous phase

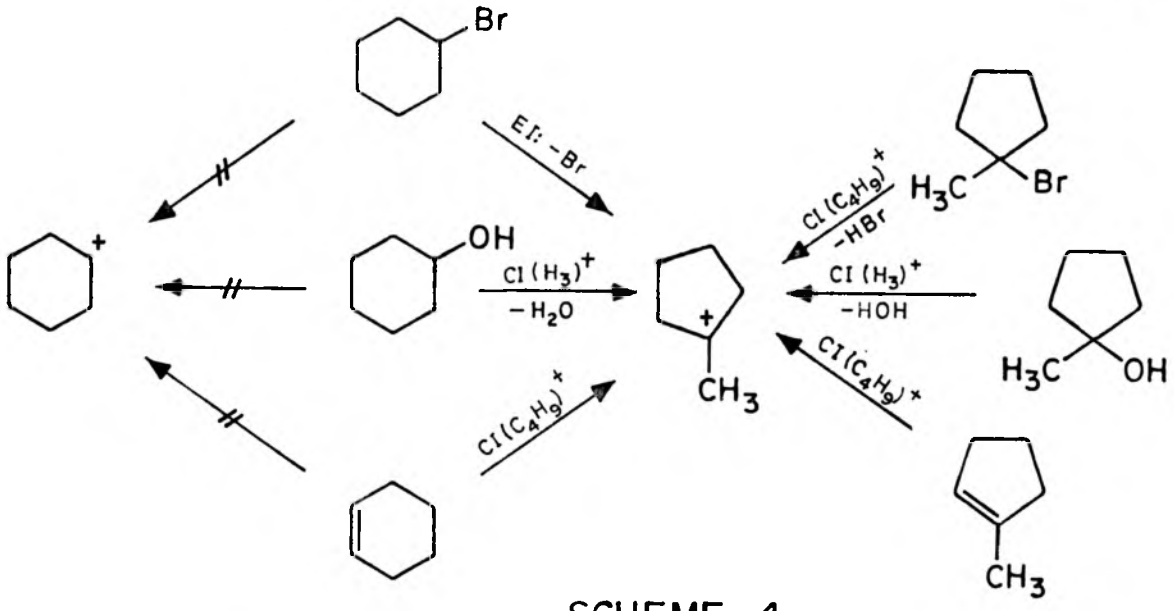
The gas phase isomerization of substituted cyclohexenyl carbonium ions to diphenyl cyclopentenyl benzyl carbonium ions was first reported by our group in 1979. Subsequently, Schwarz et al.[62] and Maquestiau et al.[63] have also invoked

isomerization of unsubstituted cyclohexenyl systems in the gas phase to explain some of their observations. Schwarz and co-workers have generated $(C_6H_{11})^+$ ions from cyclohexanol and the corresponding bromide by CI and EI methods respectively. The cyclohexyl cations from these compounds were proposed to rearrange to 1-methylcyclopentyl cations (Scheme 4). The evidence for the isomerization was obtained from the CA spectra of the $(C_6H_{11})^+$ ions produced from the compounds shown in Scheme 4. All the CA spectra were identical irrespective of the method of ionization. These results are consistent with those obtained by Olah and co-workers[37] and Arnett and Petro[39] under stable ion conditions. The kinetic energy release for the elimination of Br$^{\cdot}$ from cyclohexyl and methylcyclopentyl bromides were 2.0 K.cal and 0.31 K.cal mol^{-1} respectively. The higher value obtained for cyclohexyl system was explained by a prior rearragement involving 'open' shell ions. These rearranged ions formed by exothermic isomerization lose Br$^{\cdot}$ to give methylcyclopentyl cations (equation 24). The loss of Br$^{\cdot}$ from the cyclopentyl system is associated with a small release of kinetic energy which corresponds to a simple cleavage[64]. This is in good agreement with the data obtained for many acyclic systems[64-67].

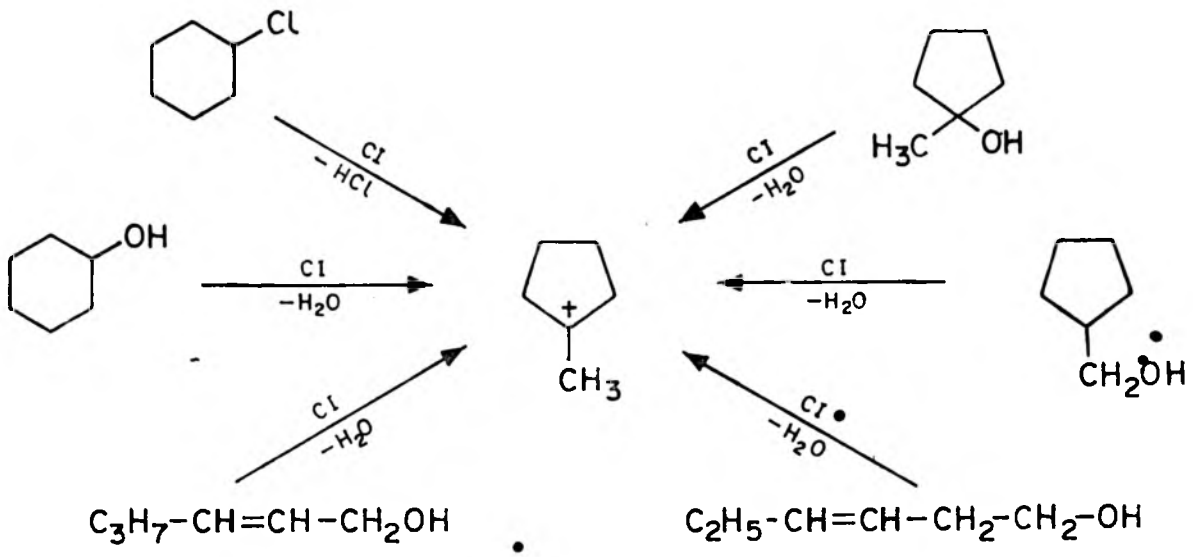
Maquestiau and co-workers[63] have carried out similar studies in the gas phase. The CA spectra of $(C_6H_{11})^+$ ions generated under CI conditions from cyclohexyl, methylcyclopentyl and acyclic hexenyl alcohols and chlorides (Scheme 5) were



(24)



SCHEME-4



$C_3H_7-CH=CH-CH_2OH$ $C_2H_5-CH=CH-CH_2-CH_2-OH$

SCHEME-5

reported. The similarity in the spectra has been used as evidence for their fast interconversion to a common structure i.e., methylcyclopentyl cation. These results imply that the energy required for primary or secondary carbonium ion to isomerise to a tertiary carbonium ion is small.

C. PRESENT WORK

The present work is on a study of the behaviour of triphenyl cyclohexenyl cations in solution and in gas phase. In solution, the nitrous acid deamination of 3,5,6-triphenyl-4-amino-Δ^1-cyclohexene and 3,6-diphenyl-5-p-tolyl-4-amino-Δ^1-cyclohexene was studied. From the deamination products the isomerized 2,5-diphenyl-cyclopent-3-en-1-yl benzyl alcohol was isolated as the major product.

For the gas phase studies the triphenyl cyclohexenyl cation was generated from the corresponding alcohol which was synthesized by a Diels-Alder reaction. The carbonium ion was generated by chemical ionization. To study the gas phase isomerization by the collisional activation technique it is necessary to generate the authentic diphenyl cyclopentenyl benzyl cation (the proposed rearranged ion) for comparison. This ion was produced by chemical ionization from the diphenyl benzyl alcohol, obtained from the deamination reaction.

D. DISCUSSION

1. Rearrangement in solution

It is interesting to find out whether the isomerization

of triaryl cyclohexenyl carbonium ion to the corresponding diaryl cyclopentenyl benzyl carbonium ion which was postulated in the gas phase takes place in solution. For this study the 3,5,6-triphenyl-4-amino-Δ^1-cyclohexene was prepared from the corresponding nitro compound by reduction with metallic tin and acetic acid[68]. The amino compound was purified by column chromatography on silica gel, and characterized from its spectral data. The nitrous acid deamination of 3,5,6-triphenyl-4-amino-Δ^1-cyclohexene was studied at 0^o in aqueous acetic acid. The amine (4 g) in aqueous acetic acid (1:1) was treated with sodium nitrite solution. After the usual work-up, a dark brown thick liquid was obtained in 97% yield (3.9 g).

Thin layer chromatography (TLC) of the reaction mixture on silica gel using benzene and chloroform mixture (9:1) showed the presence of three components, two of which appeared as the major components. In addition to these components a fast moving material was observed which travelled upto the solvent front. The reaction mixture did not contain any starting material as was evident from the TLC plate.

The pure components from the reaction mixture were isolated by column chromatography on silica gel. The reaction products were eluted with petroleum ether-benzene mixture. The percentage of benzene in the eluting solvent mixture was progressively increased. Three pure components were obtained

which accounted for 80.7% of the reaction products. A fourth component was obtained in an impure state (Table I).

All the compounds except the compound (4) were characterized from their spectral data. As it is clear from Table I the compounds 2 and 3 account for > 78% of the mixture. It is known that equatorial amines on deamination mainly give substitution products, while the axial amines predominantly yield elimination products[9-14,26]. In the present system the elimination products should be less than the substitution products since the amino function is in the equatorial conformation.

1,2,4-Triphenyl benzene (1):

The compound which was eluted from the column with petroleum ether containing 5% benzene was obtained as a white crystalline solid (0.125 g). On crystallization from petroleum ether, it melted at 121°. Both the IR and NMR spectra showed the presence of only aromatic groups in the molecule. The mass spectrum showed the molecular ion peak at m/z 306. The molecular formula was found to be $C_{24}H_{18}$ (high resolution). The molecular ion is the base peak in the spectrum. The presence of very few peaks in the spectrum suggested that the molecule is aromatic. The only peaks observed correspond to the loss of phenyl radical and a molecule of benzene from the molecular ion.

Table I

Compounds obtained from the nitrous acid deamination of 3,5,6-triphenyl-4-amino-Δ^1-cyclohexene (wt. of the reaction mixture 3.9 g).

Compound No.	Solvent system used for elution	Weight obtained in grams	Yield	M.P.	Reported M.P.
1.	5% benzene in petroleum ether	0.125	3%	121°	120°
2.	15% benzene in petroleum ether	1.180	33%	Thick liquid, BP, 222°/0.7 mm	
3.	25% benzene in petroleum ether	1.600	45%	85°	-
4.	40% benzene in petroleum ether	0.280	8%	Thick liquid	-
	Mixtures of compounds obtained while eluting	0.410			
	Total wt.	3.595 g			

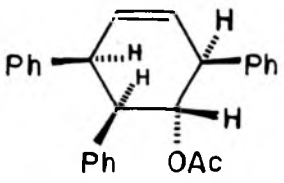
The melting point of 1,2,4-triphenyl benzene[69] reported in literature is 120°. An authentic sample of 1,2,4-triphenyl benzene was prepared[69] for comparison. The mixed melting point obtained was 121°. A comparison of the NMR and mass spectra[70] of 1,2,4-triphenyl benzene and the compound obtained by the deamination reaction gave further evidence. This compound was thus identified as 1,2,4-triphenyl benzene.

2,5-Diphenyl-cyclopent-3-en-1-yl benzyl acetate (2):

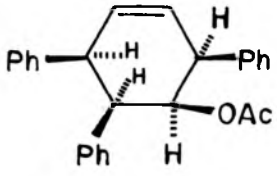
A light yellow viscous liquid was obtained by elution with petroleum ether containing 15% benzene (1.18 g). It was purified by distillation under reduced pressure. B.P. 222°/0.7 mm. From the TLC data (9:1, benzene and chloroform) it was clear that it is a single compound. The elemental analysis and mass spectral data supported the molecular formula $C_{26}H_{24}O_2$. The IR spectrum showed an absorption band at 1745 cm^{-1}, for carbonyl absorption of an acetate group.

The presence of an acetate group revealed that the compound is formed by substitution. An acetate can result by a nucleophilic substitution on either an unrearranged (triphenyl cyclohexyl) or a rearranged (diphenyl cyclopenenyl benzyl) carbonium ion formed in the reaction. In the triphenyl cyclohexenyl cation the nucleophilic attack by solvent molecule can produce the acetate (5) or (5') with retention or inversion

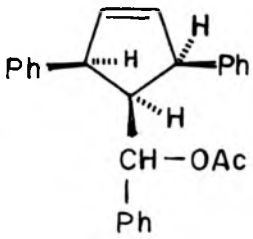
of configuration at C_4. The isomerization to the diphenyl cyclopentenyl benzyl cation can proceed via a Wagner-Meerwein type rearrangement or by homoallylic participation. This can afford either a symmetrical or an unsymmetrical diphenyl cyclopentenyl benzyl acetate (2 or 2'). Hence, the acetate obtained can have any one of the following structures 5, 5', 2 or 2'.



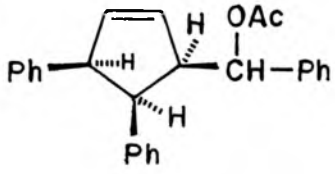
(5)



(5')



(2)



(2')

The proton NMR spectrum* was recorded in carbon tetrachloride using TMS as an internal standard. The spectrum is shown in Figure 1. Characteristic signals at 3.16 (m, 15H, ArH), 4.36 (s, 2H, olefinic H), 4.16 (d, 1H, J = 8, CH-OAc), 6.13 (m, 1H, benzylic methine H), 6.43 (m, 1H, benzylic methine H), 7.26 (q, 1H, J=6; methine H) and 8.1 (s, 3H, $-OCOCH_3$) were observed.

In the NMR spectrum the signals corresponding to the

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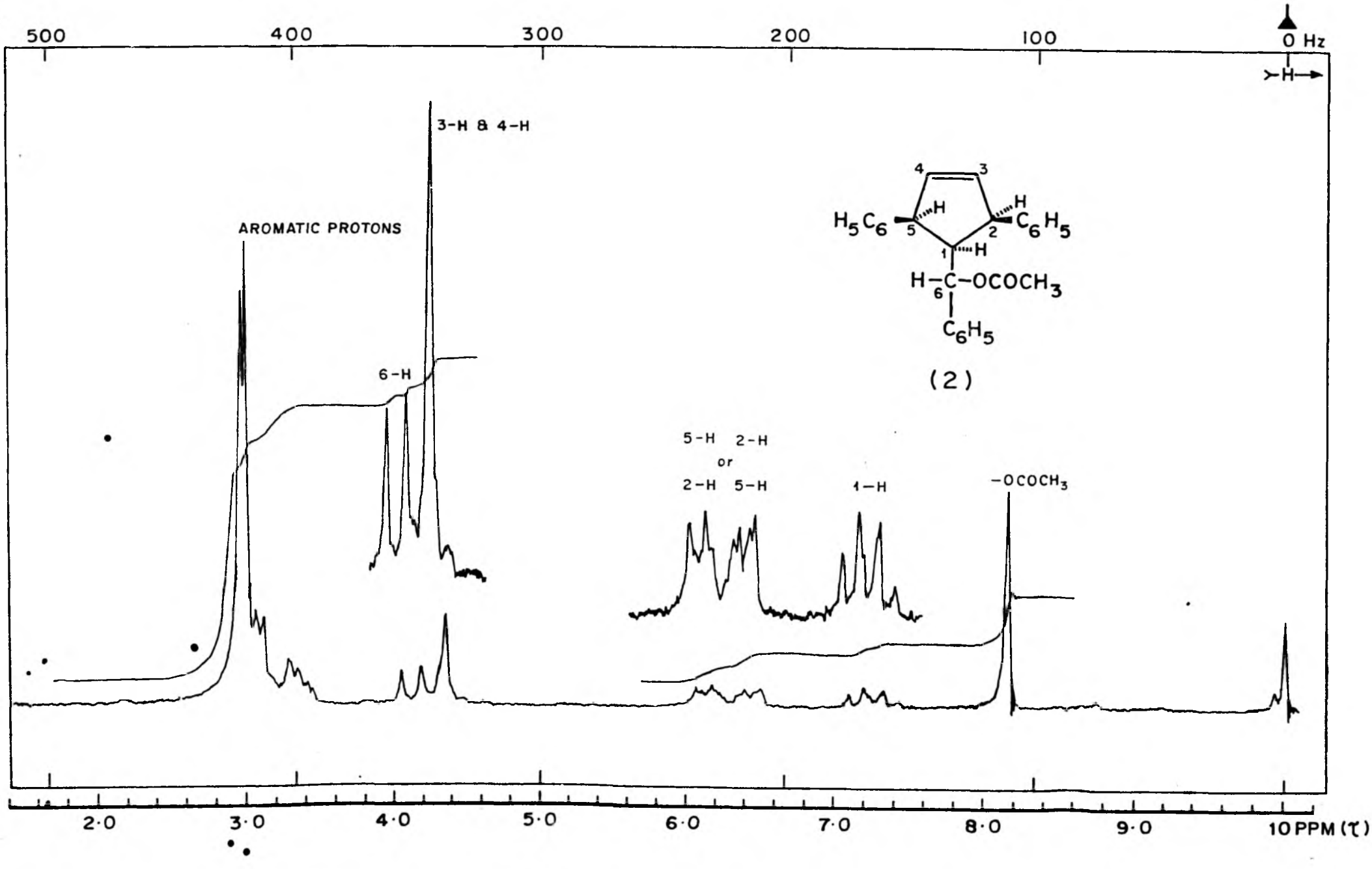
* The chemical shift values are given in τ (p.p.m.) and the coupling constants (J) in Hz.



