SOME ASPECTS OF ORGANIC MASS SPECTROMETRY

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BY

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STATEMENT

It is certified that this thesis is an authentic record of research carried out by Mr. K.P. Madhusudanan under the supervision of Dr. K. Ganesh Das in partial fulfilment of the requirements for the award of the DEGREE OF DOCTOR OF PHILOSOPHY of the UNIVERSITY OF KERALA and that it has been composed by the candidate himself.

No part of this thesis has previously formed the basis for the award of any degree, diploma, associateship, fellowship or other similar title or distinction.

(K.P. MADHUSUDANAN)
Candidate.

(K. GANESH DAS)
Research Guide

C O N T E N T S

INTRODUCTION

The thesis deals with some basic studies on the fragmentation mechanism, substituent and stereochemical effects and comparison of fragmentation mode under different ionisation conditions of some phenyl substituted nitro and amino cyclohexenes. The structures assigned to the ions are only arbitrary.

All the mass spectra, unless stated otherwise, were recorded on a CEC 21-110 B double focusing mass spectrometer at 70 eV using the direct inlet system. All the spectra were reproducible within $\pm$ 3%.

CHAPTER - I

UNIMOLECULAR ION DECOMPOSITIONS: A REVIEW

A. Ionisation

1. Franck-Condon principle

Of all the methods which have been used to ionise atoms and molecules electron impact is by far the most frequently employed. The configuration of the atomic nuclei in the molecule will change very little during the passage of the ionising electron through it, although the electrons in the molecule will change their positions and energies considerably during this interval resulting in the ejection of one of the valence electrons[1]. The transition will follow the Franck-Condon rule, which requires that the configuration and momenta of the nuclei do not change during the transition. Ionisation under electron impact is, therefore, a vertical process (Fig. 1a). Theoretical considerations show that one can not treat the ionisation process as the removal of an electron from a single bond in the molecule. The redistribution of electronic charge between the bonds takes place so rapidly that all bonds are weakened simultaneously in the ionisation process. However, there will often be some bond which is weakened much more than others, and bond

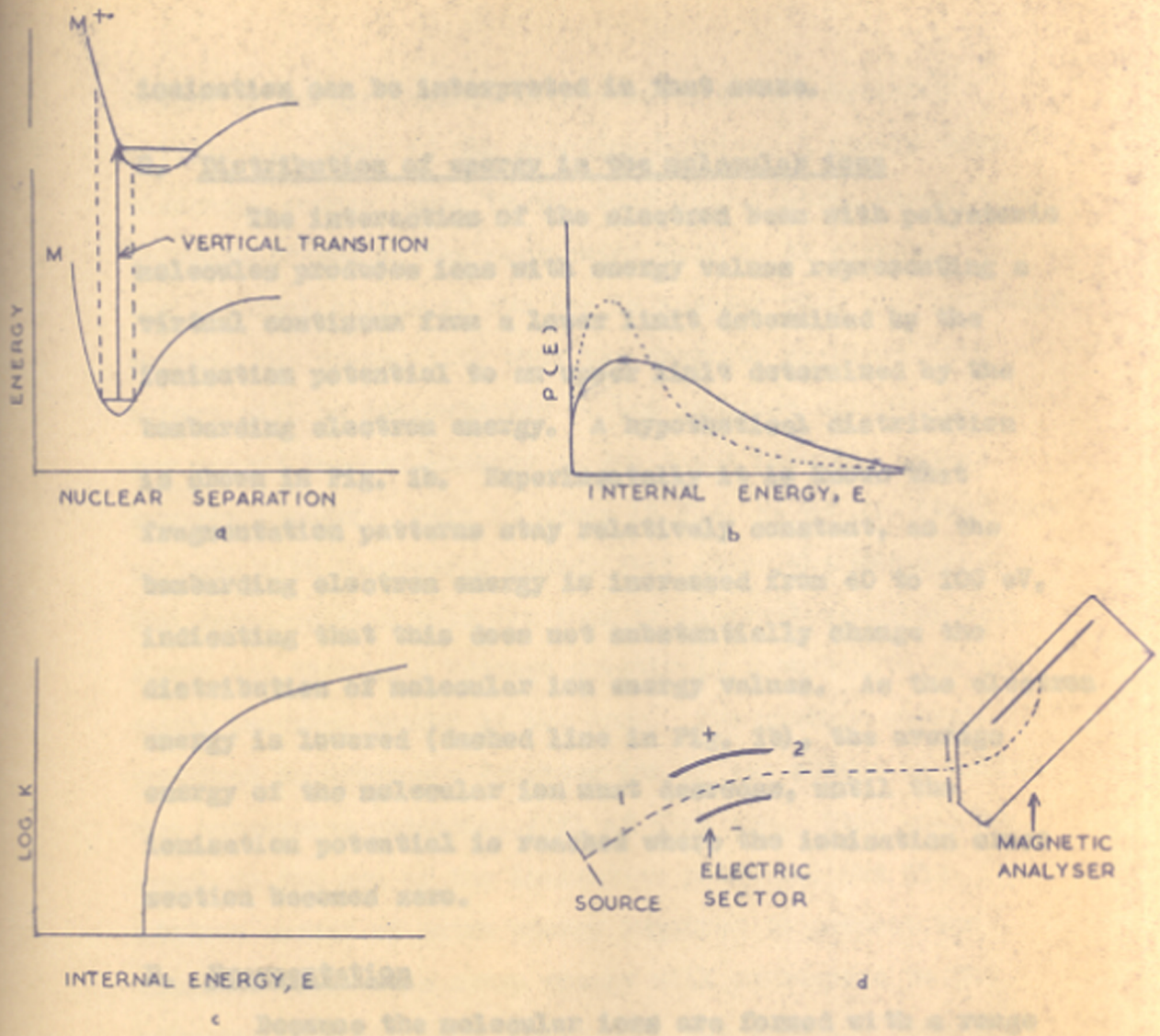

M+·
M
VERTICAL TRANSITION
ENERGY
NUCLEAR SEPARATION
a
P(E)
INTERNAL ENERGY, E
b
LOG K
INTERNAL ENERGY, E
c
+
2
1
−
SOURCE
ELECTRIC SECTOR
MAGNETIC ANALYSER
d

FIG. 1

ionisation can be interpreted in that sense.

2. Distribution of energy in the molecular ions

The interaction of the electron beam with polyatomic molecules produces ions with energy values representing a virtual continuum from a lower limit determined by the ionisation potential to an upper limit determined by the bombarding electron energy. A hypothetical distribution is shown in Fig. 1b. Experimentally it is known that fragmentation patterns stay relatively constant, as the bombarding electron energy is increased from 40 to 100 eV, indicating that this does not substantially change the distribution of molecular ion energy values. As the electron energy is lowered (dashed line in Fig. 1b), the average energy of the molecular ion must decrease, until the ionisation potential is reached where the ionisation cross section becomes zero.

B. Fragmentation

Because the molecular ions are formed with a range of energy values, for the same decomposition reaction they will exhibit a range of rates. The dependence of rate on internal energy for a particular reaction is shown in Fig. 1c. The formation of the activated complex (transition state) which can lead to decomposition requires that a particular

amount of energy becomes concentrated in the reaction coordinate. Thus if the reaction involves a simple bond cleavage, energy equal to the bond dissociation energy must be concentrated in the particular bond to be cleaved. If the internal energy of the ion is greater than the threshold energy, the probability that the required decomposition energy will be concentrated in the reaction coordinate at any moment becomes greater as the total internal energy becomes greater. This is shown in Fig. 1c by the steep rise of rate with increasing energy just above the threshold. The decomposition rate for ions of internal energies well above the threshold becomes relatively insensitive to the exact internal energy of the ions. The minimum energy required to produce a daughter ion in the source is called the appearance potential (AP) of that ion. This will be equal to the sum of the ionisation potential and the minimum amount of extra energy required to produce the daughter ion. This extra energy will correspond to the vibrational activation energy (E_o) for reaction from the ground state of $M^{+\cdot}$ and hence AP - IP = E_o.

As the precursor ions undergoing a particular decomposition have a variety of internal energy values above that required by the activation energy, the products

will also be formed with a variety of internal energy values. For a particular fragmentation the distribution of energy values can be schematically represented as in Fig. 1b and the dependence of the rates of secondary decompositions on the internal energy of the fragments can be represented as in Fig. 1c. As the electron beam energy is lowered, the energy distribution of the molecular ions becomes weighted to lower energies. Consequently, ions formed from reactions requiring more energy (whether produced in one or more steps from the molecular ion) diminish in intensity relative to the intensity of the molecular ion or disappear altogether. Low eV spectra are thus much simpler than 70 eV spectra.

1. Quasi-equilibrium theory

The quasi-equilibrium theory (QET) of mass spectra developed by Rosenstock et al.[2] is an attempt to calculate mass spectra of large, unsymmetrical polyatomic molecules using statistical methods based on a simplified model of the ionisation and fragmentation processes. The reactions leading to the formation of a mass spectrum are considered to be a series of competing and consecutive unimolecular decomposition reactions originating from the molecular ion. A fundamental postulate of the theory is that the rate constant for each reaction may be calculated by applying

the appropriate form of the absolute rate theory.

In the original and simplest form of the QET, the relationship between the rate constant k and the internal energy E was expressed as follows:

$$k = \nu (E-E_o/E)^{s-1} \qquad \text{(1)}$$

Where E_o is the activation energy for the reaction in question, ν may be regarded as the frequency factor and s is the effective number of oscillators. The failure of the theory in the quantitative aspects of mass spectra and in predicting the behaviour of molecules in the vicinity of the ionisation threshold has developed a prejudice among many organic chemists that the QET could offer them little in their attempts to understand the mass spectra of complex, polyfunctional molecules. However, it has transpired during recent years that the primary reactions occurring from the molecular ion can in many cases be very profitably looked at in terms of the fundamental assumption of the theory[3].

2. Consecutive and competitive reactions

The abundance of a particular fragment ion depends on the rates of all reactions producing this product and on the rates of all possible reactions by which this ion product subsequently decomposes. Thus in reactions (2) -(6)

$$ABC \xrightarrow{-e} ABC^{+\cdot} \xrightarrow{k_1} A^+ + BC^\cdot \quad \text{—— (2)}$$

$$\xrightarrow{k_2} A^\cdot + BC^+ \quad \text{—— (3)}$$

$$\downarrow k_2'$$

$$B^+ + C \quad \text{—— (4)}$$

$$\xrightarrow{k_3} C^\cdot + AB^+ \quad \text{—— (5)}$$

$$\downarrow k_3'$$

$$A^+ + B \quad \text{—— (6)}$$

The abundance of BC^+ ion depends on k_2, and k_2', and the abundance of A^+ ions on k_1, k_3 and k_3'. Because the rate of a particular decomposition reaction is dependent on the precursor ion energy, the probability of an ion decomposing by one of several competitive pathways is also dependent on the internal energy of the ions. As the electron beam energy is increased the energy distribution becomes more weighted to higher energies and there is a corresponding increase in the abundance of daughter ions.

3. Major factors determining reaction pathways

The three major factors determining reaction pathways are (i) location of active site (ii) stability of the products and (iii) structural factors.

(i) Location of active site:-

Both the localised positive charge and radical site trigger fragmentation reactions[4]. In many cases these are located at the same site, but the decompositions of cyclic molecules and rearrangement reactions usually involve ion species in which these sites appear to have been separated. Further, the positive charge and the unpaired electron exhibit quite different reactivities. The cation site should reflect the charge distribution in the molecule and the radical site should signify lowered electron density in a molecular orbital that is ordinarily filled.

Removal of an electron from a double bond results in an ion which can be represented by a number of resonance forms with the charge or radical on different sites.

$$C{=}C \xrightarrow{-e} C \overset{+}{-} C \longleftrightarrow C^{+} - \dot{C} \longleftrightarrow \dot{C} - C^{+}$$

To achieve overall stability it is generally more important to stabilize the positive charge than the radical site. Unsaturated groups containing heteroatoms may also be written in different forms for different types of reaction.

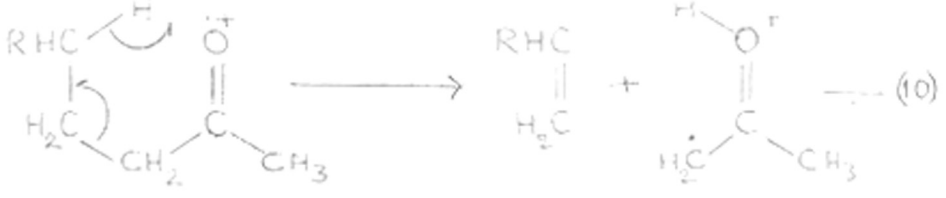
$$R - \overset{+\cdot}{\underset{\vdots}{O}} = C - R' \longrightarrow R\text{-}C{=}O^{+} + {}^{\cdot}R' \qquad (7)$$

$$R - \overset{\cdot}{\underset{\curvearrowleft}{O}} - C - R' \longrightarrow R\text{-}\overset{O}{C} + R'^{+} \qquad (8)$$

Despite the oversimplification involved in this "active site" approach it has proved useful in interpreting and predicting mass spectral data. Functional groups containing heteroatoms generally provide the most powerful directive effects in mass spectral reactions. Unsaturated moieties are also important in this regard, while saturated carbon-carbon and carbon-hydrogen bonds appear to be the least effective. Thus in locating the active site in a particular molecule, the active species of lowest energy are most probably those which arise by the removal of a non-bonding electron.

The possible reaction which an unpaired electron generated by ionisation can induce, involves the formation of a new bond. This is a powerful driving force for ion decomposition reactions. Bond formation is generally an exothermic process and thus can help offset the energy required for the cleavage of some other bond in the ion.

— (9)



— (10)

Heterolytic cleavage at the cation site and rearrangement to the cation site are also important processes in mass spectrometry.

$$R - CH_2 - \overset{+\cdot}{Cl} \longrightarrow R - CH_2^{+} + Cl \qquad (11)$$

$$H\overset{+}{O}=CH_2 \longrightarrow C_2H_4 + HO^{+}=CH_2 \qquad (12)$$

ii) Stability of the products:-

The principal peaks in the mass spectrum of a particular compound should correspond to the most stable ion products of the most favourable reaction pathways[5]. The most important general factor favouring a particular reaction is the stability of the products which are produced. Stability is important for the ion and the neutral product. The stability of the ion is important in determining the abundance of that particular ion because an increase in stability reduces further decomposition. In general, both ionic and neutral species containing an unpaired electron are less stable and more reactive than paired electron species.

iii) Structural factors:-

It has been pointed out by Junk and Svec[6] that the ionisation potential of a polyfunctional molecule is determined by the functionality of the lowest ionisation potential, provided there is no appreciable interaction

between the functional groups. If the ionisation potential and the average energy of the precursor ions are lowered by the addition of a substituent without appreciably affecting the energy-rate curves of the effective decomposition reactions the molecular ion abundance will increase. A very large reduction in the fragmentation characteristics of the keto group has been observed when an amine function is introduced in a carbonyl compound[7,8]. Structural changes also affect the energy-rate curve for a particular pathway. It may introduce a new pathway not possible in the original structure. The mass spectra of branched chain compounds show cleavage at the position of branching.

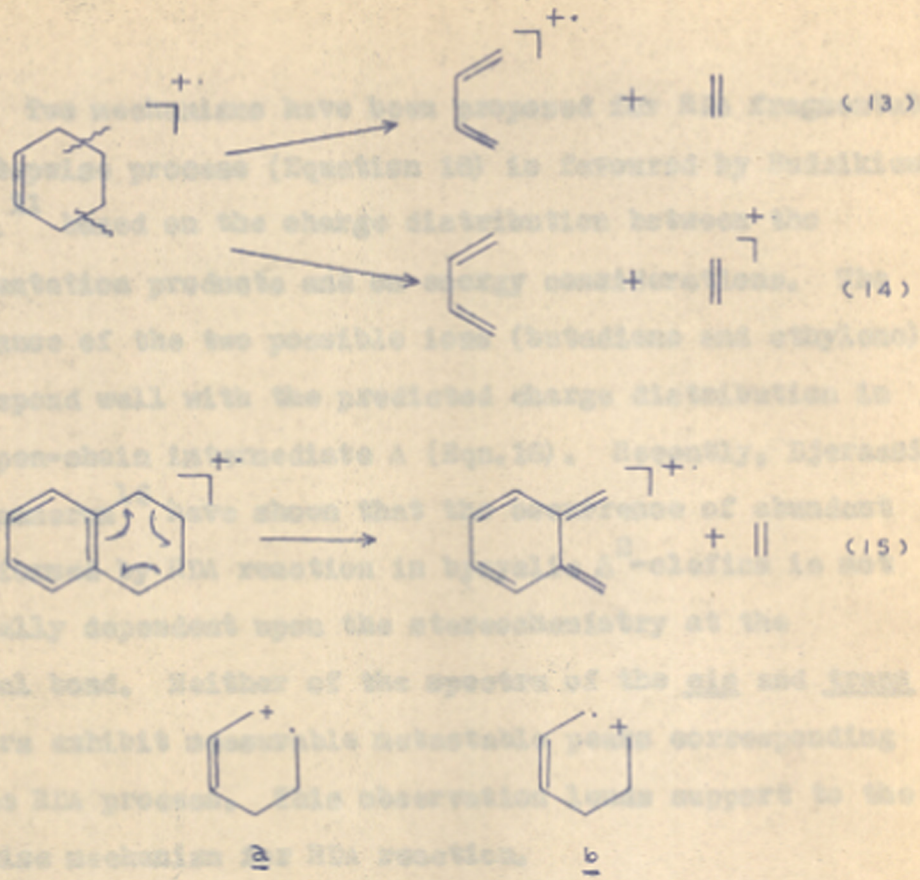
C. Retro Diels-Alder Reaction

It has been observed repeatedly that Diels-Alder adducts are thermally unstable[9]. Dissociation takes place to different extent depending upon the nature of the adducts. Electron impact induced retro Diels-Alder (RDA) reaction was first formulated by Biemann[10] and has been extensively studied by others[11].

It is one of the most important processes occurring in many organic compounds which contain a double bond in a six membered ring. Cyclohexene is the simplest molecule in which this reaction can occur. In the mass spectrum of cyclohexene[12] the ion at m/e 54, (15.5% of the total ion current)

and the m/e 28 ion, (1.6%) are the products of RDA reaction. RDA reaction appears specially favourable when the cyclohexene double bond is part of an aromatic system as for example in tetralin[11] (Scheme 1). This fragmentation process provides a unique method for structure elucidation of polycyclic compounds of considerable complexity (terpenoids, steroids, alkaloids and flavanoids)[13].

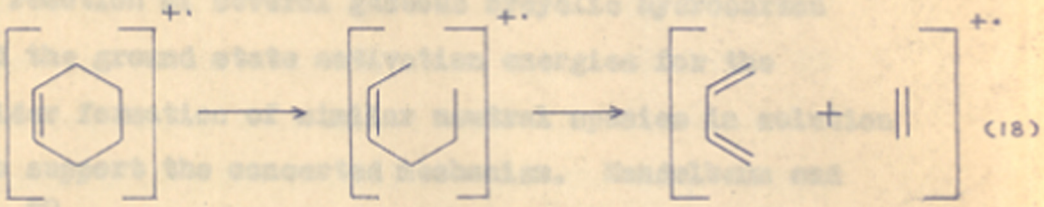
The difference in the abundances of the diene and dienophile ions in the spectrum of cyclohexene has been explained on the basis of the observed appearance potentials of the products[11]. It seems reasonable to assume that the reaction (13) involves an intermediate a and reaction (14) proceeds through an intermediate b (Scheme 1). The RDA reaction provides a suitable illustration of the application of Stevenson's rule[14]. For example, the molecular ion of ∝-terpeneol can decompose by a RDA process to form the diene and the allylic alcohol (Eqn.16). The relative ionisation potentials of the products (9.0 eV for the diene and 9.4 eV for the alcohol) lead to the prediction that the peak due to the charged diene will be more in the spectrum. This is borne out by its mass spectrum[15]. In the mass spectrum of trans -Δ^2-octalin the peaks at m/e 54 and m/e 82 due to RDA reaction are of almost equal intensity. Cyclohexene and butadiene both have ionisation potentials close to 9.1 eV.



SCHEME - I

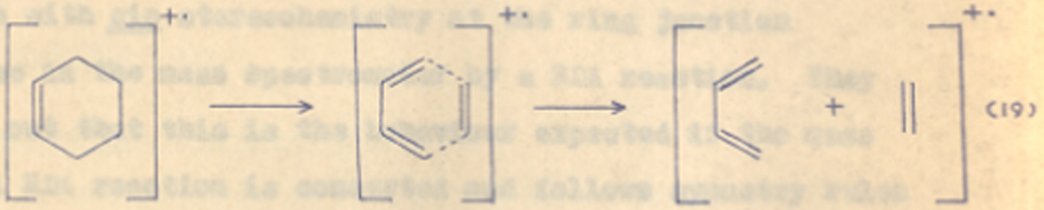
Two mechanisms have been proposed for RDA fragmentation. The stepwise process (Equation 18) is favoured by Budzikiewicz et al.[11] based on the charge distribution between the fragmentation products and on energy considerations. The abundance of the two possible ions (butadiene and ethylene) correspond well with the predicted charge distribution in the open-chain intermediate A (Eqn.18). Recently, Djerassi and Hammerum[16] have shown that the occurrence of abundant ions formed by RDA reaction in bycyclic Δ^2-olefins is not generally dependent upon the stereochemistry at the central bond. Neither of the spectra of the cis and trans isomers exhibit measurable metastable peaks corresponding to the RDA process. This observation lends support to the stepwise mechanism for RDA reaction.