(2)

FIG. 1. NMR SPECTRUM OF 2,5-DIPHENYL-CYCLOPENT-3-EN-1-YL BENZYL ACETATE IN CCl_4

aromatic and two of the benzylic protons have more or less same chemical shifts as observed in the NMR spectra of 4-substituted 3,5,6-triphenyl-Δ^1-cyclohexenes (see Chapter II). The olefinic proton signal was found to be shifted upfield by 0.3 to 0.4 ppm. In triaryl cyclohexenyl derivatives the olefinic protons appear at 4.05. A doublet centred at 4.16 can be assigned to C<u>H</u>-OAc (in cyclohexenyl acetate it appears at 4.46). It is slightly shifted to the lower field. This can be due to the aromatic ring which is directly attached to the carbon bearing this proton (C_6H_5-C<u>H</u>-OAc). The splitting pattern shows the presence of an adjacent proton. In cyclohexenyl acetate the C_4-proton (CH-OAc) is flanked by two adjacent protons and is observed as a pair of doublets. Hence, the doublet centred at 4-16 has been assigned to the methine proton of an exocyclic benzyl group containing the acetate moiety. The quartet centred at 7.2 has been assigned to the methine proton of a cyclopentyl ring which has three neighbouring benzylic protons. In the cyclohexenyl system there is no methine proton with three adjacent benzylic groups. The coupling constant of this methine proton with the neighbouring three benzylic protons is equal (6 Hz). This shows that the molecule can have a symmetrical structure. On the basis of these evidences the structure 2 is provisionally assigned to the compound. This has been confirmed.

The NMR spectrum of 3,5,6-triphenyl-4-<u>endo</u> acetoxy-Δ^1-

cyclohexene (6) is shown in Figure 3. The following signals were observed. 3.0 (m, 15H, Ar-H), 4.06 (s, 2H, olefinic H), 4.46 (dd, 1H, CH-OAc, $J_{3,4}$=6, $J_{4,5}$=11), 6.0 (m, 1H, benzylic methine H), 6.36 (d, 1H, benzylic methine H, $J_{5,6}$=11), 7.06 (t, 1H, benzylic methine H, $J_{5,4}=J_{5,6}$=11) and 8.5 (s, 3H, $-OCOCH_3$).

In the cyclohexenyl acetate (6), the CH-OAc methine proton is a pair of doublets centred at 4.46 and the third benzylic proton is a triplet centred at 7.06.

The mass spectrum of the acetate obtained by the deamination reaction is shown in Figure 2. The molecular ion is absent. The following peaks are observed at m/z 308, 219, 217, 202, 191, 178, 167, 150, 141, 115, 107 and 91. The loss of acetic acid from the parent ion is the base peak (m/z 308). Elimination of C_6H_5CHOAc by a benzylic cleavage from the molecular ion is a significant fragmentation mode (m/z 219). No retro Diels-Alder fragmentation process was observed which is a characeristic fragmentation mode of cyclohexyl derivatives. The mass spectral evidence also supports the diphenyl cyclopentyl benzyl structure.

The mass spectrum of 3,5,6-triphenyl-4-endo acetoxy-Δ^1-cyclohexene (6) showed a molecular ion peak at m/z 368. Loss of acetic acid from $M^{+\cdot}$ was noticed (m/z 308). The base peak in the spectrum corresponds to m/z 206 which arises by

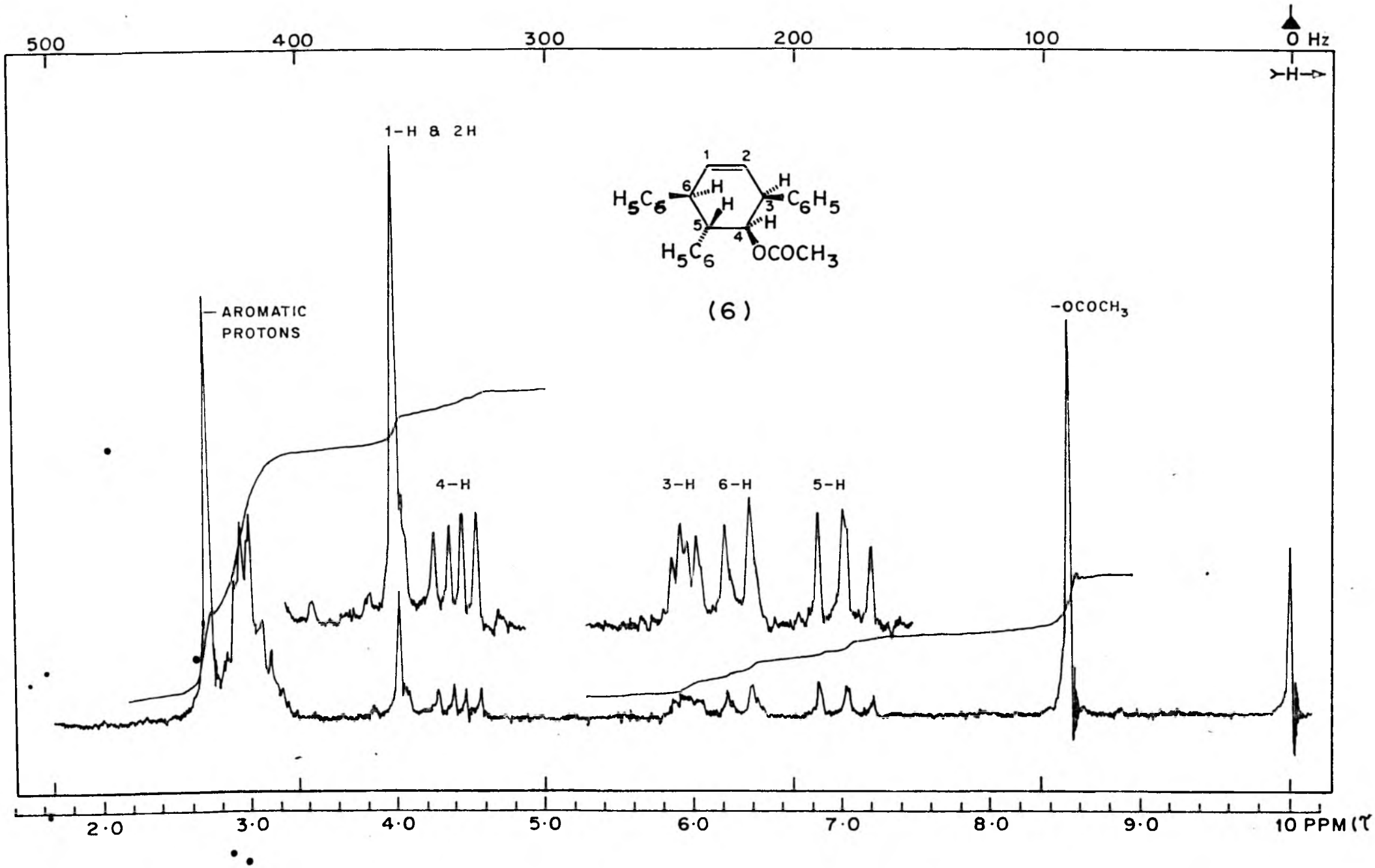


FIG. 3. NMR SPECTRUM OF 3,5,6-TRIPHENYL-4-ACETOXY-Δ^1-CYCLOHEXENE IN CCl_4

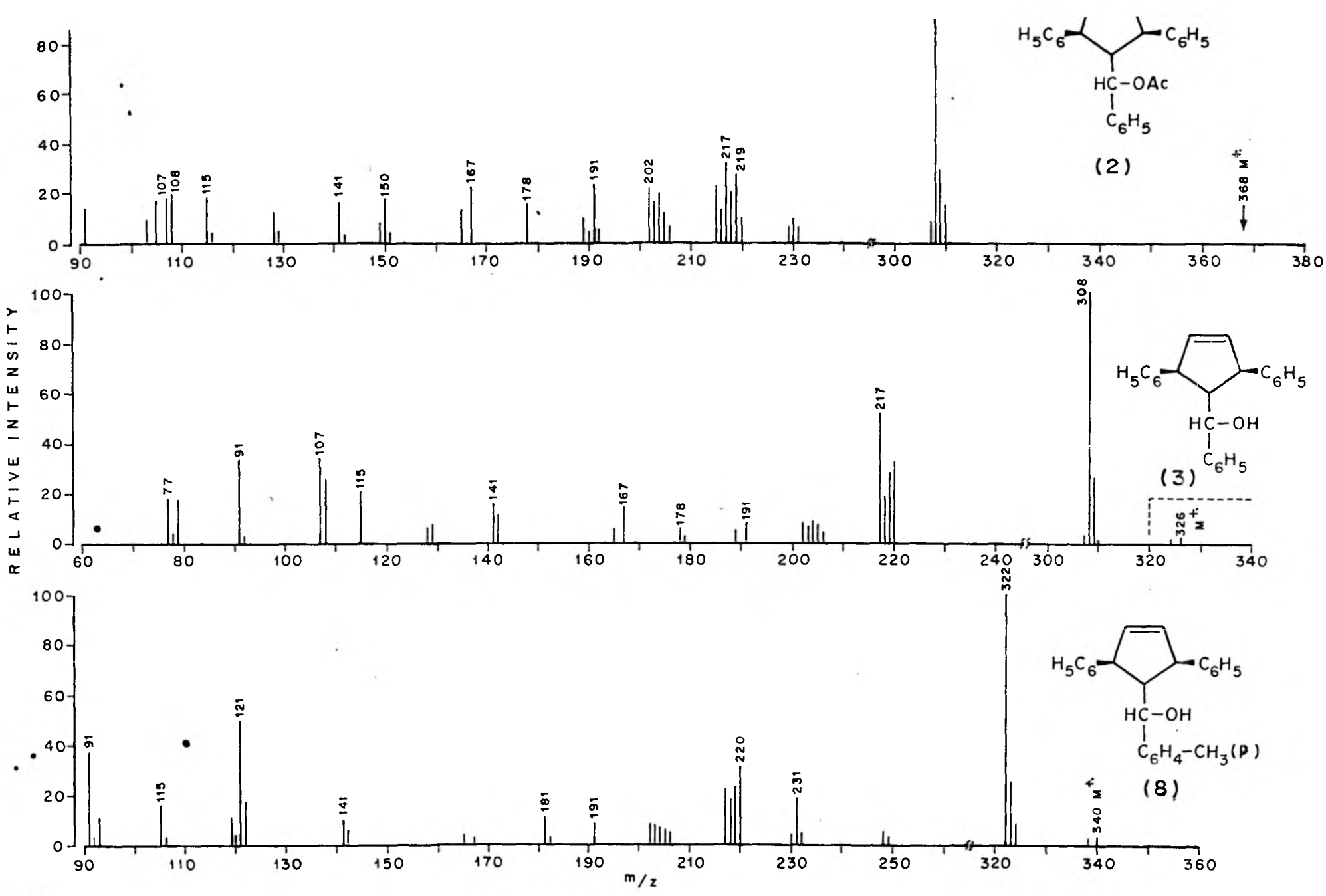

RELATIVE INTENSITY
m/z
H5C6
C6H5
HC-OAc
C6H5
(2)
368 M+
107
108
115
141
150
167
178
191
202
217
219
H5C6
C6H5
HC-OH
C6H5
(3)
326 M+
308
77
91
107
115
141
167
178
191
217
H5C6
C6H5
HC-OH
C6H4-CH3(P)
(8)
340 M+
320
91
115
121
141
181
191
220
231

FIGURE 2.

a RDA fragmentation (1,4-diphenyl-butadiene). No benzylic cleavage was observed.

The acetate (2) on hydrolysis gave an alcohol which melted at 85°C. Mixed melting point of this alcohol with the alcohol (3) obtained by the deamination was found to be 85°. The NMR and mass spectra of these two alcohols are also similar.

2,5-Diphenyl-cyclopent-3-en-1-yl benzyl alcohol (3):

This compound was obtained as a light yellow solid (1.6 g) by eluting with 25% benzene petroleum ether mixture. Crystallization from petroleum ether gave white needles which melted at 85°. The elemental analysis and mass spectral data support the molecular formula $C_{24}H_{22}O$. The IR absorbance at 3400 cm^{-1} revealed the presence of a hydroxy group. If it is a substitution product it can have a cyclohexenyl or cyclopentenyl structure.

The NMR spectrum of compound (3) was recorded in CCl_4 (Figure 4). Signals at 3.2 (m, 15H, Ar-H), 4.36 (s, 2H, olefinic H), 5.4 (d, 1H, J=7, C_6H_5-CH-OH), 6.06 (m, 1H, benzylic methine H), 6.4 (m, 1H, benzylic methine H), 7.6 (q, 1H, J=6, methine H) and 8.31 (s, 1H, -OH) were noticed.

A comparison of the NMR spectrum of this hydroxy compound (3) and acetate (2) showed the following differences. The doublet which was observed at 4.16 in the acetate was found to be shifted to 5.4 in the alcohol. Due to the deshielding effect of the acetoxy group this signal is down-field in the

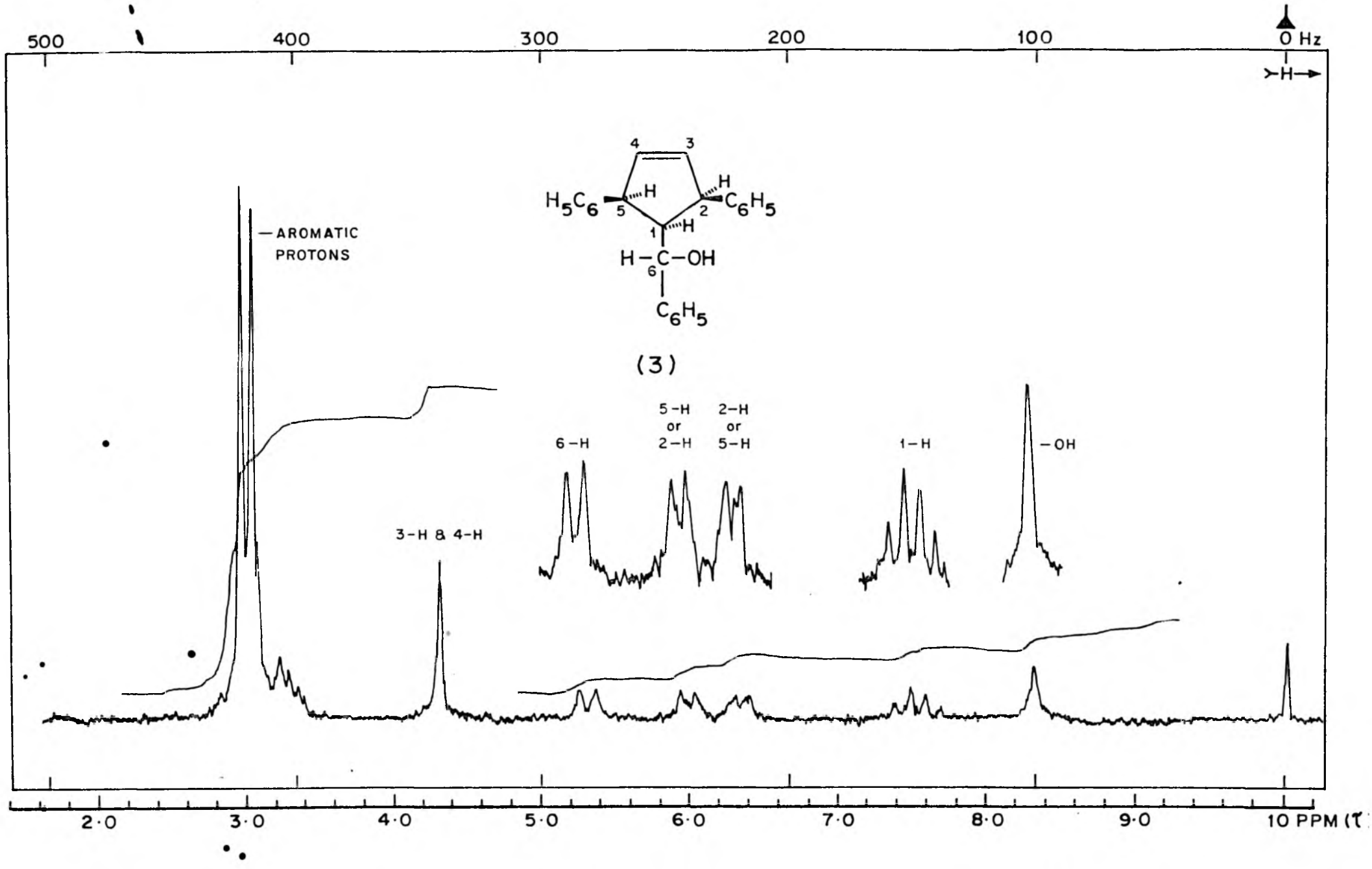


FIG. 4. NMR SPECTRUM OF 2,5-DIPHENYL-CYCLOPENT-3-EN-1-YL BENZYL ALCOHOL IN CCl_4

acetate. The singlet at 8.31 disappeared on deuteration.