The concerted mechanism (Eqn.19) is favoured by Dougherty[17] on theoretical grounds. This mechanism resembles the thermal electrocyclic RDA fragmentation. It is supported by the experimental results of Smith and Thornton[18], who found that after decomposition of 4-vinyl cyclohexene under electron impact, charge is preferentially retained in the butadiene ion which contains the vinyl group rather than in the other butadiene originating from the ring. The finding of Elwood and Beynon[19] that a correlation exists between the kinetic energy released in metastable transitions of



(18)

A



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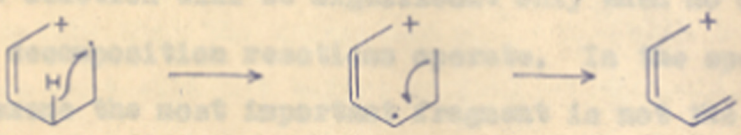

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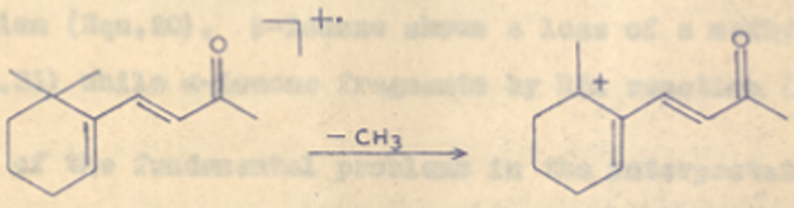
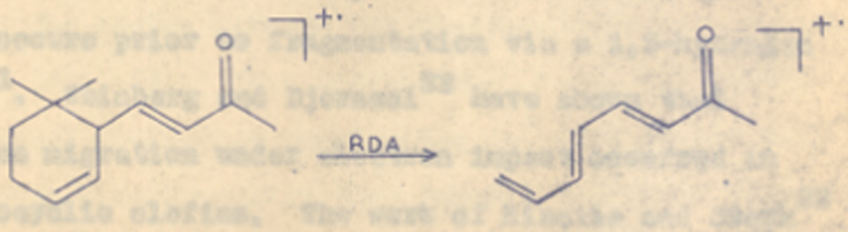


(21)

β - IONONE

$[M - CH_3]^+$



(22)

α - IONONE

DIENE

SCHEME – 2

the RDA reaction of several gaseous bycyclic hydrocarbon ions and the ground state activation energies for the Diels-Alder formation of similar neutral species in solution seems to support the concerted mechanism. Mandelbaum and coworkers[20] have shown that certain unsaturated cyclic diketons with cis stereochemistry at the ring junction decompose in the mass spectrometer by a RDA reaction. They pointed out that this is the behaviour expected if the mass spectral RDA reaction is concerted and follows symmetry rules analogous to those established for thermal reactions.

RDA reaction will be significant only when no other preferred decomposition reactions operate. In the spectrum of cyclohexene the most important fragment is not the diene but it corresponds to the loss of a methyl group from the molecular ion (Eqn.20). β-Ionone shows a loss of a methyl group (Eqn.21) while α-ionone fragments by RDA reaction (Eqn.22).

One of the fundamental problems in the interpretation of the mass spectra of unconjugated olefinic compounds is the possibility that an electron impact induced double bond migration occurs prior to fragmentation via a 1,3-hydrogen migration[21]. Weinberg and Djerassi[22] have shown that 1,3-hydrogen migration under electron impact occurred in simple monocyclic olefins. The work of Kinstle and Stark[23]

on some deuterated 1-methyl cyclohexenes has confirmed the existence of such migrations in cyclic olefins. It has also been shown that double bond migration occurs in cyclohexene before the molecules reach the field-free region of the mass spectrometer[24].

D. Metastable Ions

1. Observation of metastable ions:

If the reaction $m_1^+ \rightarrow m_2^+ + N$ occurs in the source, then m_2^+ may travel the whole of the analyser region as a mass m_2 and be recorded as an m_2^+ daughter ion. However, it is possible that the transition $m_1^+ \rightarrow m_2^+$ will occur after the source exit slit but before arrival at the collector. Ions undergoing such transitions are termed metastable ions. They will have life-times in the range 10^{-5}-10^{-6} sec.

In double focusing mass spectrometers there are two field-free regions through which ions pass after acceleration. The first field-free region is immediately before the electrostatic analyser and the second field-free region is the region between the electrostatic and magnetic analysers (Fig. 1d). If a reaction $m_1^+ \rightarrow m_2^+ + N$ occurs in the second field-free region, the m_2^+ ions formed will possess less kinetic energy than 'normal' m_2^+ ions formed in the source and are accordingly deflected more readily when traversing the magnetic analyser. They do not appear

at the normal position for m_2^+ on the mass scale, but at $m^* = m_2^2/m_1$ [25]. Factors which influence the shapes of metastable peaks have been discussed[3]. The width of the metastable peak has been used[26] to calculate the kinetic energy released during metastable decompositions using the equation,

$$m^* = \frac{m_2^2}{m_1}\left(1 \pm \sqrt{\frac{\mu T}{V e}}\right)^2 \qquad \text{——} \quad (23)$$

where V is the accelerating voltage, e is the electronic charge, $\mu = (m_1 - m_2)/m_2$, and T= kinetic energy released in electron volts. It has been shown that the kinetic energy released by metastable ions is a characteristic of ion structure and is approximately independent of internal energy[27].

If an ion m_1^+ decomposes to m_2^+ after acceleration but before entering the electrostatic analyser (in the first field-free region), then the electrostatic analyser will not transmit m_2^+ because it possesses a kinetic energy (m_2/m_1) eV instead of the required kinetic energy eV. However, m_2^+ ions formed exclusively in the first field-free region can be transmitted at the pre-set electrostatic analyser voltage of E if their kinetic energy is increased in the ratio m_1/m_2 by increasing the accelerating voltage from

its normal value V_o to V_1[28], such that

$$V_1/V_o = m_1/m_2 \quad \text{——} \quad (24)$$

In practice, the mass spectrometer is set for normal, (2 or 4 KV) operation and the magnet current is adjusted so that the m_2^+ ion of interest arrives at the collector. The accelerating voltage V is then scanned slowly towards higher values and m_2^+ will only be transmitted to the collector when the accelerating voltage is such that Eqn.24 is satisfied. Since m_2^+ is known and the ratio V_1/V_o is measured experimentally, it is possible to determine all values of m_1^+ ions which are precursors of m_2^+ ions in the first field-free region. This method of observation of metastable transition is known as metastable defocusing technique.

2. Ion kinetic energy spectroscopy

The alternative refocusing method of decreasing the electrostatic analyser potential at constant accelerating voltage is called ion kinetic energy spectroscopy[29]. This method of operation has the disadvantage that the magnetic field must first be set as if to focus a metastable, not a normal peak, as in the previous method. An advantage is that the penetrations of the source by the accelerating field is constant, and therefore the source tuning does not change

during the scan. Due to decompositions in the first field-free region, the ions entering the electrostatic analyser will have a spectrum of kinetic energies, varying downwards from the energy of the normal ion beam. If now an electron multiplier detector is placed just before the magnetic analyser, and the electrostatic voltage is continuously varied a spectrum of ion kinetic energies can be obtained[30].

The technique of ion kinetic energy spectroscopy has been applied to a variety of problems in organic mass spectrometry[31]. Since the decompositions in the first field-free region take place from ions with considerably less excitation energy than those in the ionisation chamber more subtle differences in the chemical structure could be elucidated from IKE spectra than from the normal spectra. Beynon et al.[32] have shown that IKE spectra of isomeric ortho, meta and para phenylene diamines are sufficiently different to be used as finger prints for the individual isomers. It has also been shown that 1-methyl indole could be clearly distinguished from the 4,5,6- and 7-methyl substituted isomers from their IKE spectra[33]. When a doubly charged ion fragments to two singly charged ions, the energy released can be measured. If it is assumed that all the energy released (T) in the decomposition is due to charge separation, then the distance 'r' between the two charges can be calculated using the equation $T = e^2/r$, where e is the electronic charge. This gives valuable information on the

position of charge sites and structures of doubly charged fragmenting ions[32].

B. Substituent Effects

1. Hammett equation

One of the oldest, best known, and most frequently employed quantitative correlations in solution chemistry is the Hammett equation[34]. It relates the rate of equilibria of many reactions of meta and para substituted aromatic compounds. In the form of equation 25 it allows the prediction

$$\log (k/k_0) = \rho\sigma \quad \text{——} \quad (25)$$

of a rate k of some reaction of a substituted compound from a knowledge of k_0, the rate for the similar reaction of the unsubstituted compound, σ, a substituent constant which reflects the intrinsic electron donating or electron withdrawing nature of the substituent, and ρ, a reaction constant reflecting the degree to which the influence of the substituent is transmitted to the reaction site for the particular reaction.

2. Linear free energy correlation in mass spectra

It has been shown[35] that insofar as ion intensities are a quantitative sampling of ion concentration in the source, the intensity ratios $[A]^+/[M]^+ = Z$ for the fragmentation $[M]^+ \rightarrow [A]^+ + N$ are a measure of the relative rates. Hence $Z/Z_0 = k/k_0$ —— (26)

Where Z_0 is the intensity ratio for the unsubstituted reference compound and k and k_0 are the rate constants for the fragmentation of the substituted and unsubstituted compounds respectively. The Hammett equation (25) becomes log $(Z/Z_0) = \rho\sigma$ —— (27)

There have been numerous studies of the effects of m - and p-substituents (of a benzene ring) on ion abundances associated with specific cleavage reactions[35-37]. In some cases there is good correlation between parameters designed to measure changes in ion abundance ratios and the Hammett constants for the substituents. However, there have been some debate as to the origin of these correlations and their possible mechanistic implications.

Considering the basic factors which determine the effect of substituent on ionic abundances enumerated by McLafferty[38] and others[39] Chin and Harrison[40] have used the QET to derive an expression for Z in terms of the fraction of ions capable of fragmentation. Consider a decomposition scheme

in which the further decomposition of A^+ can be neglected by working at low energies. To a good approximation, the

initial rise of k with E is so rapid (relative to the mass spectrometric time scale) that if $[M]^+$ is the molecular ion abundance recorded at the collector, and $[M_o]^+$, the initial concentration of the molecular ion, then $[M]^+ = f\,[M_o]^+$, where f is the fraction of ions in the energy distribution with sufficient energy to decompose. The abundance of A^+ is given by

$$[A]^+ = \frac{k_1}{k_t}\left([M_o]^+ - [M]^+ \right) \quad \text{---} \quad (28)$$

where k_1 is the rate constant for the formation of A^+ and k_t is the sum of all rate constants resulting in decomposition from the $M^+\cdot$. For the above equation it can be shown that

$$[A]^+/[M]^+ = \frac{k_1}{k_t}\left[(1/f) - 1 \right] \quad \text{---} \quad (29)$$

Hence, $[A]^+/[M]^+$ will depend on f and k_1/k_t (the fraction of fragmenting ions which form A^+). Thus, increase in the rates of competing reactions lead to a reduction in $[A]^+/[M]^+$, which does not necessarily reflect a change in k_1. If competing reactions are eliminated, k_1/k_t becomes unity and the substituent effect is exerted entirely through changes in f and not k_1. Therefore, direct information on the rates of a specific fragmentation reaction can not be obtained in this manner, and considerable caution must

be exercised in reaching conclusions regarding ionic structures or fragmentation mechanisms.