The NMR of the 3,5,6-triphenyl-4-endo-hydroxy-Δ^1-cyclohexene (7) (Figure 5) showed the following NMR absorptions. In the spectrum the signal corresponding to the methine proton to which the hydroxy group is attached, is a pair of doublets centred at 5.67. The third benzylic proton is a triplet centred at 7.33. The hydroxy absorption is a singlet at 9.03. Based on the NMR spectral evidences a cyclopentenyl benzylic structure is preferred for the alcohol obtained by the deamination reaction.

The mass spectrum of the alcohol obtained by deamination (Figure 2) showed an insignificant M^+ ion peak (m/z 326). The loss H_2O from the parent ion is the base peak (m/z 308). The peaks at m/z 219, 107 which can arise by a benzylic cleavage are observed. Deuteration "in situ" led to the shift of the peak at m/z 107 and m/z 326 by one mass unit. No RDA fragmentation mode was observed. Hydrogen transfer rearrangements can result in the formation of the peaks at m/z 220 and m/z 218. The peak at m/z 217 may arise by the loss of hydrogen from m/z 218.

The mass spectrum of 3,5,6-triphenyl-4-endo hydroxy-Δ^1-cyclohexene (7) exhibit a minor peak corresponding to the $M^{+\cdot}$ ion. The $(M-H_2O)^+$ was observed. RDA is a major fragmentation mode which results in the base peak (m/z 206). It is obvious

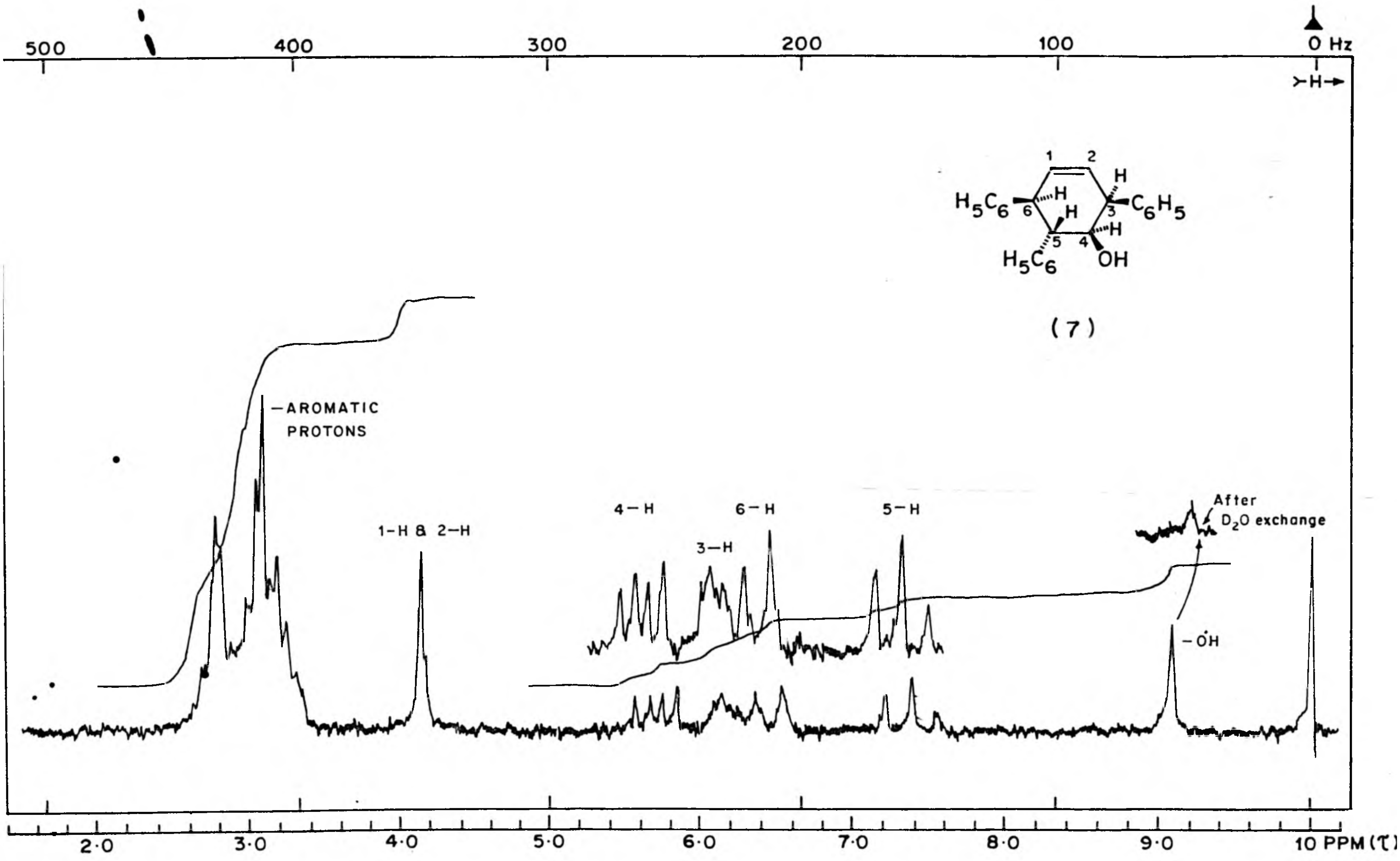


FIG. 5. NMR SPECTRUM OF 3,5,6-TRIPHENYL-4-HYDROXY-Δ^1-CYCLOHEXENE IN CCl_4

that the mass spectral data also supports a diphenyl cyclopentenyl benzyl structure to the alcohol (3).

The deamination of 3,6-diphenyl-5-(p-tolyl)-4-amino-Δ^1-cyclohexene with nitrous acid under similar conditions gave an alcohol in 40% yield. The NMR spectrum of this alcohol (Figure 6) showed the following absorptions. 3.2 (m, 14H, Ar-H), 4.36 (s, 2H, olefinic H), 5.4 (d, 1H, CH_3-C_6H_4-CH.OH, J=7), 6.06 (m, 1H, benzylic methine H), 6.4 (m, 1H, benzylic methine H), 7.6 (t, 1H, methine H, J=6), 7.76 (s, 3H, CH_3) and 8.31 (s, 1H, OH). The NMR spectral data favour the 2,5-diphenyl cyclopent-3-en-1-yl-(p-Methyl)-benzyl alcohol structure (8).

The mass spectrum of this compound gave additional evidence for the symmetrical diphenyl cyclopentenyl benzyl structure. The major fragmentation mode corresponds to the loss of p-methyl benzyl acetate moiety and not the benzyl acetate group. This fragmentation mode can be explained only if the alcohol has got the symmetrical structure (8). The alcohol obtained by the nitrous acid deamination reaction is the symmetrical 2,5-diphenyl-cyclopent-3-en-1-yl benzyl alcohol.

Mechanism

When 3,5,6-triphenyl-4-amino-Δ^1-cyclohexene is treated with nitrous acid, an intermediate diazonium ion (A, Scheme 6) is formed, which loses nitrogen to give the corresponding triphenyl cyclohexenyl cation (B). This carbocation on

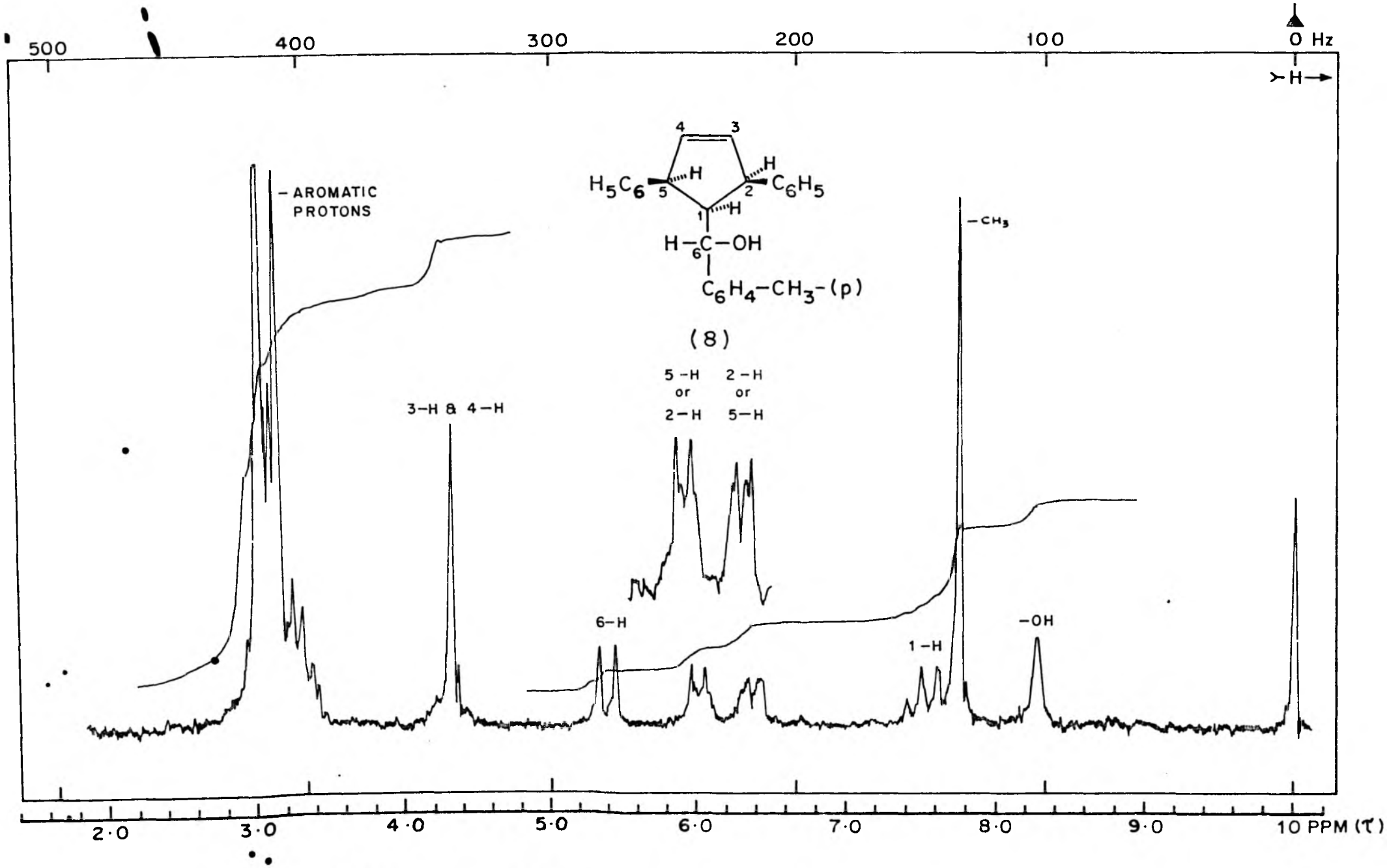
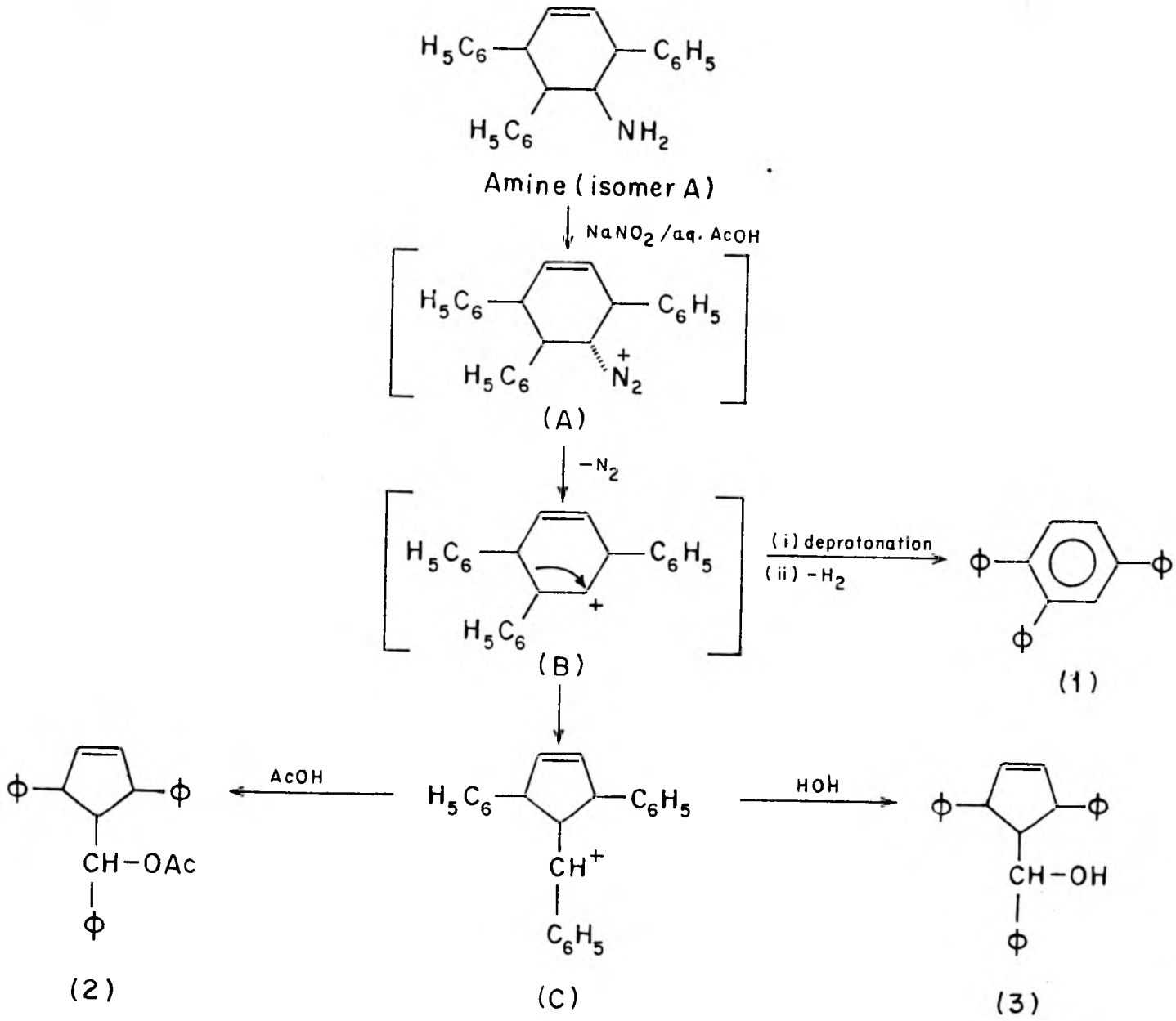
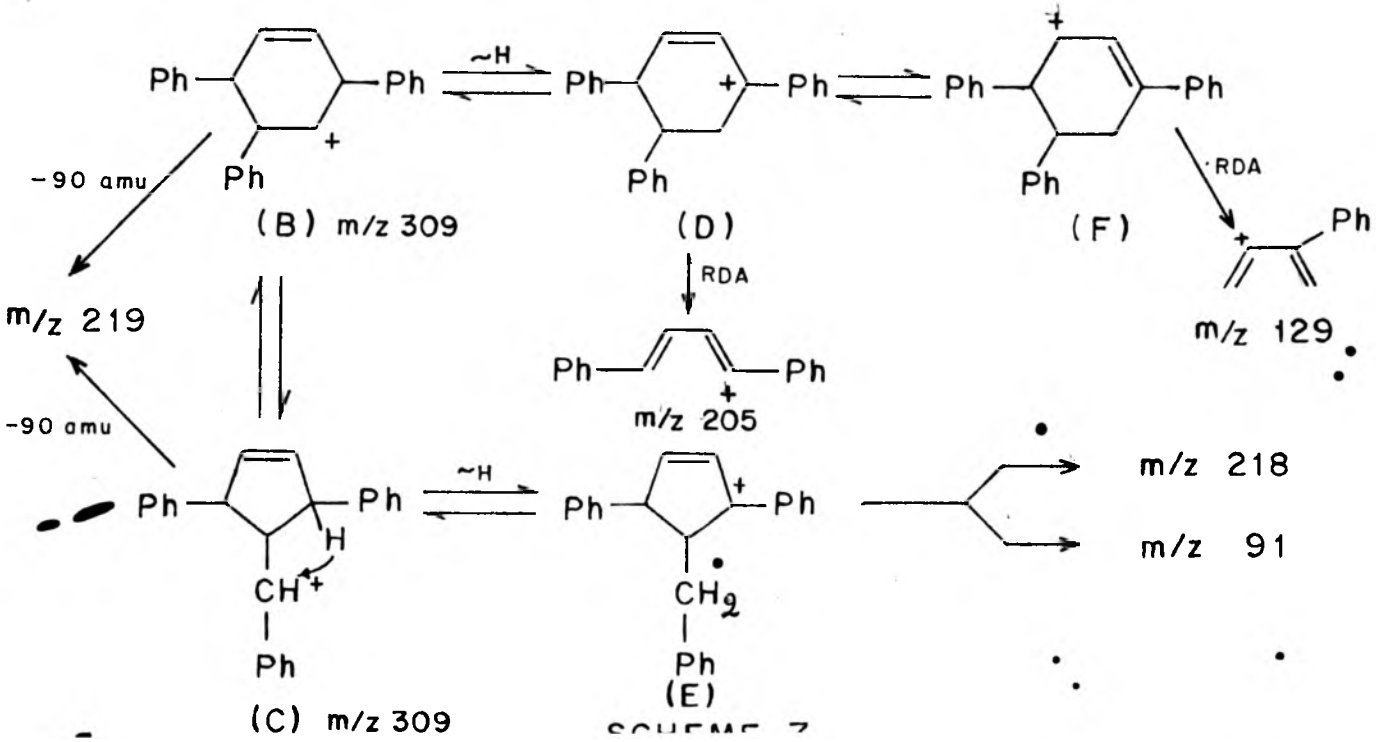