Substituent effects on competing cleavages of the same molecular ion have been studied[41-44]. McLafferty et al.[41] obtained a correlation when log Y $C_7H_6^+/C_7H_7^+$ from the spectra of substituted bibenzyls were plotted against Brown's σ^+ constants. Log Y $C_6H_4\overset{+}{N}\langle^{CH_2}_{CH_3}$ $/C_6H_5\overset{+}{N}\langle^{CH_2}_{CH_3}$ from the spectra of N,N'-diaryl ethylene diamines gave a good correlation with Taft's σ° constants[42]. These ratios were assumed to represent the ratios of the averaged rate constants for the formation of these ions. Einolf and Munson[43,44] from a kinetic analysis have shown that the ratio of the products of two competing decompositions of the same molecular ion represents the ratio of the rate constants for the formation of the non-decomposing product ions. The ratios Y $C_7H_4O^+/C_7H_5O^+$ were determined for several benzophenones for electron energies from 15 to 70 eV. Plots of log Y $C_7H_4O^+/C_7H_5O^+$ vs σ^+ gave good straight lines at all energies.

F. Newer Ionisation Techniques

1. Field desorption

Extremely high electric fields - of the order of 10^8 V/cm - acting on atoms or molecules have the effect of changing the atomic or molecular potentials in such a way that valence electrons may penetrate the potential wells. Positively charged ions are formed in this way. This process, called "field ionisation" (FI), is based on the quantum mechanical tunneling effect[45]. Field desorption (FD) mass spectrometry is a modification of the FI technique[45]. The solid sample is deposited directly on the field anode by dipping it in a solution of the sample and then evaporating off the solvent. For the adsorption of the sample the emitter tip is activated by a special technique. This involves field polymerisation of benzonitrile on the metal resulting in the growth of microneedles on the emitter surface. On applying the high electric field the organic molecules become mobile and diffuse along the shanks of the microneedles into the emitter region. The temperature required for this is only the heat of surface diffusion which is less than the heat of vaporisation. Even the heat of ionic desorption of the sample is reduced by the strong electric field[46,47]. The parent or $(M+1)^+$ ion formed by FD or field induced protonation undergo very little fragmentation. A striking illustration of the advantage of this method is shown in Fig.2.

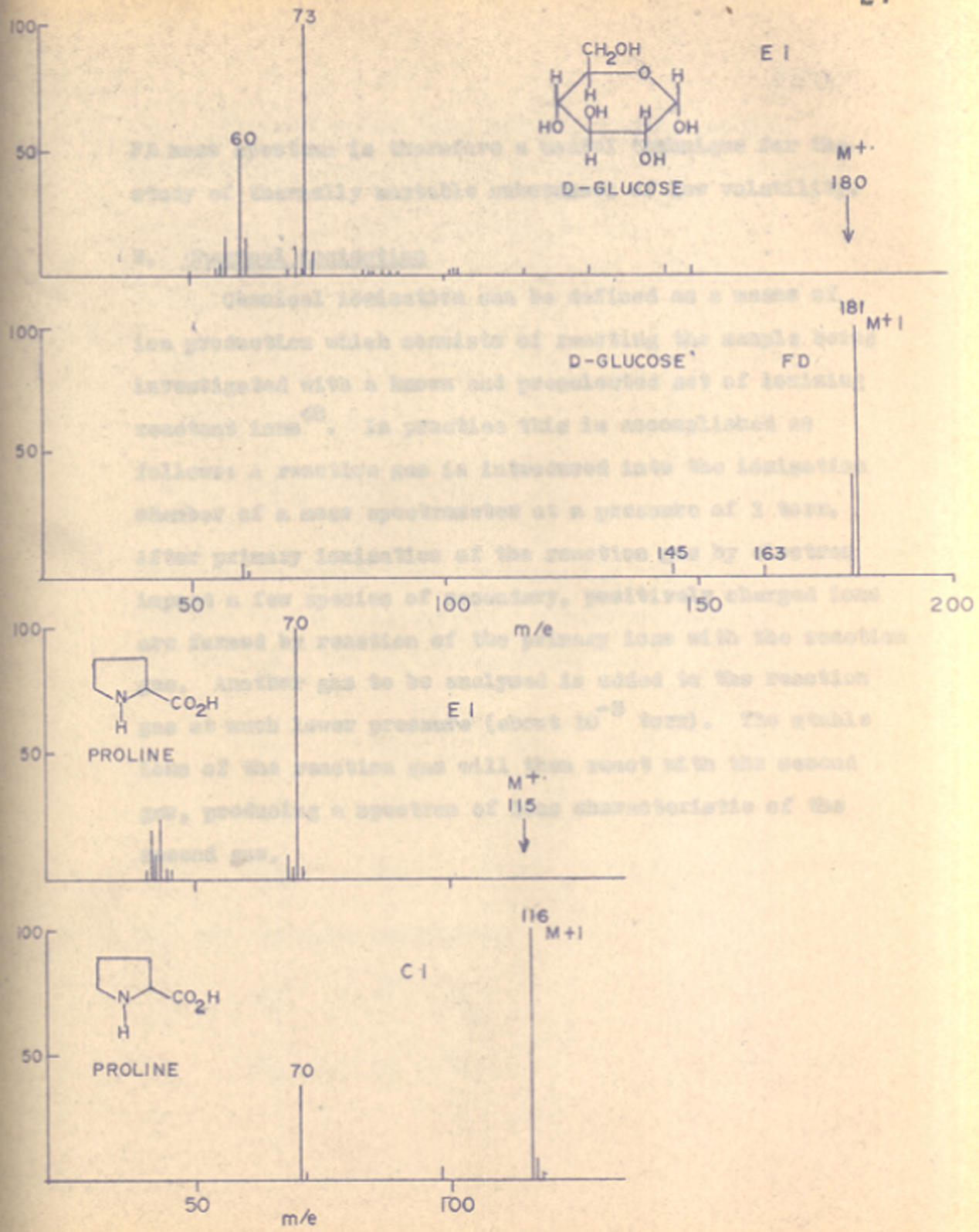

RELATIVE INTENSITY
100
50
73
60
CH2OH
O
H
OH
HO
E I
M+·
180
D-GLUCOSE
181
M+1
FD
145
163
50
100
150
200
m/e
70
N
H
CO2H
PROLINE
E I
M+·
115
116
M+1
C I
PROLINE
70
50
m/e
100

FIG. 2.

FD mass spectrum is therefore a useful technique for the study of thermally unstable substances of low volatility.

2. Chemical ionisation

Chemical ionisation can be defined as a means of ion production which consists of reacting the sample being investigated with a known and preselected set of ionising reactant ions[48]. In practice this is accomplished as follows: A reaction gas is introduced into the ionisation chamber of a mass spectrometer at a pressure of 1 torr. After primary ionisation of the reaction gas by electron impact a few species of secondary, positively charged ions are formed by reaction of the primary ions with the reaction gas. Another gas to be analysed is added to the reaction gas at much lower pressure (about 10^{-3} torr). The stable ions of the reaction gas will then react with the second gas, producing a spectrum of ions characteristic of the second gas.

The most widely used reactant gas is methane. The principal ionic processes in methane are as follows:[49]

$$CH_4 + e \rightarrow CH_4^{+\cdot}, CH_3^+, CH_2^{+\cdot} \text{ etc.} \quad \text{—— (30)}$$

$$CH_4^{+\cdot} + CH_4 \rightarrow CH_5^+ + \cdot CH_3 \quad \text{—— (31)}$$

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2 \quad \text{—— (32)}$$

$$CH_2^{+\cdot} + CH_4 \rightarrow C_2H_3^+ + H_2 + H^\cdot \quad \text{—— (33)}$$

$$C_2H_3^+ + CH_4 \rightarrow C_3H_5^+ + H_2 \quad \text{—— (34)}$$

The major secondary ions are CH_5^+, $C_2H_5^+$ and $C_3H_5^+$. The reaction between a hypothetical sample molecule BH and CH_5^+ and $C_2H_5^+$ can be written as follows.

$$CH_5^+ + BH \rightarrow BH_2^+ + CH_4 \quad \text{—— (35)}$$

$$C_2H_5^+ + BH \rightarrow BH_2^+ + C_2H_4 \quad \text{—— (36)}$$

$$C_2H_5^+ + BH \rightarrow B^+ + C_2H_6 \quad \text{—— (37)}$$

BH_2^+ may decompose as follows.

$$BH_2^+ \rightarrow B^+ + H_2 \quad \text{—— (38)}$$

$$BH_2^+ \rightarrow A_i^+ + C_i \quad \text{—— (39)}$$

The mass spectra produced in this way by chemical reaction are usually quite different from those obtained by electron impact. Generally, the relative abundance of fragment ions is much smaller in the case of CI mass spectra. An illustrative example is the spectrum of prolin[50] (Fig.2). When electron impact spectrum does not show the molecular ion, the $(M+H)^+$ ion is the base peak in the CI spectrum. It has been reported[51] that CI mass spectra of many underivatised peptides can be obtained by introducing the sample directly into the ion plasma of the CI source. The sample is deposited on the surface of an extended tip of the conventional sample probe as a drop of dilute solution which is allowed to evaporate and the mass spectrum thus obtained contain abundant N- and C-terminal sequence peaks as well as the $(M+H)^+$ peak. The CI method seems to be especially promising in structure elucidation of organic compounds because CI mass spectrum is complementary to EI mass spectrum and because the CI mass spectrum can be explained in many cases by simple postulates of the reaction occurring as shown by Field, Munson and Becker[52].

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CHAPTER - II

ELECTRON IMPACT STUDIES ON SOME SUBSTITUTED NITRO CYCLOHEXENES

A. Present Work

In the mass spectrum of cyclohexene the rearrangement process involving the loss of a methyl radical from the molecular ion results in the base peak[1]. The retro Diels-Alder reaction is one of the major competing reactions. The peak due to the diene ion is 80% of the base peak. The mass spectrum of 4-nitro-Δ^1-cyclohexene shows that the major fragmentation mode is the elimination reaction resulting in the loss of HNO_2, while RDA reaction is only a very minor process (5.5%). A minor peak due to the loss of NO is observed. Peaks corresponding to the expulsion of $^{\cdot}NO_2$ and $^{\cdot}H_2NO_2$ are also significant.

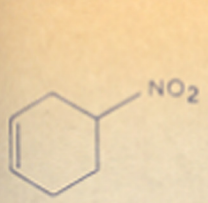
The present work was undertaken to study the effect of substituents, stereochemistry and saturation of the double bond on the major fragmentation modes of 4-nitro cyclohexene. The introduction of phenyl groups in the molecule, as expected, has resulted in the formation of the m/e 91, 117 and 167 ions. In the triphenyl compounds peaks at m/e 193 and 206 are significant. A characteristic

fragmentation mode of the isomeric 3,6-diphenyl-4-nitro cyclohexenes is the loss of $^{\cdot}NO$ from the molecular ion. Considerable substituent effects were observed for the loss of $^{\cdot}NO$, $^{\cdot}NO_2$, HNO_2 and H_2NO_2 and for the formation of RCH_2^+ (R corresponds to the substituent on C_5). Significant steric effects were observed for the formation of $[M-HNO_2]^{+\cdot}$ and $[M-H_2NO_2]^+$ ions in the fragmentation of the isomeric 3,6-diphenyl-4-nitro cyclohexenes. Saturation of the double bond of the cyclohexene ring was found to have some effect on the loss of $^{\cdot}NO$. In all the compounds except the triphenyl nitro cyclohexanes considerable reduction of this fragmentation mode was observed. The compounds examined are shown in Fig.1.

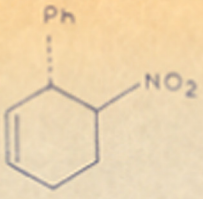
1. Discussion

4-Nitro-Δ^1-cyclohexene (I)

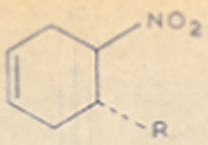
The molecular ion peak is practically absent in the spectrum of 4-nitro-Δ^1-cyclohexene (Fig.2). Loss of nitric oxide from the molecular ion is a minor process. The preferred fragmentation mode is the loss of HNO_2 by a rearrangement process in which the C_3 or C_5 hydrogen atom is involved. Metastable transitions were observed in the first field-free region for the direct loss of HNO_2 from the molecular ion and for the loss of $^{\cdot}OH$ from the $[M-NO]^+$ ion. Hence, the $[M-HNO_2]^{+\cdot}$ ion is formed by both one



I



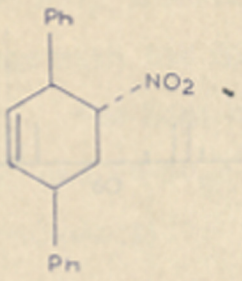
II



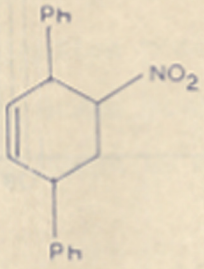
III, R = C_6H_5

IV, R = p-MeC_6H_4 ; V, R = p-ClC_6H_4

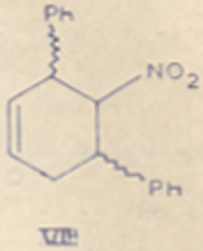
VI, R = p-CNC_6H_4 ; VII, R = p-$NO_2C_6H_4$



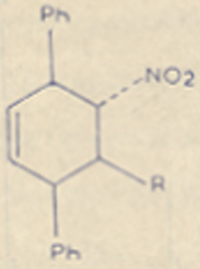
IX A



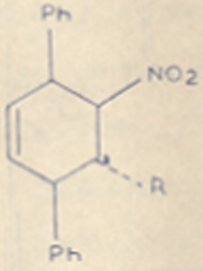
IX B



VIII



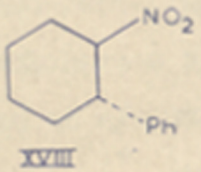
(A)



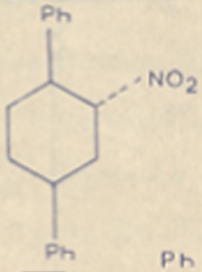
(B)

X A, R = p-$MeOC_6H_4$
XI A, R = 2-THIENYL
XII A, R = p-MeC_6H_4
XIII A, R = 2-FURYL
XIV A, R = p-BrC_6H_4
XV A, R = p-ClC_6H_4
XVI A, R = C_6H_5
XVII A, R = p-CNC_6H_4

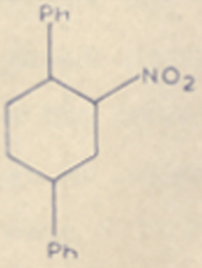
XI B, R = 2-THIENYL
XII B, R = p-MeC_6H_4
XIII B, R = 2-FURYL
XIV B, R = p-BrC_6H_4
XV B, R = p-ClC_6H_4
XVI B, R = C_6H_5



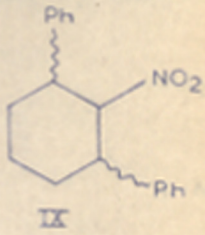
XVIII



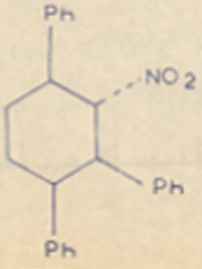
XX A



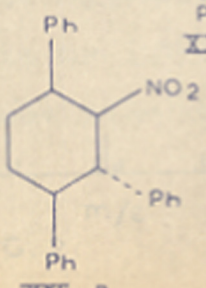
XX B



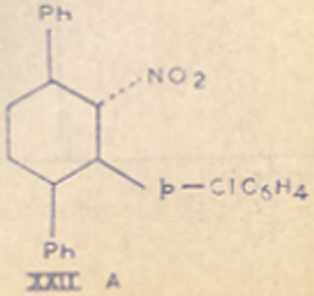
IX



XXI A



XXI B



XXII A

FIG. 1

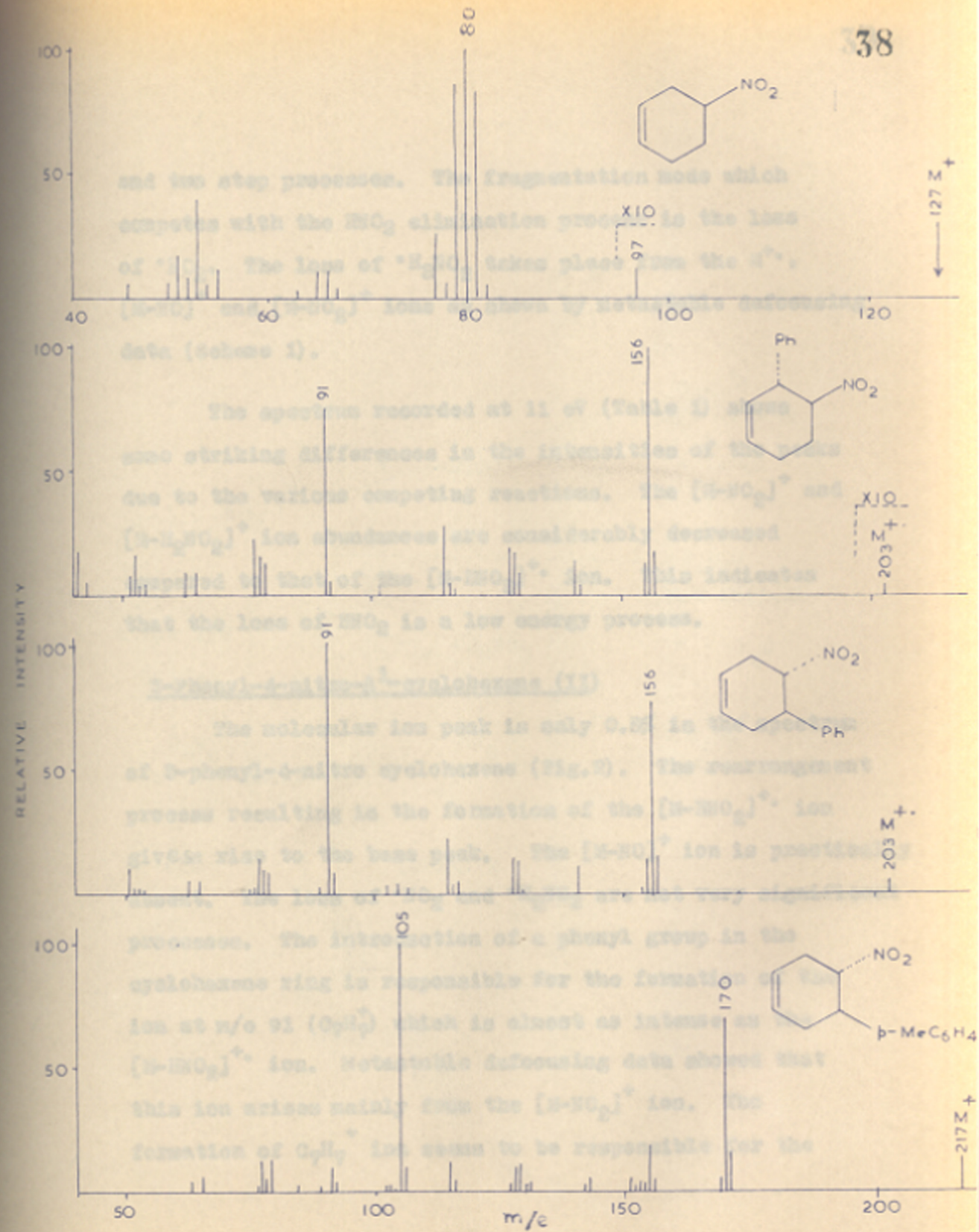

RELATIVE INTENSITY
100
50
80
NO_2
X10
97
127 M^+
40
60
80
100
120
156
91
Ph
NO_2
X10
M^+
203
91
156
NO_2
Ph
M^+
203
105
170
NO_2
p-MeC_6H_4
217 M^+
50
100
150
200
m/e

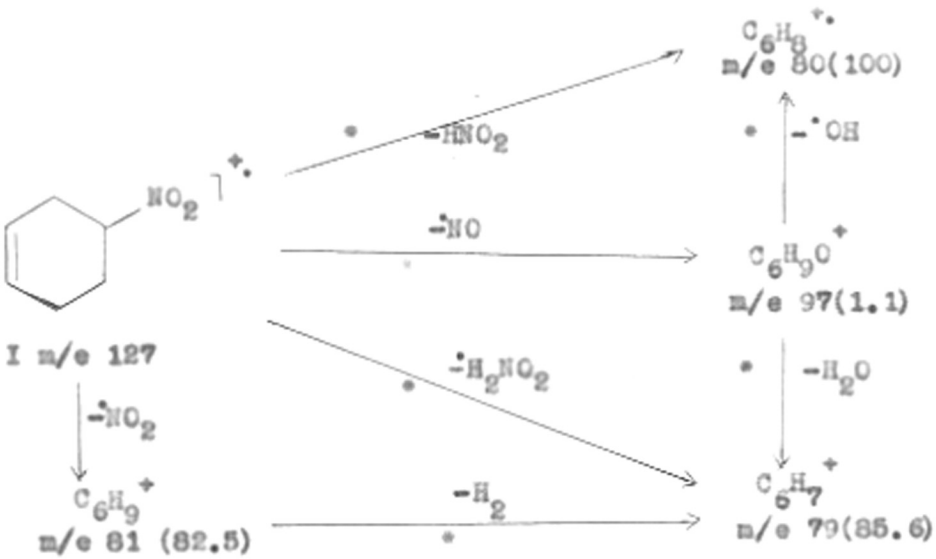
FIG. 2

and two step processes. The fragmentation mode which competes with the HNO_2 elimination process is the loss of $\cdot NO_2$. The loss of $\cdot H_2NO_2$ takes place from the $M^{+\cdot}$, $[M-NO]^+$ and $[M-NO_2]^+$ ions as shown by metastable defocusing data (Scheme 1).