FIG. 6. NMR SPECTRUM OF 2,5-DIPHENYL-CYCLOPENT-3-EN-1-YL p-METHYLBENZYL ALCOHOL IN CCl_4


Amine (isomer A)
NaNO2 /aq. AcOH
(A)
-N2
(B)
(i) deprotonation
(ii) -H2
(1)
AcOH
HOH
(2)
(C)
(3)

SCHEME 6


~H
-90 amu
(B) m/z 309
(D)
(F)
RDA
m/z 219
m/z 129
m/z 205
m/z 218
m/z 91
(C) m/z 309
(E)

deprotonation followed by the expulsion of a hydrogen molecule can result in 1,2,4-triphenyl benzene (1). The cation B can also undergo a Wagner-Meerwein type rearrangement to give the corresponding ring contracted diphenyl cyclopentenyl benzyl cation (C). This rearrangement involves the migration of the C_5-C_6 bond to the cationic site in B. It may be due to (i) the C_5-C_6 bond is <u>trans</u> to the leaving group which is an ideal situation[27,28] for ring contraction, (ii) the stability of the resulting substituted benzylic cation. The presence of phenyl group[22,23] may also be responsible for ring contraction.

Since the reaction was carried out in aqueous acetic acid medium the nucleophilic attack by acetic acid or water molecule on cation C would result in the formation of compounds 2 and 3. These compounds account for ~ 78% of the mixture of products. A possible mechanism for this reaction is shown in Scheme 6.

The deamination reaction of 3,5,6-triphenyl-4-amino-Δ^1-cyclohexene has been shown to proceed <u>via</u> ring contraction to give the isomerised alcohol in high yields. This reaction appears to have some synthetic value in organic chemistry, since cyclopentenyl derivatives are starting materials for the synthesis of many natural products.

2. Rearrangement in the gas phase

The 3,5,6-triphenyl-4-hydroxy-Δ^1-cyclohexene (7) and 2,5-diphenyl-cyclohex-3-en-1-yl benzyl alcohol (3) exhibit loss of a molecule of water from their protonated molecular ions under CI conditions. The protonation takes place on the hydroxy group in both the compounds. Thus it is possible to produce the triphenyl cyclohexenyl (B) and diphenyl cyclopentenyl benzyl (C) cations in the gas phase. The isomerization of these cations generated from model compounds (3 and 7) was studied in the gas phase by kinetic energy release measurements (T) and collisional activation (CA) spectroscopy.

The CA spectra* of $(MH-H_2O)^+$ ions from the $(MH)^+$ ions of compounds 3 and 7 were recorded by B/E linked scan. The spectra are tabulated in Table II. It is obvious from the table that the two spectra are more or less similar. Some differences are observed especially in the relative abundances of the fragments m/z 307, 218, 217, 205, 167 and 91.

Similarities observed in the CA spectra suggest that one of the following situations may be possible: (i) $(MH-H_2O)^+$ ions from both 3 and 7 give rise to a single ionic product, (ii) A mixture of rapidly interconverting ions is formed and (iii) distinct ionic structures are formed from both

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* The author is grateful to Prof. Dr.H. Schwarz, Technical University of Berlin, West Germany, for CA spectra.

Table II

Collisional activation spectra[a] of $(MH-H_2O)^+$ ions (m/z 309) formed from the $(MH)^+$ ions of compounds 3 and 7.

Fragment ions m/z	$(MH-H_2O)^+$ ions from	
	3	7
308	b	b
307	4.4	2.2
232	2.8	2.8
231	5.7	4.7
230	0.9	0.9
229	1.5	1.5
219	1.4	1.4
218	9.9	7.8
217	11.5	8.4
216	3.1	2.2
215	3.5	2.8
205	9.2	7.8
204	2.0	2.0
203	2.2	2.1
202	2.7	2.7
191	2.1	2.1
178	1.9	2.0
168	2.7	3.4
167	17.7	25.3
166	1.2	2.2
165	2.1	2.1
141	1.3	1.5
129	1.2	1.0
115	1.3	1.5
91	8.0	6.6

a. Relative abundances are normalized to a total of 100 units over the mass range 91 - 308.

b. More abundant and not taken in the scale.

the compounds and the CA spectra are similar either by chance or the ions isomerize after collision.

From the CA spectral data alone it is difficult to decide which of the alternatives mentioned above hold good in the present case. Relatively abundant fragment ions at m/z 91, 205, 218 and 231 in the CA spectra may be due to the interconversion of ions B and C. In Scheme 1 some of the possible structures for the non-decomposing $(MH-H_2O)^+$ ions from compounds 3 and 7 are shown.

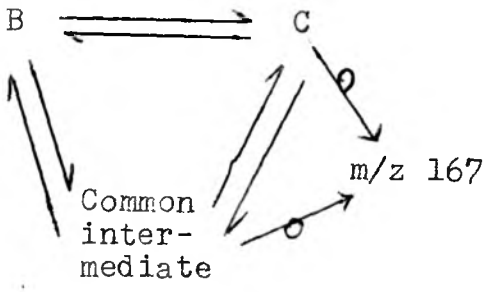
It is known that CA fragmentations proceed through simple cleavages due to the availability of excess internal energy in the collision induced ions. Some cleavage processes may precede hydrogen shifts. Thus the ions at m/z 218 and 91 in the CA spectrum of ion C can arise from a rearranged precursor ion (E). The ion E itself may result from a hydrogen shift. These ions are also encountered in the CA spectrum of ion B. The formation of the ions at m/z 218 and 91 in the spectrum of B can be explained by assuming that the ion B isomerizes to C. The relative abundance of these ions in the CA spectrum of ion B is comparatively less.

The ions at m/z 205 can arise from ion D by retro Diels-Alder fragmentation. The ion B can isomerize to ion D by a hydrogen shift. It can also give rise to ion F which can further decompose by RDA to afford diene ions at m/z 129.

The RDA fragments (m/z 205 and 129) are also observed in the CA spectrum of C. These fragmentation processes are only possible if C isomerises to B.

The formation of diphenyl methyl cation (m/z 167) is a favoured process in the CA spectra of both the ions. As indicated earlier these ions appear to be formed from ion C by skeletal rearrangement processes. The relative abundance of these ions is more in the CA spectrum of ion B. This is due to the fact that ion B undergoes an exothermic isomerization[64,72] to a more stable ion C. The driving force for this isomerization process may be the stability of benzyl cation C. Isomerization of a secondary carbonium ion B to a benzyl carbonium ion C may be associated with a release of excess energy which can be utilized for further fragmentation of the resulting cations. Thus, the cyclopentenyl benzyl cations formed from the corresponding cyclohexenyl cations by isomerization have relatively more energy than those cyclopentenyl benzyl cations formed directly from the corresponding alcohol. This interpretation is substantiated by the observation of relatively more abundant ions at m/z 167 in the CA spectra of $(MH-H_2O)^+$ ions generated from compound 7. The CA spectral data support the equilibration of the two ions B and C. The formation of a common intermediate cannot be ruled out. If one considers this possibility, the formation of ions at m/z 167 can be explained as follows. The ions B

and C may isomerize either directly or through a common intermediate or intermediates. The skeletal rearrangement ion can arise either from the common intermediate or from ion C (Scheme 8).



Scheme 8

The kinetic energy release* (T) was measured for elimination of water molecule from the $(MH)^+$ ions of compounds 3 and 7. It was also measured for the formation of m/z 167 from both the ions B and C. The data is given in Table III. It is known that the kinetic energy release data provide information on the structure of decomposing metastable ions.

From the T values it is clear that the decomposing $(MH)^+$ ions do not isomerise prior to or during the loss of water under CI conditions. If it were the case, relatively large difference in the T values would have resulted.

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* The author is thankful to Prof. Dr.H. Schwarz for T data.

Schwarz et al.[62] based on the measured T values have reported that in the gas phase the incipient cyclohexyl cation produced by dissociative ionization of cyclohexyl bromide spontaneously rearranged to 1-methyl cyclopentyl cation. The more kinetic energy release in the loss of Br from the cyclohexyl bromide molecular ion was attributed to an exothermic isomerization to the corresponding ring contracted ion. This results in line broadening of metastable peaks. Such line broadening was not observed for the loss of water from the $(MH)^+$ ions of compounds 3 and 7. The isomerization does not take place before or during the loss of water. Comparatively more kinetic energy is released in case of cyclopentenyl derivative (3).

The kinetic energy released in the formation of diphenyl methyl cations from the $(MH-H_2O)^+$ ions in both the compounds (3 and 7) is of the same order. This observation supports the view that a common ion is involved in the rearrangement process.

Conclusion:

The present work has shown that the triphenyl cyclohexenyl carbonium ion (B) isomerizes to diphenyl cyclopentenyl benzyl cation (C) under deamination conditions and in the gas phase. An analogy is observed in this isomerization which takes place in the condensed and isolated

phases. In the present study the nitrous acid deamination was carried out with the endo phenyl amino compounds while the endo hydroxy alcohol was employed in the gas phase studies.

The gas phase studies have shown that the triphenyl cyclohexenyl and diphenyl cyclopentenyl benzyl carbonium ions are interconverting directly or through a common intermediate. The precursor for skeletal rearrangement ions can be either diphenyl cyclopentenyl benzyl cation or the common intermediate ion.

Homoallylic carbonium ions are known to rearrange to allylic and tertiary carbonium ions under solvolytic and stable ion conditions. In the present system a secondary triphenyl cyclohexenyl cation is found to rearrange to a diphenyl cyclopentenyl benzyl cation. The presence of a phenyl group at C_5-position may be responsible for this phenomenon. It is interesting to study the low temperature NMR spectra of these carbocations under stable ion conditions to investigate whether these rearrangements take place in super acid media.

EXPERIMENTAL

3,5,6-Triphenyl-4-amino-Δ^1-cyclohexene

9 g of 3,5,6-triphenyl-4-nitrocyclohexene was dissolved in 80 ml of warm glacial acetic acid. In a 250 ml three necked flask which was provided with a mechanical stirrer and a dropping funnel 6 g of metallic tin and 20 ml glacial acetic acid were added. The contents were heated on a water bath and the amine dissolved in acetic acid was added dropwise from the dropping funnel in 1 hour. Stirring and heating were continued for 3 hours. The reaction mixture was filtered while hot. The filtrate was cooled and basified with 10N sodium hydroxide solution. The solution was then extracted with ethyl acetate and the ethyl acetate solution was washed with water to remove metallic salts if any. The ethyl acetate solution was concentrated to 5 ml, when 48% aqueous hydrobromic acid was added with stirring until the aqueous layer was acidic. The amine hydrobromide was collected on a Buchner funnel, washed several times with distilled water and dried in a vacuum desiccator (8.5 g). It was then washed with benzene to remove unreacted nitro compound. The amine hydrobromide salt was then suspended in 50 ml benzene and refluxed for half-an-hour. It was again collected on a Buchner funnel, washed 4 to 5 times with hot benzene. The free amine was generated by adding aqueous ammonia solution to the hydrobromide salt suspended in chloroform. The chloroform layer was separated,

washed with distilled water and dried over anhydrous sodium sulfate. The solvent removal gave 6 g of pure amine. It was crystallised from ether-petroleum ether mixture, colourless crystals, M.P. 141°C. Lit.[68] 140°.

MW (mass spectrum), 325.

IR ($CHCl_3$) ν 3510, 3420 ($-NH_2$).

NMR ($CDCl_3$) τ 3.0 (m, 15H, aromatic protons), 4.5 (bs, 2H, H-1 and H-2), 6.5 (m, 4H), 9.1 (s, 2H, NH_2).

3,6-Diphenyl-5-(p-tolyl)-4-amino-Δ^1-cyclohexene

5 g of the corresponding nitrocyclohexene was reduced with 4 g of metallic tin in 500 ml glacial acetic acid. The same procedure was followed as described previously. The amine obtained was 3.1 g. It was recrystallized from ethyl acetate in petroleum ether mixture. Colourless crystals, 2.5 g. M.P. 84°.

MW (Mass spectrum), 339.

IR ($CHCl_3$) ν 3500, 3410 ($-NH_2$).

NMR (CCl_4) τ 3.2 (m, 14H, aromatic protons), 4.2 (bs, 2H, H-1 and H-2), 6.6 (m, 4H), 7.8 (s, 3H, CH_3), 9.2 (s, 2H, NH_2).

Nitrous acid deamination of 3,5,6-triphenyl-4-amino-Δ^1-cyclohexene

4.0 g of the amine cyclohexene was taken in a 250 ml two necked round bottom flask and dissolved by adding 68 ml of 1:1 acetic acid and water mixture. The solution was stirred at -5° to 0°C when 6.4 g of sodium nitrite dissolved in 24 ml of water was added slowly over a period of 15-20 minutes.

Temperature was maintained below -5°C. After the addition of some sodium nitrite solution, a gummy material is formed in the reaction flask. A small amount of ether (10 ml) was added to the reaction mixture to make it homogeneous. After the addition the reaction mixture was brought to the room temperature and stirring continued for 3 hours. It was then warmed on a water bath at 50-60°C for 30 minutes to complete the reaction. The acid solution was carefully neutralized under cold conditions with saturated sodium bicarbonate solution. It was then saturated with common salt.

Reaction mixture was extracted with 3x50 ml of ether. It was washed twice with 10% HCl, 10% $NaHCO_3$ and water. Ethereal layer was then dried over anhydrous sodium sulfate. Solvent was removed under reduced pressure to give 3.9 g of a gummy dark brown residue. TLC of this reaction mixture in benzene:chloroform (9:1) on silica gel showed a two major and one minor components. A minor component was also noticed which was carried to the solvent front. All the components were separated by column chromatography on 160 g of silica gel. Eluted with benzene - petroleum ether mixture, the concentration of benzene was progressively increased to elute all the components in the order as shown below:

(i) Elution with 5% benzene-petroleum ether gave a colourless crystalline material, 0.125 g (1).

(ii) Elution with 15% benzene-petroleum ether gave (1.18 g), a thick liquid (2).

(iii) Compound 3 was obtained by eluting with 25% benzene - petroleum ether mixture, 1.6 g, a pale yellow crystalline powder.

(iv) Compound 4 was obtained by eluting with 40% benzene - petroleum ether, a thick resinous material, light yellow, 280 mgs.

1,2,4-Triphenyl benzene (1), 0.125 g was recrystallized from petroleum ether, colourless crystals, 0.1 g, M.P. 121°, Lit.[69] 120°.

MW (mass spectrum), 308.

Analysis calculated for $C_{24}H_{18}$: C, 93.5; H, 6.51; Found: C, 93.2; H, 6.31%.

2,5-Diphenyl cyclopent-3-en-1-yl-benzyl acetate (2), 1.18 g, BP, 222°/0.7 mm.

MW (mass spectrum), 368.

IR (Nujol) ν 1745 (C=O)

NMR (CCl_4) τ 3.16 (m, 15H, ArH) 4.16 (d, 1H, H-6), 4.36 (s, 2H, H-3 and H-4), 6.13 (m, 1H, H-2 or H-5), 6.43 (m, 1H, H-5 or H-2) 7.26 (q, 1H, H-1), 8.1 (s, 3H, $-OCH_3$).

Analysis calculated for $C_{26}H_{24}O_2$: C, 84.8; H, 6.5.

Found: C, 84.01; H, 6.3%.

2,5-Diphenyl cyclopent-3-en-1-yl benzyl alcohol (3) 1.6 g was recrystallized from petroleum ether, colourless crystals, 1.4 g.

M.P. 85°.

MW (mass spectrum), 326.

IR (Nujol) ν 3400 (-OH)

NMR (CCl_4) τ 3.1 (m, 15H aromatic), 5.3 (d, 1H, H-6), 4.3 (s, 2H, H-3 and H-4), 6.0 (m, 1H, H-2 or H-5) 6.3 (m, 1H, H-5 or H-2), 7.53 (q, 1H, H-1), 8.3 (s, 1H, -OH).

Analysis calculated for $C_{24}H_{22}O$: C, 88.4; H, 6.7.

Found: C, 88.91; H, 6.82%.

Compound 4: It was obtained in impure form as a thick liquid, 0.280 g. No attempt was made to characterize it.

Nitrous acid deamination of 3,6-diphenyl-5-(p-tolyl)-4-amino-Δ^1-cyclohexene.

1 g of amine was deaminated as described above and the usual work-up gave about 1 g of gummy dark brown residue. TLC of this reaction mixture in benzene:chloroform (9:1) on silica gel showed two major components and a minor component. All the components were separated by column chromatography on silica gel and only the fraction corresponding to alcohol was characterized. Elution with benzene - petroleum ether mixture gave all the components in the order as shown below:

(i) Elution with 5% benzene - petroleum ether gave a colourless solid, 0.045 g. It was not characterized.

(ii) Elution with 15% benzene-petroleum ether gave a thick liquid, 0.34 g and it was also not characterized.

(iii) 2,5-Diphenyl-cyclopent-3-en-1-yl-p-methyl-benzyl alcohol (8): Elution with 25% benzene - petroleum ether gave a white crystalline compound, 0.4 g.

It was recrystallized from petroleum ether.

M.P. 105°.

MW (mass spectrum), 340.

IR (Nujol) ν 3400 (-OH).

NMR (CCl_4) τ 3.2 (m, 14H, aromatic protons), 4.36 (s, 2H, H-3 and H-4); 5.4 (d, 1H, H-6, J=7), 0.06 (m, 1H, H-2 or H-5), 6.4 (m, 1H, H-5 or H-2), 7.6 (t, 1H, H-1, J=6), 7.76 (s, 3H, $-CH_3$), 8.31 (s, 1H, -OH).

Analysis calculated for $C_{25}H_{24}O$ C, 88.24; H, 7.06.

Found: C, 87.68; H, 6.98%.

3,5,6-Triphenyl-4-hydroxy-Δ^1-cyclohexene (7) was prepared by the hydrolysis of the corresponding acetate which was obtained by Diels-Alder reaction between 1,4-diphenyl-1,3-butadiene and styryl acetate. The latter compound was prepared from phenyl acetaldehyde by a well described procedure[73].

Styryl acetate

20 g of phenyl acetaldehyde and 33.6 g of acetic anhydride were taken in a clean 100 ml round bottom flask. 4 g of freshly fused potassium acetate was added to the reaction flask and the contents were heated on an oil bath at 165°C for 4 hours. The mixture was cooled and diluted with 150 ml of 2:1 pentane and ether mixture. 100 ml of 25% sodium hydroxide solution was slowly added to the reaction mixture with continuous stirring and cooling. Organic layer was washed with water and dried over anhydrous sodium sulphate

for 2 hours. Removal of the solvent gave 28 g of residue. It was distilled under reduced pressure. The fraction boiling at 96-98°C/5 mm was collected. A colourless liquid, 14 g.

3,5,6-Triphenyl-4-acetoxy-Δ^1-cyclohexene (6)

15 g of 1,4-diphenyl-1,3-butadiene, 10 g of styryl acetate and 50 mgs of hydroquinone were taken in a clean two necked 100 ml round bottom flask. A reflux condensor was attached to one neck and a nitrogen inlet tube was provided in the other neck. The contents were heated with stirring at 200-210°C on an oil bath for 7 hrs. under nitrogen atmosphere. The unreacted styryl acetate was removed from the reaction mixture by distilling under reduced pressure (3.8 g b.p. 95°C/5 mm). The residue was chromatographed on 450 g of silica gel. Elution with 20% benzene in petroleum ether gave unreacted diene (7.6 g) as a thick liquid. Elution with equal volumes of benzene and petroleum ether gave 4.4 g of adduct, a yellow resinous material. This yellow material after 2 or 3 triturations with petroleum ether - ethyl acetate gave a white crystalline adduct, 1.61 g. It was recrystallised from petroleum ether-ethyl acetate mixture, 1.4 g. M.P. 118°C. MW (Mass spectrum), 368.

IR (Nujol) ν 1740 (CO), 1040, 1360 (C-O stretching).

NMR (CCl_4) τ 3.0 (m, 5H, aromatic protons), 4.06 (bs, 2H, H-1 and H-2), 4.46 (dd, 1H, H-4), 6.0 (m, 1H, H-3), 6.36 (1H, H-6), 7.06 (t, 1H, H-5), 8.5 (s, 3H, $OCOCH_3$).

Analysis calculated for $C_{26}H_{24}O_2$: C, 84.8; H, 6.5.
Found: C, 84.93; H, 6.56%.

3,5,6-Triphenyl-4-hydroxy-Δ^1-cyclohexene (7)

The 3,5,6-Triphenyl-4-acetoxy-Δ^1-cyclohexene was hydrolysed in basic medium according to a reported procedure[74].

0.6 g of the corresponding acetate was taken in a 25 ml round bottom flask fitted with a reflux condensor. 6 ml of 5% alcoholic caustic potash (prepared by dissolving 300 mgs of potassium hydroxide in 6 ml of methanol) was added to the reaction flask and the contents were refluxed for 2 hours. The solvent was removed under reduced pressure. 5 ml of water was added to the flask. Separated solid material was collected on a Buchner funnel, washed several times with cold distilled water until the filtrate is free from base. The alcohol was dried in a desiccator. Colourless crystals, 0.53 g. Recrystallized from petroleum ether and ethyl acetate mixture. 0.45 g, M.P. 95°C.

MW (mass spectrum), 326.

IR ($CHCl_3$) ν 3350 (-OH).

NMR (CCl_4): τ 2.84 (m, 15H, aromatic protons), 4.04 (bs, 2H, H-1 and H-2), 5.58 (m, 1H, H-4), 6.04 (q, 1H, H-3), 6.36 (d, 1H, H-6, J=12), 7.28 (t, 1H, H-5, J=12), 8.88 (bs, 1H, OH).

Analysis calculated for $C_{24}H_{22}O$: C, 88.4; H, 6.7.
Found: C, 88.18; H, 6.78%.

Preparation of 1,2,4-Triphenyl benzene (1)

It was prepared according to a procedure described by Herz and Lewis[69]. A mixture of 3 g of 3,4-diphenyl-4-hydroxy-2-cyclopentenone[75], 6 g of freshly fused potassium bisulfate and 3 g of phenyl acetylene[76] was taken in a 20 ml round bottomed flask fitted with a reflux condensor and a guard tube. The contents were heated on an oil bath at 180° for 8 hrs. The potassium bisulfate was filtered and washed with benzene. The combined filtrate and washings were concentrated using an oil bath at 230-240°. The residue was chromatographed on alumina column. Elution with petroleum ether gave a crystalline product, 0.15 g. It was recrystallized from petroleum ether, MP, 119-120°. Lit. 120°.

MW (mass spectrum), 308.

Analysis calculated for $C_{24}H_{18}$: C, 93.5; H, 6.51.

Found: C, 92.98, H, 6.41%.

Hydrolysis of 2,5-diphenyl cyclopent-3-en-1-yl-benzyl acetate (2)

95 mgs of the corresponding acetate was dissolved in 0.5 ml of methanol containing 40 mgs potassium hydroxide. The resultant solution was refluxed on water bath for two hours. TLC monitering showed the quantitative conversion of acetate to alcohol. The solvent was removed and 2 ml of water was added. No solid separated out. The alcohol was dissolved in ether and washed with water thrice to remove alkali. Ethereal solution was dried over anhydrous sodium sulfate

and solvent was removed to give 80 mgs of alcohol (3) a white crystalline material. It was recrystallized from petroleum ether. MP, 85°C.

MW (mass spectrum), 326.

IR (Nujol) ν 3400 (-OH).

NMR (CCl_4) τ 3.1 (m, 15H aromatic protons), 5.3 (d, 1H, H-6), 4.3 (s, 2H, H-3 and H-4), 6.0 (m, 1H, H-2 or H-5), 6.3 (m, 1H, H-5 or H-2), 7.53 (q, 1H, H-1), 8.3 (s, 1H, -OH).

Analysis calculated for $C_{24}H_{22}O$: C, 88.4; H, 6.7.

Found: C, 88.7; H, 6.82%.

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CHAPTER IV : STUDIES ON THE STRUCTURE OF $[C_6H_6O]^{+\cdot}$ RADICAL CATIONS

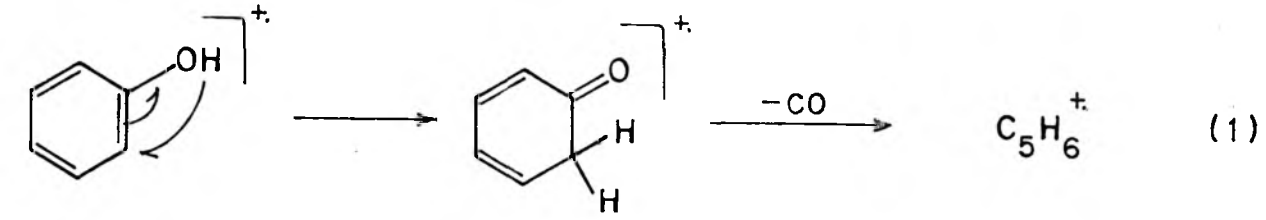
A. INTRODUCTION

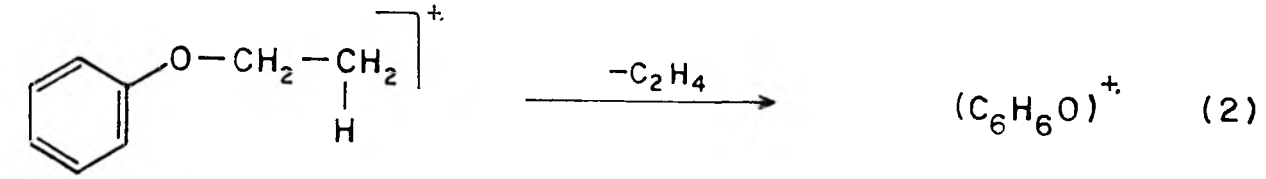
The $(C_6H_6O)^{+\cdot}$ radical cation can be generated in the gas phase by direct ionisation of phenol. Elimination of carbon monoxide from the molecular ion of phenol is an important fragmentation mode. This process is rationalised by the following mechanism in which the cyclohexadienone intermediate is formed (equation 1) by an 1,3-hydrogen migration[1,2]. Carbon monoxide loss takes place from the intermediate ion.

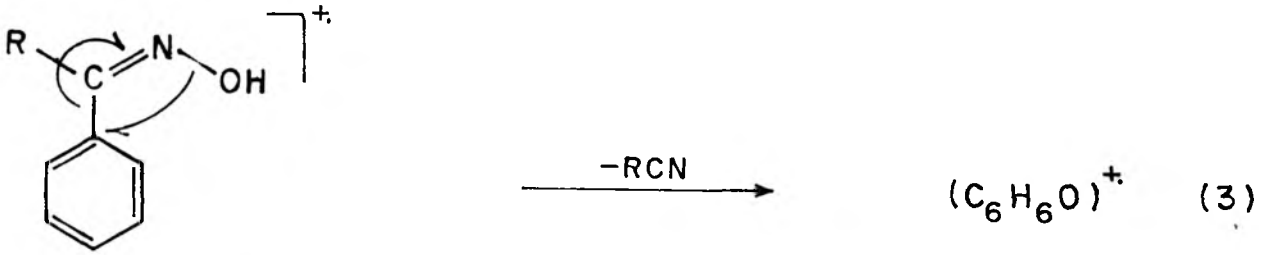
The $(C_6H_6O)^{+\cdot}$ ion can also be generated from various precursors either by fragmentation or by rearrangement. Alkyl phenyl ethers produce $(C_6H_6O)^{+\cdot}$ ions as fragment ions by a hydrogen transfer rearrangement. For example phenetole[3] loses ethylene from its molecular ion (equation 2).

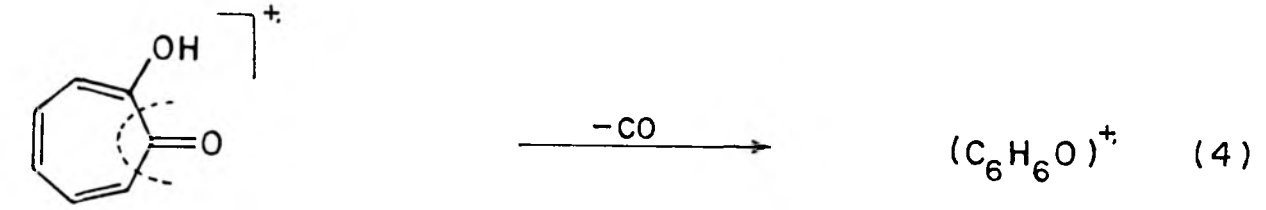
Skeletal rearrangement process can lead to the formation of $(C_6H_6O)^{+\cdot}$ ions. Elimination of RCN from the molecular ions of oximes of the type $C_6H_5-\overset{R}{\overset{|}{C}}=NOH$ results in these ions[4,5]. This involves the migration of a hydroxy group.