The spectrum recorded at 11 eV (Table 1) shows some striking differences in the intensities of the peaks due to the various competing reactions. The $[M-NO_2]^+$ and $[M-H_2NO_2]^+$ ion abundances are considerably decreased compared to that of the $[M-HNO_2]^{+\cdot}$ ion. This indicates that the loss of HNO_2 is a low energy process.

3-Phenyl-4-nitro-Δ^1-cyclohexene (II)

The molecular ion peak is only 0.5% in the spectrum of 3-phenyl-4-nitro cyclohexene (Fig.2). The rearrangement process resulting in the formation of the $[M-HNO_2]^{+\cdot}$ ion gives rise to the base peak. The $[M-NO]^+$ ion is practically absent. The loss of $\cdot NO_2$ and $\cdot H_2NO_2$ are not very significant processes. The introduction of a phenyl group in the cyclohexene ring is responsible for the formation of the ion at m/e 91 ($C_7H_7^+$) which is almost as intense as the $[M-HNO_2]^{+\cdot}$ ion. Metastable defocusing data showed that this ion arises mainly from the $[M-NO_2]^+$ ion. The formation of $C_7H_7^+$ ion seems to be responsible for the


$C_6H_8^{+\cdot}$
m/e 80(100)
$-HNO_2$
$-^{\cdot}OH$
NO_2
$-NO$
$C_6H_9O^+$
m/e 97(1.1)
I m/e 127
$-H_2NO_2$
$-H_2O$
$-NO_2$
$C_6H_9^+$
m/e 81 (82.5)
$-H_2$
$C_6H_7^+$
m/e 79(85.6)

SCHEME 1

TABLE – 1

Abundances of the major ions in the 11 eV spectra of the nitro cyclohexenes (as % base peak).

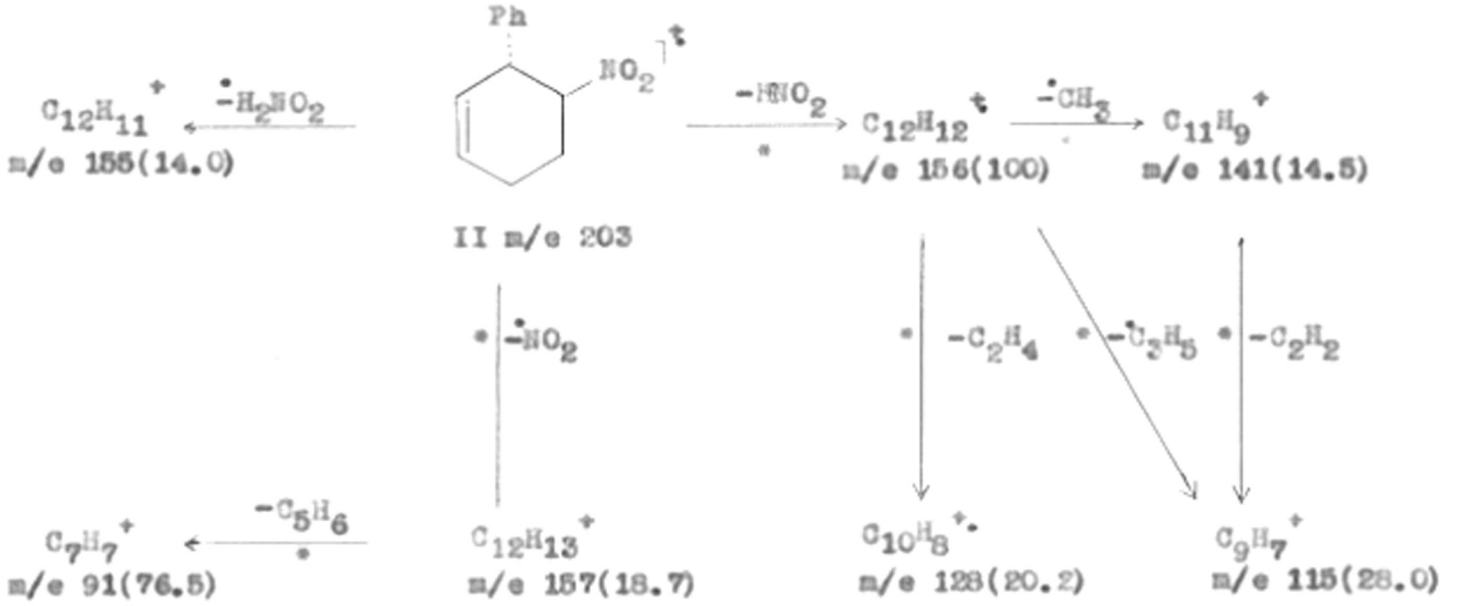
Compound	$M^{+\cdot}$	$[M-NO]^+$	$[M-NO_2]^+$	$[M-HNO_2]^{+\cdot}$	$[M-H_2NO_2]^+$	$C_7H_7^+$	$C_9H_9^+$	$C_{13}H_{11}^+$	$C_{15}H_{13}^+$	Diene
I	–	3.4	43.0	100	22.0	–	–	–	–	–
II	0.3	–	16.0	100	2.0	5.1	–	–	–	0.7
III	6.7	2.3	21.0	100	14.4	54.0	3.5	–	–	–
VIII	2.0	6.9	8.7	21.0	4.6	29.0	100	18.0	–	4.3
IXA	–	57.0	24.0	95.0	44.5	100	14.3	5.70	–	–
IXB	14.7	53.0	20.0	40.5	26.4	100	19.6	7.2	–	–
XVIA	–	27.5	10.5	33.0	33.0	7.2	–	9.9	11.7	100
XVIB	0.1	0.7	0.5	2.0	1.3	1.0	–	2.0	52.0	100

reduction in the relative intensity of the $[M-NO_2]^+$ ion. Scheme 2 shows the fragmentation modes of 3-phenyl-4-nitro cyclohexene.

A comparative study of the 70 eV and 11 eV spectra has shown that the abundance of the $[M-HNO_2]^{+\cdot}$ ion is considerably more than that of the $C_7H_7^+$ ion at 11 eV. This again shows that the formation of $[M-HNO_2]^{+\cdot}$ is a low energy process. It can also be due to the fact that the further fragmentation of the $[M-HNO_2]^{+\cdot}$ ion is comparatively less at low eV. The daughter ions of the $[M-HNO_2]^{+\cdot}$ ion viz., the m/e 141 ion formed by the loss of $\cdot CH_3$ and the m/e 115 ion formed both by the direct loss of $\cdot C_3H_5$ and by the successive loss of $\cdot CH_3$ and C_2H_2 (these fragmentation processes are supported by the observation of metastable transitions) are less abundant at low eV. The intensity of the $[M-H_2NO_2]^+$ ion is also considerably reduced at low eV.

5-Phenyl-4-nitro-Δ^1-cyclohexene (II)

The molecular ion peak is more intense than that of 3-phenyl-4-nitro-Δ^1-cyclohexene (Fig.2). The $[M-NO]^+$ ion is very insignificant. The formation of $[M-HNO_2]^{+\cdot}$ ion is an important process. The base peak corresponds to $C_7H_7^+$ ion. This may be due to the fact that both allylic

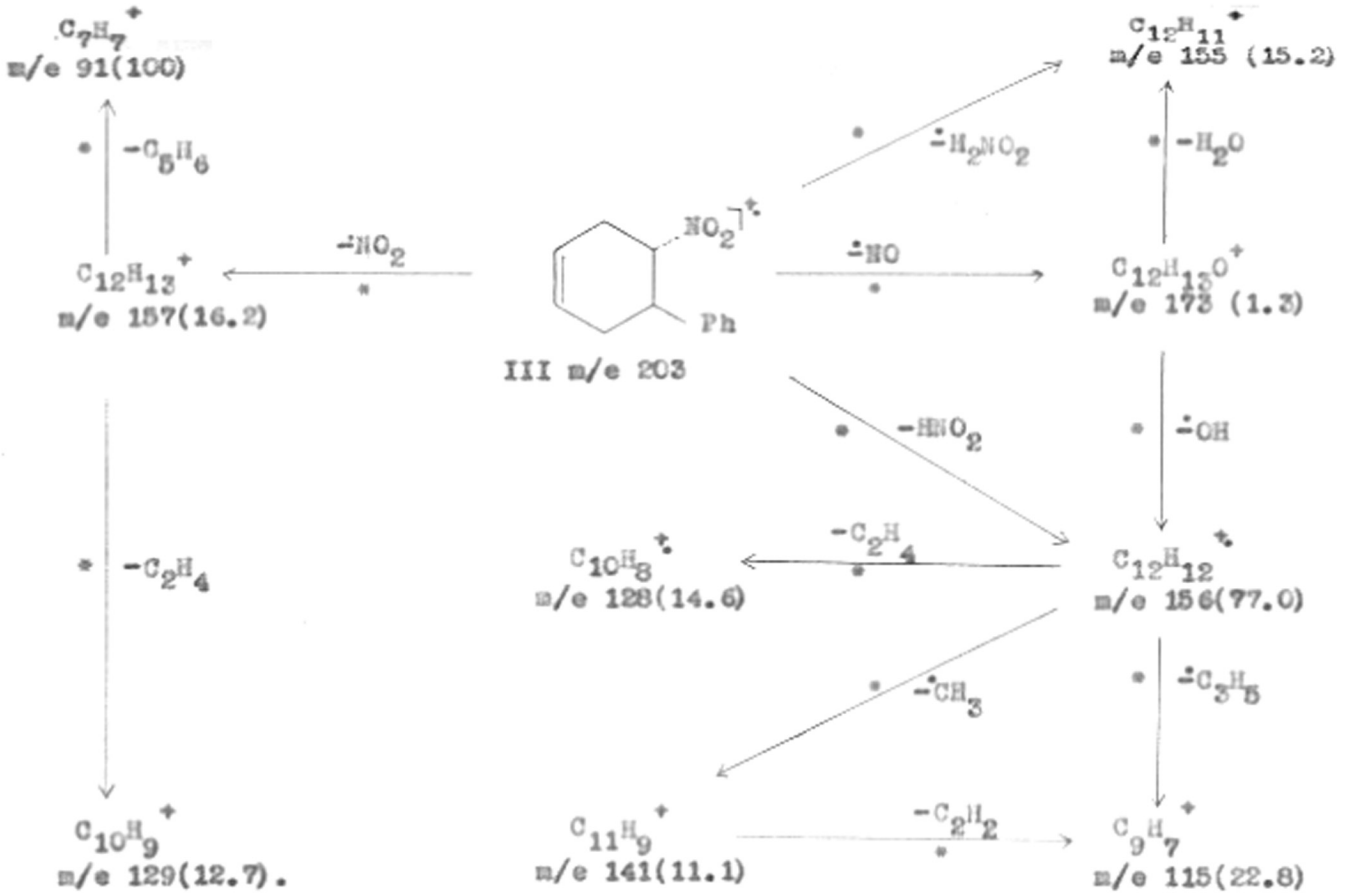

Ph
NO2
II m/e 203
C12H11+
m/e 155(14.0)
-H2NO2
-HNO2
C12H12+
m/e 156(100)
-CH3
C11H9+
m/e 141(14.5)
-NO2
-C2H4
-C3H5
-C2H2
C7H7+
m/e 91(76.5)
-C5H6
C12H13+
m/e 157(18.7)
C10H8+·
m/e 128(20.2)
C9H7+
m/e 115(28.0)

SCHEME 2

and benzylic cleavages favour the formation of m/e 91 ion. Metastable defocusing data showed that it is formed mainly from the $[M-NO_2]^+$ ion (Scheme 3). The abundances of the $[M-NO_2]^+$ and $[M-H_2NO_2]^+$ ions are comparable to those observed in the spectrum of 3-phenyl-4-nitro cyclohexene.