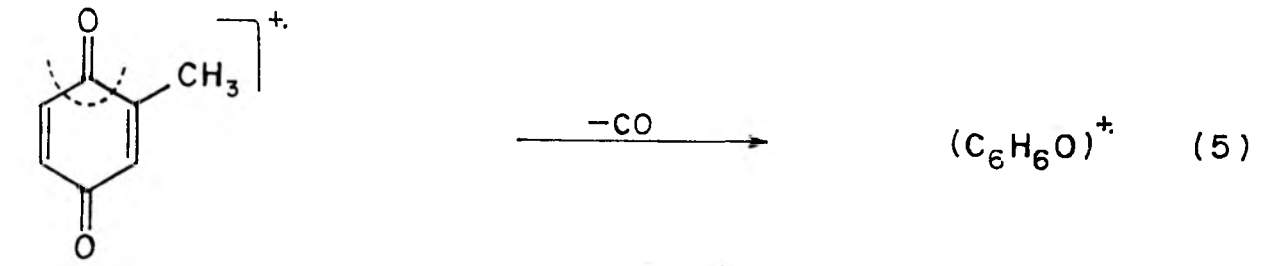
A few rearrangements accompanying the loss of small molecules can also produce $(C_6H_6O)^{+\cdot}$ radical cations. The molecular ions of tropolone expel carbon monoxide to give abundant $(C_6H_6O)^{+\cdot}$ ions (equation 4). A similar fragmentation takes place from the molecular ions of methyl p-benzoquinone[6] (equation 5). The loss of ketene from the molecular ion of

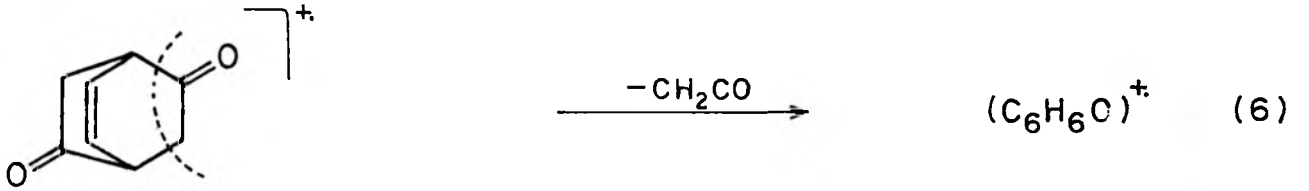


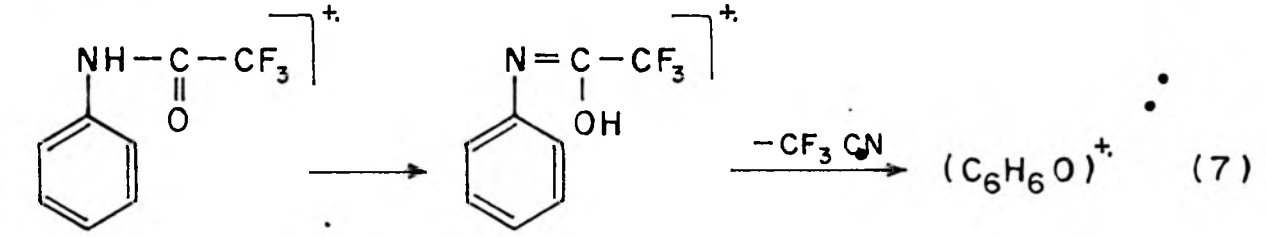












FORMATION OF $(C_6H_6O)^{+\cdot}$ ION FROM DIFFERENT PRECURSORS

bicyclo(2.2.2)oct-2-en-5,7-dione[7] affords $(C_6H_6O)^{+\cdot}$ ions (Equation 6).

N-trifluoracetanilide undergoes enolization followed by skeletal rearrangement to give $(C_6H_6O)^{+\cdot}$ ions (equation 7).

B. PREVIOUS WORK

In 1959, McLafferty[3] reported a hydrogen transfer rearrangement in the EI spectrum of ethyl phenyl ether, which results in the formation of $(C_6H_6O)^{+\cdot}$ radical cations. This led to a large number of investigations on the structure and formation of $(C_6H_6O)^{+\cdot}$ ions. Almost all modern mass spectral techniques have been employed to study this system in the gas phase.

MacLafferty and Schiff[8] have studied the effect of ring substituents on the formation of $(Y\text{-}C_6H_5O)^{+\cdot}$ ions from a series of m- and p-substituted aryl alkyl ethers. They found that for several substituents the relative abundance of $(Y\text{-}C_6H_5O)^{+\cdot}$ ions is independent of ring position, which could be due to isomerisation. It was observed that the $(Y\text{-}C_6H_5O)^{+\cdot}$ ions formed by rearrangement and by direct ionisation exhibit nearly identical metastable ion characteristics. Based on these data, it was concluded that $(Y\text{-}C_6H_5O)^{+\cdot}$ ions formed in the spectra of substituted aryl alkyl ethers have phenolic structure without loss of ring position identity. Similar conclusions were drawn by Shapiro and Tomer[9].

Based on metastable ion abundance data and labelling studies[10], it was shown that the formation of $(C_6H_6O)^{+\cdot}$ ions from ionized p-bromophenetole proceeds *via* a 4-membered transition state and the resulting ion has a phenol structure. Using (1- ^{13}C) phenol[11], it was demonstrated that there is no loss of ring carbon identity in the ionized phenol before the elimination of CO. Woodgate and Djerassi[12] reported that no scrambling takes place in the molecular ions of (1-^{13}C) phenyl n-butyl ether. They concluded that $(C_6H_6O)^{+\cdot}$ ions formed from phenyl butyl ether have phenol like structure.

The formation of $(C_6H_6O)^{+\cdot}$ ions from ionized phenyl-n-butyl ethers was studied using labelled compounds[13]. It was proposed that competing specific hydrogen transfer processes operate which result in both phenol and cyclohexadienone ions. The results showed that the hydrogen transfer from different positions is due to transition states of different ring sizes rather than to the intervention of scrambling of the hydrogen before fragmentation. Deuterium labelling of phenyl valerate in the α-position indicated 87% of the hydrogen is from the α-position and only 13% come from other positions[14]. Six centred as well as four centred cyclic transitions were proposed to rationalize these observations.

Later investigations clearly demonstrated that in the formation of $C_6H_6O^{+\cdot}$ ions from ionized alkyl phenyl ethers and their analogs, the hydrogen transfer takes place to the

oxygen only and not to the phenyl ring. Benoit and Harrison[15], using specifically labelled compounds, studied the elimination of propene from phenyl n-propyl ether under electron ionization and chemical ionization conditions. It was suggested that the hydrogen comes from all the three positions of the side chain but is exclusively transferred to the oxygen. A similar mechanism was proposed under chemical ionisation.

The results obtained by Levsen and co-workers[16] using field ionization kinetics also support the hydrogen transfer to the oxygen and not to the ring in phenyl-n-propyl ether.

On the basis of the IP and AP values of a series of ring substituted halophenetoles and the $(M-28)^{+\cdot}$ ions, Bursey and Parker[17] favoured a four centred mechanism. No substituent effect was reported. From the energetics of formation of $(C_6H_6O)^{+\cdot}$ ions from alkoxy benzenes[18], it was shown that none of the fragment ions have enthalpies as low as the corresponding phenol molecular ion. The formation of a fragment having a cyclohexadienone ion structure or a structure of similar enthalpy was postulated to explain the observations. Similarly, kinetic energy release measurements[19] for the formation of $(C_6H_6O)^{+\cdot}$ ions from phenetole have supported the cyclohexadienone structure.

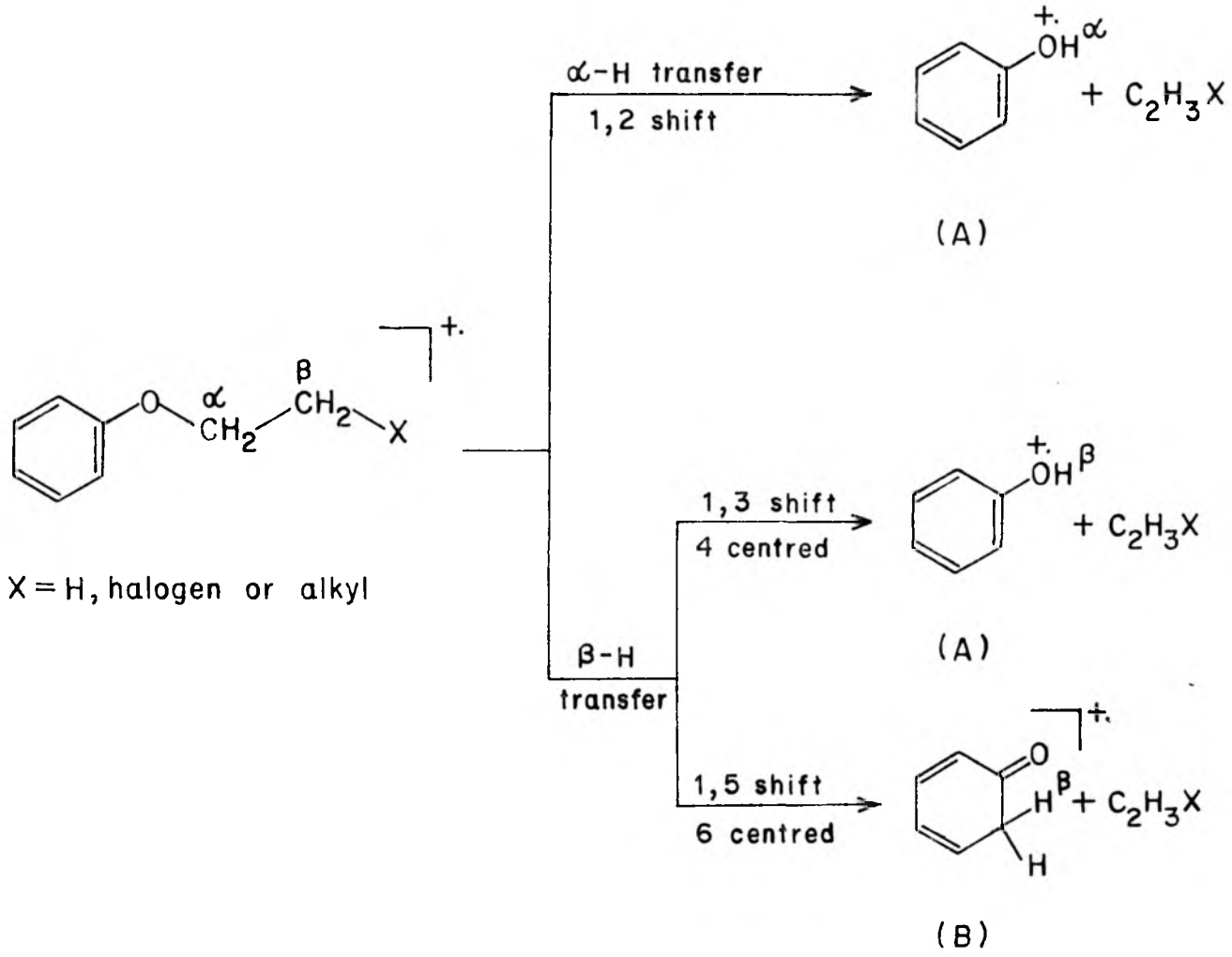
Ion cyclotron resonance (ICR) studies[20] provided

evidence for the phenolic structure for the $(C_6H_6O)^{+\cdot}$ ions from phenyl ethyl ether. Several deuterated analogs were examined. There was no evidence for the formation of cyclohexadienone ions from these precursors. Tomer and Djerassi[7] used the same technique. They suggested that the two ionic structures are distinct and exhibit characteristic ion molecule reactions of their own in the ICR cell. Partial interconvertion of hexadienone ion to the enol form was proposed. Based on ICR studies on $(C_6H_6O)^{+\cdot}$ ions from phenyl acetate it was concluded that a four centred mechanism is involved in the elimination of ketene.

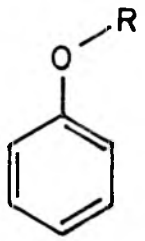
The two structures of the $(C_6H_6O)^{+\cdot}$ ions from alkyl phenyl ethers and analog are shown in Scheme 1.

C. PRESENT STUDY

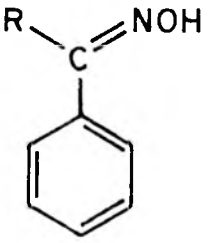
In the present investigation, the $(C_6H_6O)^{+\cdot}$ radical cations from ten compounds with different structures were generated and studied by the MIKE technique. The kinetic energy released in the decarbonylation reaction of the decomposing $(C_6H_6O)^{+\cdot}$ ions was measured. Similarly, the non-decomposing $(C_6H_6O)^{+\cdot}$ ions were activated by collision with neutral gas and the decomposition products were analyzed by MIKE technique. The compounds examined are shown in Scheme 2.


α-H transfer
1,2 shift
+ C_2H_3X
(A)
1,3 shift
4 centred
+ C_2H_3X
(A)
β-H
transfer
1,5 shift
6 centred
+ C_2H_3X
(B)
X = H, halogen or alkyl

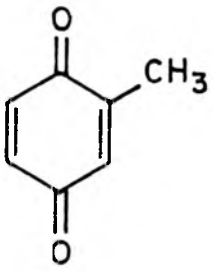
SCHEME 1



1. R = H
2. R = C_2H_5
3. R = $-\overset{\overset{O}{\|}}{C}-CH_3$
4. R = C_6H_5



5. R = H
6. R = CH_3



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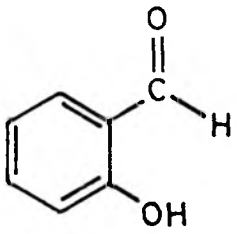

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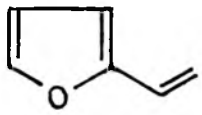

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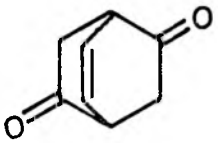

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SCHEME 2

D. DISCUSSION

1. Kinetic energy release measurements

All the compounds 1-10 examined in the present study produce abundant $(C_6H_6O)^{+\cdot}$ radical cations at m/z 94 in their normal 70 eV electron impact mass spectra. Simple ionization of compounds 1 and 9 leads to the formation of these ions, while fragmentation processes are involved in the case of compounds (2-8 and 10). These ions further decompose by the elimination of carbon monoxide (CO) to give abundant ionic signals at m/z 66. The kinetic energy release (T) associated with this fragmentation mode was measured for all the compounds 1-10 (Table I).

The kinetic energy release values obtained for these compounds are relatively large (0.50 eV). This is consistent with rearrangement processes which proceed through activated complexes via tight transition states containing large excess of reverse activation energy $E^{\neq}_{o}$. In addition, the activated complex may contain non-fixed excess energy $E^{\dagger\dagger}$ due to kinetic shift[19].

During the course of this investigation, Hoffman et al.[21] have also reported the kinetic energy release values for the loss of carbon monoxide from $C_6H_6O^{+\cdot}$ ions generated from six different precursors. They have shown that these reactive ions exist at least in two different forms (ionized phenol

Table I

Kinetic energy release measurements for the reaction $[C_6H_6O]^{+\cdot} \rightarrow [C_5H_6]^{+} + CO$

Compd. No.	Compound	T_{CO} (eV)[a]
1.	Phenol	0.49
2.	Phenetole	0.50
3.	Phenylacetate	0.52
4.	Diphenyl ether	0.50
5.[b]	Syn-Benzaldoxime	c
6.	Acetophenone oxime	0.56
7.	Methyl-p-benzoquinone	0.50
8.	Salicylaldehyde	d
9.	Vinylfuran	0.47
10.	Bicyclo[2.2.2.]oct-2-en-5,7-dione	0.42

a: Values obtained by scanning the electric sector voltage and calculated from the width of the peaks at half-height (uncorrected for main beam width). Previously reported values for 1, 2 and 4 are respectively 480, 505 and 514 meV [22].

b: Anti-Benzaldoxime behaves similarly. The data reported throughout this work concern the syn-isomer.

c: Interfering isotope fragmentation $[93]^{+} \rightarrow [66]^{+} + HCN$ excludes a correct measurement of T. The shape of the metastable peak is nevertheless similar to that of the other compounds.

d: A reliable value cannot be determined because of an interfering fragmentation $[93]^{+} \rightarrow [65]^{+} + CO$.

and cyclohexadienone). Experimental values reported by these workers are in agreement with some of the data collected in the present study.

It is clear from Table I, that the compounds 1-9 give similar T values but the bicyclic diketone released comparatively less energy (0.42 eV) for the loss of carbon monoxide from the $C_6H_6O^{+\cdot}$. The $(C_6H_6O)^{+\cdot}$ ions produced by fragmentation are likely to contain more internal energy[19,22] than those produced by direct ionization. This excess internal energy is then channeled into translational energy release of the products. The kinetic energy release data obtained for the compounds 1-9 shows that this is valid for all the compounds except 10 for which the energy is much less (T_{co} = 0.42 eV). The similar T values obtained for compounds 1-9 indicate that the reactive $(C_6H_6O)^{+}$ ions generated from these compounds rearrange to a common intermediate prior to the loss of carbon monoxide.

The bicyclo(2.2.2)oct-2-en-5,7-dione (10) was chosen by Tomer and Djerassi[7] in their ICR study as a model compound to generate authentic cyclohexadienone ion (B). The $(C_6H_6O)^{+\cdot}$ ions generated from 10 further fragment by the elimination of CO and a methyl group. The latter fragmentation supports a non-phenolic structure for the $(C_6H_6O)^{+\cdot}$ ion produced from bicyclic ketone (10). In the ICR experiments[7,13] tautomerism of keto form (B) to phenolic structure (A) has been suggested.