The low eV behaviour of 5-phenyl-4-nitro cyclohexene is similar to that of 3-phenyl-4-nitro cyclohexene.

The effect of substituted 5-phenyl groups on the major fragmentation processes was studied from the spectra of 5-aryl-4-nitro cyclohexenes (IV-VII). The intensities of the major peaks in the 11 eV spectra are given in Table 2. As expected, the molecular ion peak intensity increases with increasing electron donating nature of the substituent. Loss of NO is less when the substituent is electron donating in nature and is more if the substituent is electron attracting. The $[M-HNO_2]^{+\cdot}$ ion is the base peak in the spectra of all these compounds. The $[M-NO_2]^+$ and the $[M-H_2NO_2]^+$ ion abundances are more when electron withdrawing groups are attached to C_5-phenyl. RCH_2^+ ion abundance is also influenced by substituents. Its abundance is considerably decreased by electron withdrawing groups. This is expected since benzylic cleavage is less preferred when electron attracting groups are attached to the phenyl ring[2].


$C_7H_7^+$
m/e 91(100)
$-C_5H_6$
$C_{12}H_{13}^+$
m/e 157(16.2)
$-NO_2$
$-C_2H_4$
$C_{10}H_9^+$
m/e 129(12.7).
NO_2
Ph
III m/e 203
$-H_2NO_2$
$-NO$
$-HNO_2$
$-C_2H_4$
$C_{10}H_8^{+\cdot}$
m/e 128(14.6)
$-CH_3$
$C_{11}H_9^+$
m/e 141(11.1)
$-C_2H_2$
$C_{12}H_{11}^+$
m/e 155 (15.2)
$-H_2O$
$C_{12}H_{11}O^+$
m/e 173 (1.3)
$-OH$
$C_{12}H_{12}^{+\cdot}$
m/e 156(77.0)
$-C_3H_5$
$C_9H_7^+$
m/e 115(22.8)

SCHEME 3

TABLE - 2.

Abundances of the major peaks in the 11 eV spectra of 5-aryl-4-nitro-Δ-cyclohexenes (as % base peak)

Compound (R)	$M^{+\cdot}$	$[M-NO]^+$	$[M-NO_2]^+$	$[M-HNO_2]^{+\cdot}$	$[M-H_2NO_2]^+$	RCH_2^+
IV (p-MeC_6H_4)	14.7	0.2	18.0	100	2.2	32.5
V (p-ClC_6H_4)	11.7	0.2	15.0	100	2.0	29.0
III (C_6H_5)	6.7	2.3	21.0	100	4.6	29.0
VI (p-CNC_6H_4)	2.7	7.7	22.0	100	30.0	24.0
VII (p-$NO_2C_6H_4$)	0.7	9.7	23.0	100	15.0	7.0

3,5-Diphenyl-4-nitro-Δ^1-cyclohexene (VIII)

In the spectrum of 3,5-diphenyl-4-nitro-Δ^1-cyclohexene (Fig.3) the molecular ion and the $[M-NO]^+$ ion are insignificant. The $C_7H_7^+$ ion is the base peak. The next intense peak (m/e 117) corresponds to the $C_9H_9^+$ ion. It was found by metastable defocusing technique that this ion has three precursors, viz., the $M^{+\cdot}$, $[M-NO]^+$ and $[M-NO_2]^+$ ions. In the spectra of 1-phenyl heptene[2] and trans- 10-phenyl-2-decalone[4] the m/e 117 ion has been assigned a phenyl propenyl ion structure. A metastable transition was observed for the further fragmentation of this ion to give the m/e 115 ion in the spectra of 3,5-diphenyl-4-nitro cyclohexene and 1-phenyl heptene[3]. Hence, the ion at m/e 117 in the spectrum of the nitro cyclohexene may have a structure similar to that of phenyl propenyl cation, $C_6H_5-\overset{+}{C}H-CH=CH_2$. Loss of $^{\cdot}NO_2$ and $^{\cdot}H_2NO_2$ from the molecular ion are not very significant processes. The $[M-HNO_2]^{+\cdot}$ ion is fairly abundant. A peak at m/e 167 ($C_{13}H_{11}^+$) was observed. The $C_{13}H_{11}^+$ ion is characteristic of compounds containing two phenyl groups[5] and is formed by a skeletal rearrangement process. It was found from metastable data that the $C_{13}H_{11}^+$ ion is formed from both the $[M-NO]^+$ and $[M-HNO_2]^{+\cdot}$ ions (Scheme 4).

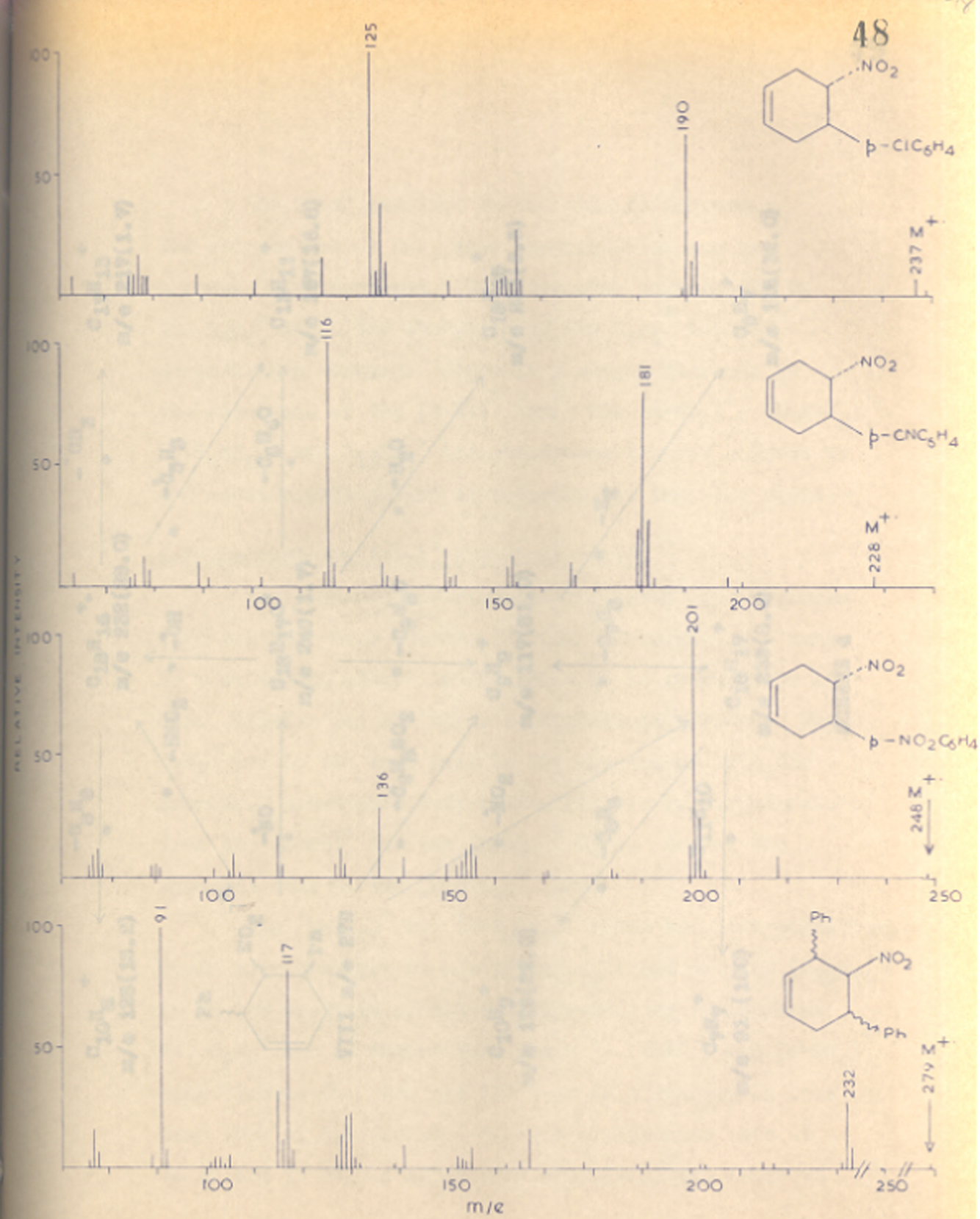
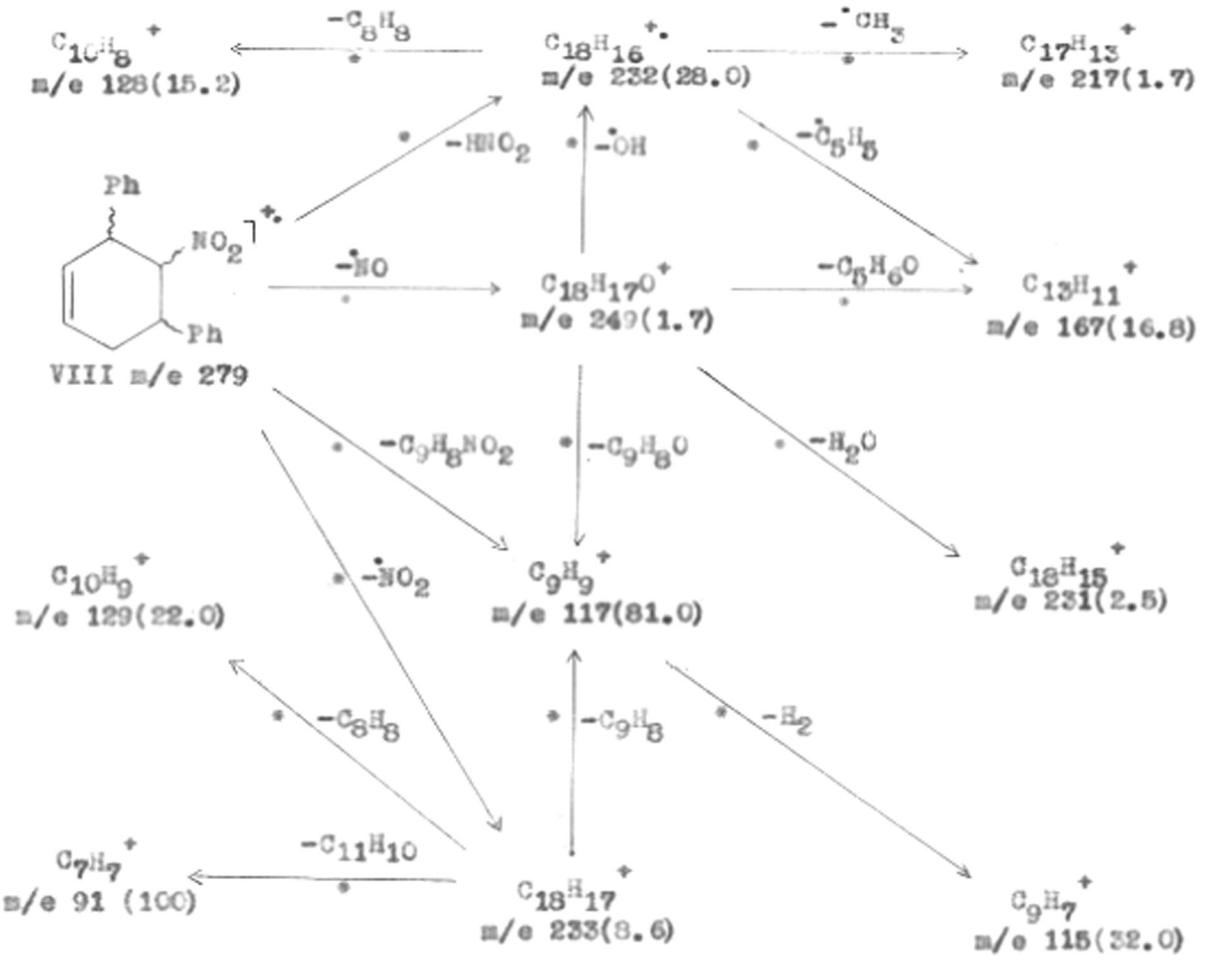