As there appears to be some apparent contradiction in these observations, the bicyclic diketone (10) was reexamined under electron ionization. The mass spectrum of this compound is shown in Figure 1. The base peak in the spectrum is due to an ion at m/z 66. It is formed from $(C_6H_6O)^{+\cdot}$ ion by the elimination of CO. The molecular ion (m/z 136) is stable and exhibits significant loss of CO competing with two other processes. They are the elimination of ketene and acetaldehyde. The expulsion of ketene from the molecular ion proceeds by retro Diels-Alder reaction. Such fragmentation processes have been reported in various bicyclic ketones[23]. The MIKE spectrum obtained for the molecular ion of compound 10 has confirmed all the transitions discussed above. Thus, it may be assumed that the $(C_6H_6O)^{+\cdot}$ ions generated from the molecular ions of 10 by a RDA elimination of ketene[24], have a cyclohexadienone structure (B). If this is really the case, the low T_{co} value (Table I) indicates that ions B and A are distinct and non-interconverting species. This result also shows that all decomposing $(C_6H_6O)^{+\cdot}$ ions generated from 1 to 9 isomerize to a common intermediate prior to the expulsion of CO, which may be structurally distinct from the cyclohexadienone ion (B).

These results are in good agreement with a situation

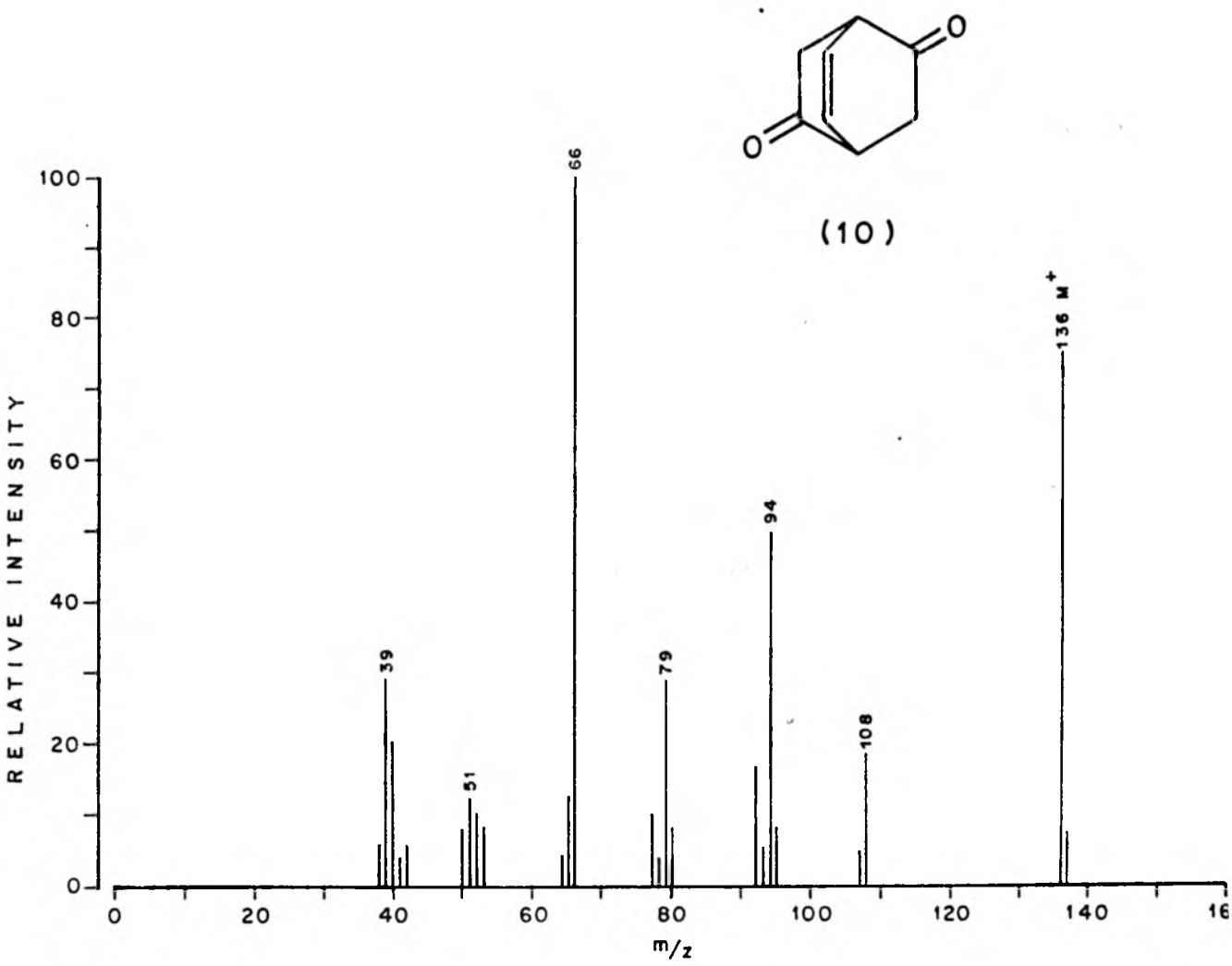

O
O
(10)
RELATIVE INTENSITY
100
80
60
40
20
0
66
136 M+
94
39
79
108
51
0
20
40
60
80
100
120
140
m/z

FIGURE - 1

where A isomerizes to B in a rate determining step[25,26]. Thus, B produced from A would undergo loss of CO with excess energy in the transition state some of which is in the reaction co-ordinate. This leads to broadening of the metastable peak. However, the following observations do not support isomerization of these two ions, (i) no isotope effect for CO loss is observed for phenol O-d_1 , (ii) the ion abundance ratio $(C_5H_6)^{+\cdot}/(C_6H_6O)^{+\cdot}$ is far greater (> 1) for 10 than for 1 (< 1), and (iii) isomerization of the $(C_6H_6O)^{+\cdot}$ ions generated from 7,8 and 9 to a phenol structure would have to precede the rate determining isomerization of enol ion to keto structure in order to account for the higher kinetic energy values. This is a complex situation that appears rather unlikely.

From the above discussion it can be concluded that the isomerization of reactive phenol (A) and cyclohexadienone ions (B) before the decarbonylation reaction is unlikely. The isomerization barrier between these two ions is greater than their decomposition barrier.

2. Collisional activation spectra

The conclusions based on kinetic energy release values for reactive $(C_6H_6O)^{+\cdot}$ ions can not be extrapolated to another energy scale. Therefore it was necessary to investigate the structure and reactivities of the non-decomposing ions. On an average, these ions would

relatively have lower internal energy content than the decomposing ions discussed in the previous section. Hence, these ions, in general, do not reveal the phenomenon of isomerization. But the isomerization is quite likely, if the energy required for isomerization is comparatively less than the maximum energy (E_{max}) available in the ions. Tomer and Djerassi[7], based on ICR experiments have proposed partial isomerization of keto to enol form on the ICR time scale (~ 10^{-3} s). It was therefore , interesting to find out whether or not, the ionized cyclohexadienone species (B) have rearranged to ionized phenol (A), within 10^{-5} seconds (CA time scale) as compared to ICR time scale. Application of the technique of collisional activation to the problem of structures of non-decomposing ions has been discussed in detail by Levsen and Schwarz[27].

The CA spectra of $(C_6H_6O)^{+\cdot}$ ions generated from compounds 1-10 are shown in Table II. They have also recorded[28] the CA spectra of 1 and 10. The spectra reported here are similar to those obtained by Levsen et al. for $(C_6H_6O)^{+\cdot}$ ions. The following general observations are made before discussing each CA spectrum in detail.

(i) The CA spectra of $C_6H_6O^{+\cdot}$ ions generated from compounds 1-9 are similar. The fragments with m/z 93, 65, 55, 51, 39 and 27 are present in the spectra of all these compounds in more or less the same abundances. The CA spectrum of 10 is

Table II

The Collisional Activation Spectra[a] of $(C_6H_6O)^{+\cdot}$ ions (m/z 94) generated from compounds 1-10[b].

Compd. No.	m/z 93	92	81	80	79	77	76	75	74	65	63[c]	55	53	51	42	39	29	27	26
1.	20.9	2.5	-	-	0.7	2.0	1.6	-	1.6	37.0	5.2	4.8	3.5	5.1	1.0	11.9	0.8	1.4	-
2.	17.1	2.4	-	-	0.8	1.9	1.6	-	1.7	40.1	5.7	5.0	3.5	5.2	0.9	12.1	0.8	1.3	-
3.	18.7	2.5	-	-	0.7	2.1	1.7	-	1.7	35.3	5.9	4.9	3.6	5.6	1.2	13.6	0.9	1.6	-
4.	17.8	2.5	-	-	d	d	d	d	d	37.0	5.5	4.9	3.6	5.4	1.5	13.3	1.2	1.9	-
5.	25.2	2.2	0.6	-	1.0	1.2	1.2	-	1.3	37.9	4.4	4.2	3.0	4.4	0.9	10.6	0.8	1.3	-
6.	19.4	2.7	-	-	1.1	2.1	1.6	-	1.7	33.6	5.5	5.1	4.0	5.5	1.1	13.7	1.1	1.8	-
7.	11.3	2.3	-	-	2.8	1.0	-	2.1	1.6	39.0	6.4	2.7	8.8	6.7	0.7	12.8	0.8	1.1	-
8.	13.7	1.7	-	-	-	-	12.2	4.1	3.0	43.8	4.9	1.7	3.0	4.1	0.4	6.2	0.4	0.5	-
9.	18.3	2.7	-	0.7	0.8	-	-	-	-	33.8	7.7	3.3	-	4.2	-	18.9	1.2	3.4	-
10.	4.9	-	-	-	0.4	0.6	-	1.0	-	67.9	4.3	0.6	-	4.0	-	12.6	-	1.8	1.6

a: For operating conditions see Experimental section. Abundances relative to total ion current excluding m/z 66.

b: Refer to Scheme 2.

c: Unresolved peaks = m/z 63 or 62.

d: Interferences with first field free region metastable fragmentations. The abundances are normalized with m/z 65 taken as 37% (value obtained in the case of phenol).

different from the other spectra. It shows less abundant peaks at m/z 77 and 55.

(ii) The elemental compositions of the fragments have been assigned as shown below.

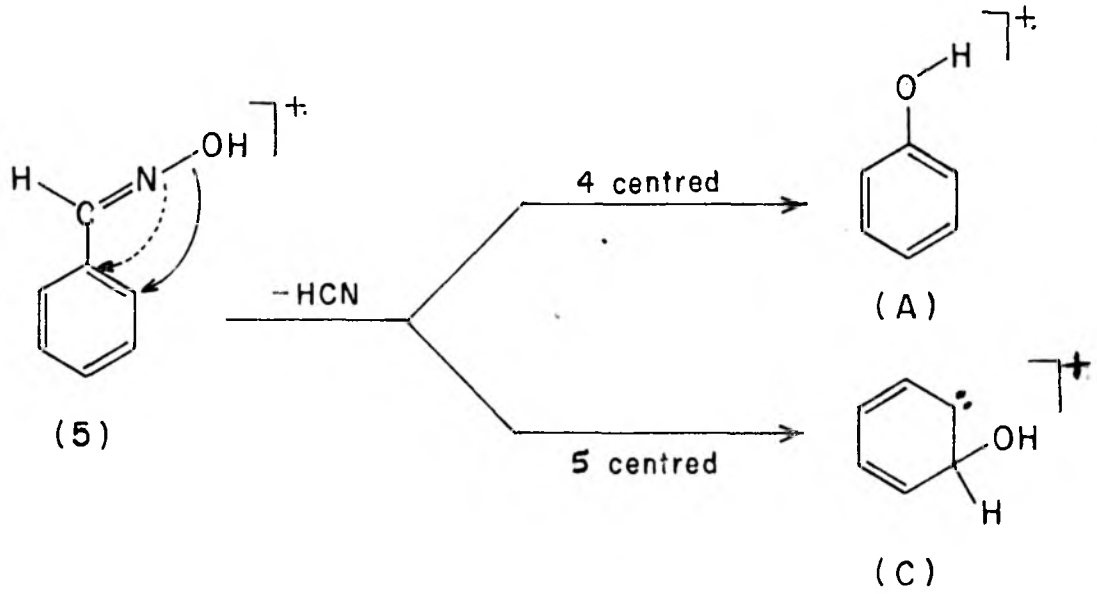
m/z	Elemental composition	Fragmentation process
65	$(C_5H_5)^+$	$(C_6H_6O)^{+\cdot} \rightarrow (C_5H_5)^+ + CHO^{\cdot}$
55	$(C_3H_3O)^+$	$(C_6H_6O)^{+\cdot} \rightarrow (C_3H_3O)^+ + C_3H_3^{\cdot}$
51	$(C_4H_3)^+$	$(C_6H_6O)^{+\cdot} \rightarrow (C_4H_3)^+ + C_2H_3O^{\cdot}$
39	$(C_3H_3)^+$	$(C_6H_6O)^{+\cdot} \rightarrow (C_3H_3)^+ + C_3H_3O^{\cdot}$

(iii) Depending on the structure of the precursor ion, some small differences are observed in the relative intensities of the fragments from m/z 81 to m/z 74, which reflects the structural characteristics of isomeric $(C_6H_6O)^{+\cdot}$ ions.

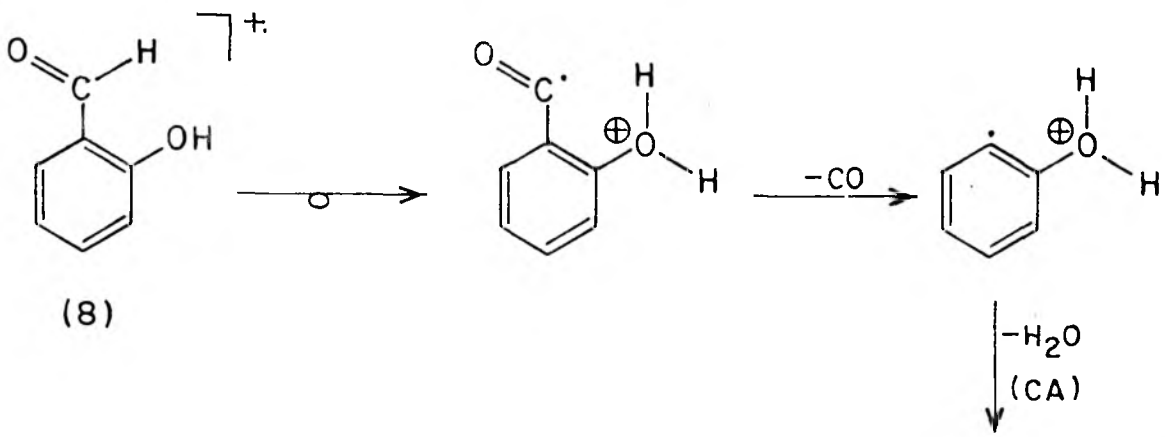
The CA spectra of $(C_6H_6O)^{+\cdot}$ ions generated from compounds 1-4 are similar suggesting identical structures to these ions. An abundant ion at m/z 77 in all these compounds supports the phenol-like structure (A). The peak at m/z 77 was not shifted in the O-d_1 analog. The

hydrogen atom lost in the elimination of hydroxy radical comes exclusively from the original phenolic -OH group. This also explains the absence of scrambling between the aromatic and phenolic protons prior to loss of OH radical. If the keto species generated from 10 undergoes keto-enol tautomerism on the CA time scale then, one would expect a fragment at m/z 77. This was not observed. It clearly demonstrates that the non-reactive ions do not isomerize in the gas phase. The maximum available energy (E_{max}) is less than the activation energy barrier for isomerization. Based on ICR experiments[7,10,29] it was shown that phenetole and phenyl acetate generate $(C_6H_6O)^{+\cdot}$ ions by a four centred mechanism to give phenol-like structure (A). Similarly compounds 2-4 appear to give rise to ionized phenol by a four centred mechanism on CA time scale.

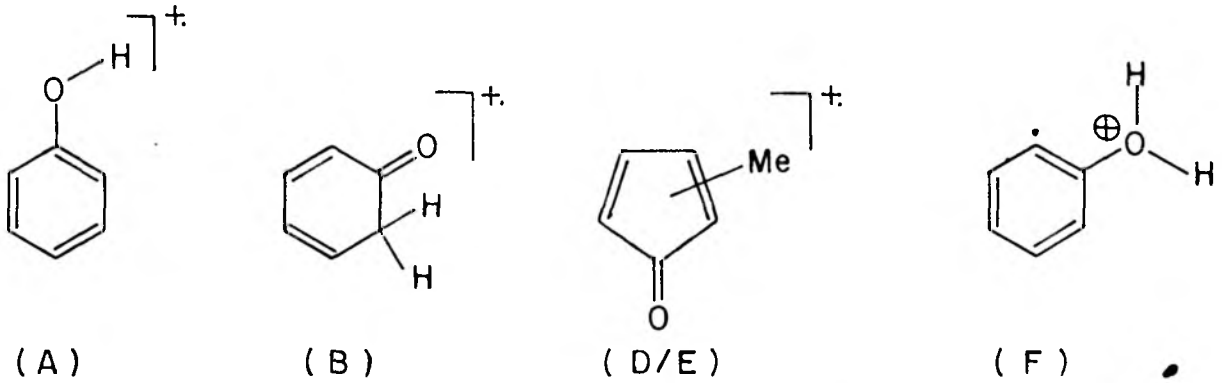
The expulsion of RCN (R = H, Me) from 5 and 6 also produces $(C_6H_6O)^{+\cdot}$ ions. Their CA spectra are similar to those of compounds 1-4. Dijkstra[30,31] have postulated four and five membered transition states in the elimination of hydrogen cyanide from molecular ion of benzaldoxime (5) to account for the composite metastable peak (Scheme 3). The wide component of the metastable peak being more abundant than the narrow one. Expulsion of methyl cyanide from the molecular ions of acetophenone oxime (6) also showed composite metastable peak but a reverse trend was observed

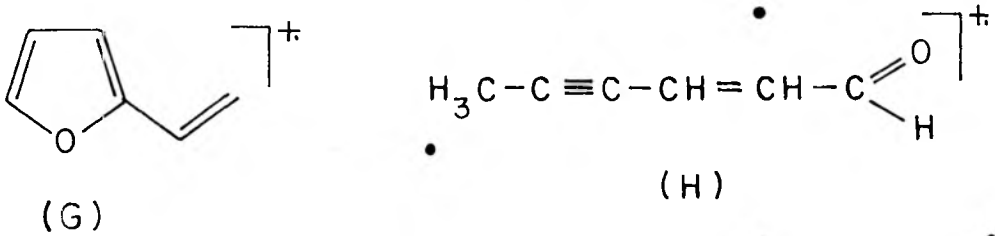


SCHEME 3



SCHEME 4





SCHEME 5

i.e., the wide component being less abundant than the narrow one. Similar metastable peak shapes have been observed for the elimination of RCN from compound 5 and 6.

In general composite metastable peaks are due to different structures for the reactive ions or products. In the present case the composite metastable peak shapes could be ascribed to different $(C_6H_6O)^{+\cdot}$ ion structures arising from different transition states. Thus, the elimination of RCN from $(C_6H_6O)^{+\cdot}$ ions form 5 or 6 through a four centred transition state would give rise to ion A whereas five membered transition state leads to the formation of carbene type structure C (Scheme 3). Beynon et al.[33,34] have offered similar explanation for composite metastable peak shapes in the expulsion of CH_2O from $(M-HCN)^{+\cdot}$ fragment ions produced from benzaldoxime o-methyl ethers. Despite the fact that four and five membered transition states give rise to different product ions, the CA spectra of 5 and 6 are similar to those of compounds 1-4. No evidence for carbene structure (C) nor for possible isomerization to a cyclohexadienone ion (B) was evident from the CA spectral data. The CA fragment at m/z 81 observed only for benzaldoxime (5), cannot reflect a carbene structure since this compound loses HCN predominantly via a four centred mechanism. Probably the carbene type intermediate ions (C) have sufficient activation energy to isomerize into a

thermodynamically stable phenol ion structure by a rapid 1,2-hydride shift. Hence the non-decomposing $(C_6H_6O)^{+\cdot}$ ions generated from 5 and 6 may also have phenol like structure (A).

Methyl-p-benzoquinone (7) generates $(C_6H_6O)^{+\cdot}$ ions by the expulsion of CO from the molecular ions[6]. It is apparent that the CO loss from the molecular ions takes place in two ways leading to a mixture of 2- and 3-methyl cyclopentadienones (D and E, Scheme 5) or to the corresponding acyclic species. The ions at m/z 51 $(C_4H_3)^+$, 53 $(C_4H_5)^+$ and 79 reflect the structural features of the ions D and E.

The major fragmentation process of salicylaldehyde (8) under electron ionization is the loss of H$^{\cdot}$, which is followed by the elimination of CO to give an abundant ion at m/z 93[35]. A minor fragment ion at m/z 94 is formed in the spectrum which arises from the expulsion of CO from the molecular ion as shown in Scheme 4. A significant ion at m/z 76 can result from the loss of water from $(C_6H_6O)^{+\cdot}$ ion by an ortho effect[36]. The radical cation F appears to be unique and is different from ion A. The absence of a fragment ion at m/z 77 and very intense ion at m/z 76 support this assumption.

2-Vinyl furan (9) on electron impact forms $(C_6H_6O)^{+\cdot}$ ions. From the CA spectrum it is concluded that this ion has a different structure G. Some of the characteristic features of this ion are: (i) absence of ions at m/z 76 and 77; (ii) a peak at m/z 80 which may correspond to the

loss of methylene from the side chain, and (iii) very intense peaks at m/z 39 and 51.

Thus the CA spectral studies on the non-decomposing $(C_6H_6O)^{+\cdot}$ ions showed the existence of at least five (A-G) different stable ions (Scheme 5), whose structural assignments have been made on the basis of the analysis of CA spectra in the region m/z 81 to m/z 74.

To explain these results, a low energy isomerization step was considered so that CA spectra result in the superposition of fragment ions originating from a stable 'initial' species and also from an isomerized common ion structure. The latter may probably give rise to the common fragment ions at m/z 93, 92, 65, 55, 51 and 39 whatever the precursor may be. In an attempt to determine the structure of the isomerized $(C_6H_6O)^{+\cdot}$ ions, the CA spectra of several linear $(C_6H_6O)^{+\cdot}$ ions with different functional groups have been recorded and studied. Molecules with keto and alcohol functions are known to fragment by α- and β-cleavages[35], and these structures appeared unlikely as precursor ions for the loss of CO. Dipropargyl ether also behaved in a different way under EI conditions. It showed no elimination of CO. In the absence of suitable α,β-unsaturated aldehydes, the CA spectrum of crotonaldehyde was recorded and examined. The molecular ion exhibits the intense loss of CO and CHO in the second field free region. Since this behaviour is

analogous to the present system, it can be suggested that the isomerized reactive ion for 1-9 may have an ionized α,β-unsaturated aldehyde like structure H (Scheme 5), but not a cyclohexadienone.

Conclusion

Kinetic energy release (T) measurements and CA spectral studies on $(C_6H_6O)^{+\cdot}$ ions generated from ten different precursors suggest that the ion B is unique and that ionized phenol (A) does not ketonize prior to the loss of carbon monoxide. Both these structures exist in deep potential wells.

The CA spectra of the non-decomposing $(C_6H_6O)^{+\cdot}$ ions exhibit five stable ionic structures in the gas phase. These species however partly isomerize to a common structure before losing CO. The assumptions made here regarding the ion structures are tentative, since the acyclic model compounds are not available. An α,β-unsaturated aldehyde like structure (H) has been proposed to the common ion which is shown to be formed from all the compounds except the bicyclic diketone.

After the present work was published, Gross et al.[37] investigated the structural problem on $C_6H_6O^{+\cdot}$ ions. They have postulated the keto-enol tautomerism to explain the chemistry of $(C_6H_6O)^{+\cdot}$ ions generated from ethyl phenyl ether

and bicyclo(2,2,2)oct-2-ene-5,7-dione. The $(C_6H_6O)^{+\cdot}$ ions generated from the above compounds were studied by measurement of [redacted] kinetic energy release for the reaction $C_6H_6O^{+\cdot} \rightarrow C_5H_6^{+\cdot} + CO$. Contrary to the previous reports, it was shown that both phenol and cyclohexadienone ions isomerize if they are sufficiently activated to expel carbon monoxide. The phenol ion was shown to isomerize to keto form by a high energy 1,3-hydrogen shift, a symmetry forbidden process. It is the rate-determining step for CO loss. If the isomerization takes place by a rate-determining step and fragmentation occurs from keto form, then there would be substantial kinetic shift for ions having shorter life time. There would be then unusual contributions from the excess internal energy $E^{\ddagger}$ and the reverse activation $E_o^{\ddagger}$ energy to the kinetic energy released. This hypothesis is supported by the fact that the values of kinetic energy release at long ion life times for the enol form of $(C_6H_6O)^{+\cdot}$ ions converge to the value measured for ions generated from the keto form. Because of the large kinetic barrier for the ketonization, a large fraction (~ 20%) of excess energy in the transition state is released as kinetic energy in the expulsion of CO from the $(C_6H_6O)^{+\cdot}$ ions. The tautomerism was not detected for stable ions, but only for those having sufficient activation to undergo loss of CO.

Maquestiau and co-workers[38] have measured the kinetic energy released during the decarbonylation reaction of

decomposing $(C_6H_6O)^{+\cdot}$ ions generated from phenol. The measurements were carried out on three different double focusing instruments. Contrary to the results obtained by Gross et al.[37] it was observed that the kinetic energy release for CO loss from phenol does not decrease as the ion accelerating voltage is decreased. In fact, an increase was observed which was attributed to an instrumental descrimination against off-axis ions at low voltage. They have further concluded that the kinetic energy release data obtained for $(C_6H_6O)^{+\cdot}$ ions generated from phenol do not demand the tautomerism before decarbonylation reaction.

EXPERIMENTAL

The MIKE and CA spectra were recorded on a Varian MAT 311A reversed geometry instrument equipped with a small collision chamber. The samples were introduced through the direct inlet system and volatilized at the lowest temperature possible. The spectra were measured at 70 eV with an accelerating voltage of 3 KV and an initial electric sector voltage of 505 volts. The MIKE spectra were obtained by scanning the electric sector voltage. The kinetic energy release (T) values were calculated from the width at half-height of the metastable peaks[39]. The CA spectra of the metastable ions in the field free region were also obtained by scanning the electric sector voltage at a preselected magnetic field value. Air was used as collision gas at a pressure of 2×10^{-4} torr.

Samples 1, 4 and 8 were purchased from Aldrich and used after further purification. The other compounds were prepared according to well described procedures. Their purity and identity were established by physical constants and spectral data. The IR spectra were recorded on a Perkin Elmer Infracord Spectrophotometer. The melting points were determined in silicone oil (melting point apparatus) and are uncorrected.

Phenetole (2)

It was prepared according to the procedure described

by King and Wright[40]. 3.9 g of potassium was dissolved in 30 ml of methanol under cold conditions in 100 ml round bottomed flask. 9.4 g of freshly distilled phenol and 22 g of ethyl phthalate were added to the flask. The excess methanol was removed from the reaction flask under reduced pressure. A thick residue obtained was heated at 190-200° (oil bath), using an air condensor for 3 hours. 50 ml of cold water was added after cooling. The contents were extracted with ether. Ethereal layer was washed with 2N sodium hydroxide and water. It was dried on anhydrous sodium sulphate. Removal of the solvent gave a light brown residue. It was distilled under reduced pressure. Fraction boiling at 170-175° was collected as colourless liquid. Yield 7.0 g.
BP, lit.[40] 170°.
MW (mass spectrum), 122.

Phenyl acetate (3)

It was prepared as described in literature[41]. 5.9 g of phenol dissolved in 40 ml of 10% sodium hydroxide were placed in a 150 ml reagent bottle. 50 g of crushed ice was added to it and the contents were shaken vigorously for 5 minutes. The reaction mixture was extracted with 20 ml of carbon tetrachloride. It was washed with 10% sodium carbonate and saturated sodium bicarbonate solutions until effervescence ceased. The carbon tetrachloride layer after drying on sodium sulphate was removed under suction.

The residue was distilled under reduced pressure. A fraction boiling at 194-196° was collected as colourless liquid. Yield 8 g.

α-Benzaldoxime (5)

10.5 g of benzaldehyde was placed in a 2 necked 100 ml round bottomed flask fitted with a mechanical stirrer. The other neck of the flask was used for additions. 7 g of sodium hydroxide dissolved in water was added to the flask. Then 7.5 g of hydroxylamine hydrochloride was added in small portions with stirring at room temperature (15 minutes). Some heat was developed in the reaction mixture. Upon, cooling, a crystalline sodium derivative separated out. Sufficient water was added to make the solution clear and it was saturated with carbon dioxide. The solution was extracted with ether. The ethereal solution was dried on magnesium sulphate. Removal of ether on water bath gave a residue which was distilled under diminished pressure. A fraction boiling 120°/10 mm was collected. It was solidifed on cooling. Yield, 5.6 g, colourless crystals.
MP, 34°. Lit.[42] 35°.

Acetophenone oxime (6)

It was prepared from acetophenone. Same procedure was followed as described above. 12 g of acetophenone and 7 g of sodium hydroxide dissolved in 20 ml of water were

taken in a 2 necked round bottomed flask. 7.5 g of hydroxylamine hydrochloride was added to the flask in portions with stirring in 15 minutes. It was worked up as mentioned above. Yield, 6.1 g, colourless crystals. MP, 58°, Lit.[42] 60°.

Methyl p-benzoquinone

A method described by Chattaway and Parkes[43], was employed in the preparation of this compound. 450 ml of distilled water was placed in a 2 necked 1 litre flask fitted with a mechanical stirrer and a 125 ml separating funnel. The flask was in a freezing bath. 120 g of conc. sulphuric acid was added dropwise to the flask to prepare dilute acid. When the contents of the flask were cooled to 5°, 15 g of o-toludine was added dropwise through the separating funnel with continuous stirring. After the addition was over, 39 g of powdered potassium dichromate was added in one gram batches with stirring during the period of 4 hours at 5°. After dichromate addition the stirring was continued for half an hour more and the content of the flask were left aside for 12 hours. The separated p-toluquinone was filtered and distilled in small portions at a time in a current of super heated steam. It was recrystallized from petroleum ether. Yield 10 g, light yellow plates. MP, 68-70° Lit.[43], 70°.

2-Vinyl furan (9)

It was prepared by the procedure described by Hachihama and Imato[44]. 10 g of freshly distilled furfural, 20 g of acetic anhydride and 20 g of anhydrous sodium acetate were taken in a 100 ml round bottomed flask attached with a reflux condensor. The contents were heated at 150-160° (oil bath) for 20 hours. The basic reaction mixture was extracted with ether (100 ml) to remove the unreacted furfural. 50 ml of water was added to it and acidified with 10% dilute hydrochloric acid. On cooling crystalline furan acrylic acid was separated. It was filtered. Yield 9 g. Thus obtained acid was distilled slowly in the presence of 1.5 g of anhydrous copper sulphate and 39 g of quinoline. A fraction distilled at 96-102° was collected. It was dried on calcium chloride, and redistilled. BP, 98-100°, yield, 2 g. Lit.[44], 99-101°.

Bicyclo(2,2,2)oct-2-en-5,7-dione (10)

This compound was synthesized by cyclo addition of maleic anhydride to hydroquinone followed by hydrolysis[45] and oxidative decarboxylation using lead tetraacetate[46].

A mixture of 20 g of hydroquinone and 40 g of maleic anhydride was placed in a 2 necked 250 ml round bottomed flask attached with a reflux condensor and a $CaCl_2$ guard tube. The second neck of the flask was provided with a gas inlet tube for passing carbon dioxide. The contents were

heated for 1.5 hours at 200-205°. 200 ml of ether was added after cooling. The insoluble solid was filtered and washed several times with ether. Removal of ether gave a brown residue. Three crystallizations of the residue from anhydrous acetone gave pure adduct, bicyclo(2,2,2)octane-2,5-dioxo-7,8-dicarboxylic anhydride, 3.6 g. Colourless plates, MP, 270-72° (decomp), Lit.[45] 251-253° (decomp). This adduct was hydrolysed by crystallizing it in water to the corresponding cis-acid, colourless crystals, 3.0 g. MP, 250-255° (decomp). Lit.[45], 248-253° (decomp).

2.26 g of above obtained bicyclo(2,2,2)octane-2,5-dioxo-7,8-cis-dicarboxylic acid was taken in a 50 ml round bottomed flask provided with a guard tube and a magnetic stirring needle. 10 ml of acetonitrile and 1.6 g of anhydrous pyridine were added with stirring when a good suspension was resulted. 4.43 g of freshly prepared lead tetraacetate was added to the reaction flask in batches. A precipitate started forming and the temperature rose with evolution of carbon dioxide. The reaction mixture was kept at 50° till the evolution of carbon dioxide ceased. Stirring was continued for 1 hour more. Thus resulted light brown mass was dissolved in 30 ml of 10% cold nitric acid and the clear solution was extracted with ether for 24 hours by a continuous liquid liquid extracting apparatus. The ether phase was washed five times with 2.5 ml portions of 50% potassium hydroxide solution and then with saturated

ammonium sulphate solution. The ethereal solution was dried over sodium sulphate. Solvent was removed to give a crude material, 1.1 g. MP, 85-90°. It was purified by subliming at 80°/11 mm. MP, 97°. Lit.[46], 99°.

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