125
190
237 M+
NO2
p-ClC6H4
116
181
228 M+
p-CNC6H4
201
136
246 M+
p-NO2C6H4
91
117
232
274 M+
Ph
Ph
RELATIVE INTENSITY
m/e

FIG. 3


$C_{10}H_8^+$
m/e 128(15.2)
$-C_8H_8$
$C_{18}H_{16}^{+\cdot}$
m/e 232(28.0)
$-\dot{C}H_3$
$C_{17}H_{13}^+$
m/e 217(1.7)
$-HNO_2$
$-\dot{O}H$
$-\dot{C}_5H_5$
Ph
NO_2
Ph
VIII m/e 279
$-\dot{N}O$
$C_{18}H_{17}O^+$
m/e 249(1.7)
$-C_5H_6O$
$C_{13}H_{11}^+$
m/e 167(16.8)
$-C_9H_8NO_2$
$-C_9H_8O$
$-H_2O$
$C_{10}H_9^+$
m/e 129(22.0)
$-\dot{N}O_2$
$C_9H_9^+$
m/e 117(81.0)
$C_{18}H_{15}^+$
m/e 231(2.5)
$-C_8H_8$
$-C_9H_8$
$-H_2$
$C_7H_7^+$
m/e 91 (100)
$-C_{11}H_{10}$
$C_{18}H_{17}^+$
m/e 233(8.6)
$C_9H_7^+$
m/e 115(32.0)

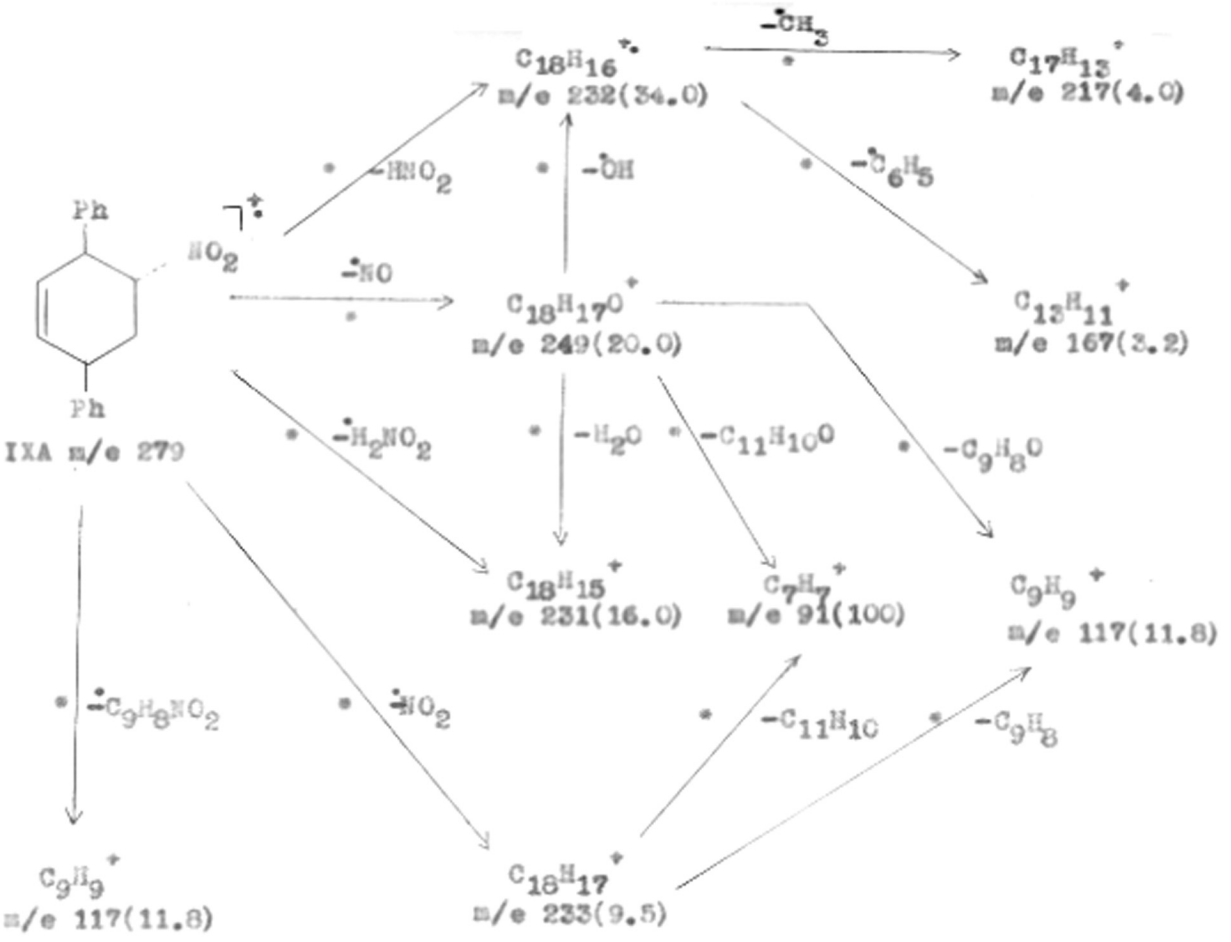
SCHEME 4

The 11 eV spectrum showed some differences. The elimination of HNO_2 from the molecular ion is slightly less favoured. The base peak corresponds to the $C_9H_9^+$ ion. The abundance of the $C_7H_7^+$ ion is considerably reduced. There is a slight increase in the abundance of the $[M-NO]^+$ ion. The $[M-NO_2]^+$, $[M-HNO_2]^{+\cdot}$, $[M-H_2NO_2]^+$ and $C_{13}H_{11}^+$ ion abundances are not altered to any considerable extent by reducing the ionising voltage.

3,6-Diphenyl-4-nitro-Δ^1-cyclohexene (IX)

Two isomeric 3,6-diphenyl-4-nitro-Δ^1-cyclohexenes (IXA and IXB) were studied (Fig.4). Molecular ion peak is practically absent in IXA while it is appreciable in IXB. Elimination of $^{\cdot}NO$ is a significant process. The $C_7H_7^+$ ion is the base peak in the spectra of both the isomers. Metastable data showed that it is formed mainly from the $[M-NO]^+$ and the $[M-NO_2]^+$ ions. One of the abundant ions is the $[M-HNO_2]^{+\cdot}$ ion.

The $[M-NO_2]^+$ and $[M-H_2NO_2]^{+\cdot}$ ions are less significant. Peaks were observed at m/e 117 ($C_9H_9^+$) and m/e 167 ($C_{13}H_{11}^+$). As in the spectrum of 3,5-diphenyl-4-nitro cyclohexene the $C_9H_9^+$ ion is formed from the $M^{+\cdot}$, $[M-NO]^+$ and $[M-NO_2]^+$ ions (Scheme 5). The m/e 117 peak is considerably less than that of 3,5-diphenyl-4-nitro cyclohexene both at 70 eV and 11 eV. A metastable transition was observed


Ph
Ph
IXA m/e 279
$C_{18}H_{16}^{+\cdot}$ m/e 232(34.0)
$C_{17}H_{13}^{+}$ m/e 217(4.0)
$C_{18}H_{17}O^{+}$ m/e 249(20.0)
$C_{13}H_{11}^{+}$ m/e 167(3.2)
$C_{18}H_{15}^{+}$ m/e 231(16.0)
$C_7H_7^{+}$ m/e 91(100)
$C_9H_9^{+}$ m/e 117(11.8)
$C_9H_9^{+}$ m/e 117(11.8)
$C_{18}H_{17}^{+}$ m/e 233(9.5)
$-\dot{C}H_3$
$-HNO_2$
$-\dot{O}H$
$-\dot{C}_6H_5$
$-\dot{N}O$
$-\dot{H}_2NO_2$
$-H_2O$
$-C_{11}H_{10}O$
$-C_9H_8O$
$-\dot{C}_9H_8NO_2$
$-\dot{N}O_2$
$-C_{11}H_{10}$
$-C_9H_8$

SCHEME 5

for the formation of the $C_{13}H_{11}^+$ ion from the $[M-HNO_2]^+$ ion.

The $C_7H_7^+$ ion is the base peak even in the low eV spectra of both the isomers (Table 1). The $[M-NO]^+$, $[M-NO_2]^+$, $[M-HNO_2]^{+\cdot}$ and $[M-H_2NO_2]^+$ ion abundances are considerably increased by reducing the ionising voltage.

3,5,6-Triphenyl-4-nitro-Δ^1-cyclohexene (XVIA and XVIB)

The mass spectra of the isomeric triphenyl nitro cyclohexenes (XVIA and XVIB) are shown in Fig. 4. Molecular ion abundance is negligible. Loss of NO is a significant process only in XVIA. The retro Diels-Alder reaction is the most favoured decomposition pathway. The base peaks in the spectra of both the isomers correspond to the diene ion ($C_{16}H_{14}^{+\cdot}$, m/e 206). Since the nitro group is not a charge-stabilising moiety the dienophile ion is not observed in the spectra of these compounds. It is interesting, however, to point out that when the nitro group is reduced to the amino group both the diene and the dienophile ions are observed.

Another important process is the formation of the $C_7H_7^+$ ion. Its formation from the $[M-NO]^+$, the $[M-NO_2]^+$ and the diene ions is supported by the observation of metastable transitions. Loss of $^{\cdot}NO_2$, HNO_2 and $^{\cdot}H_2NO_2$ are significant only in XVIA. The abundance of the $C_{13}H_{11}^+$ (m/e 167) is appreciable, while the $C_9H_9^+$ (m/e 117) ion is not significant. A peak is observed at m/e 193 ($C_{15}H_{13}^+$). The formation of

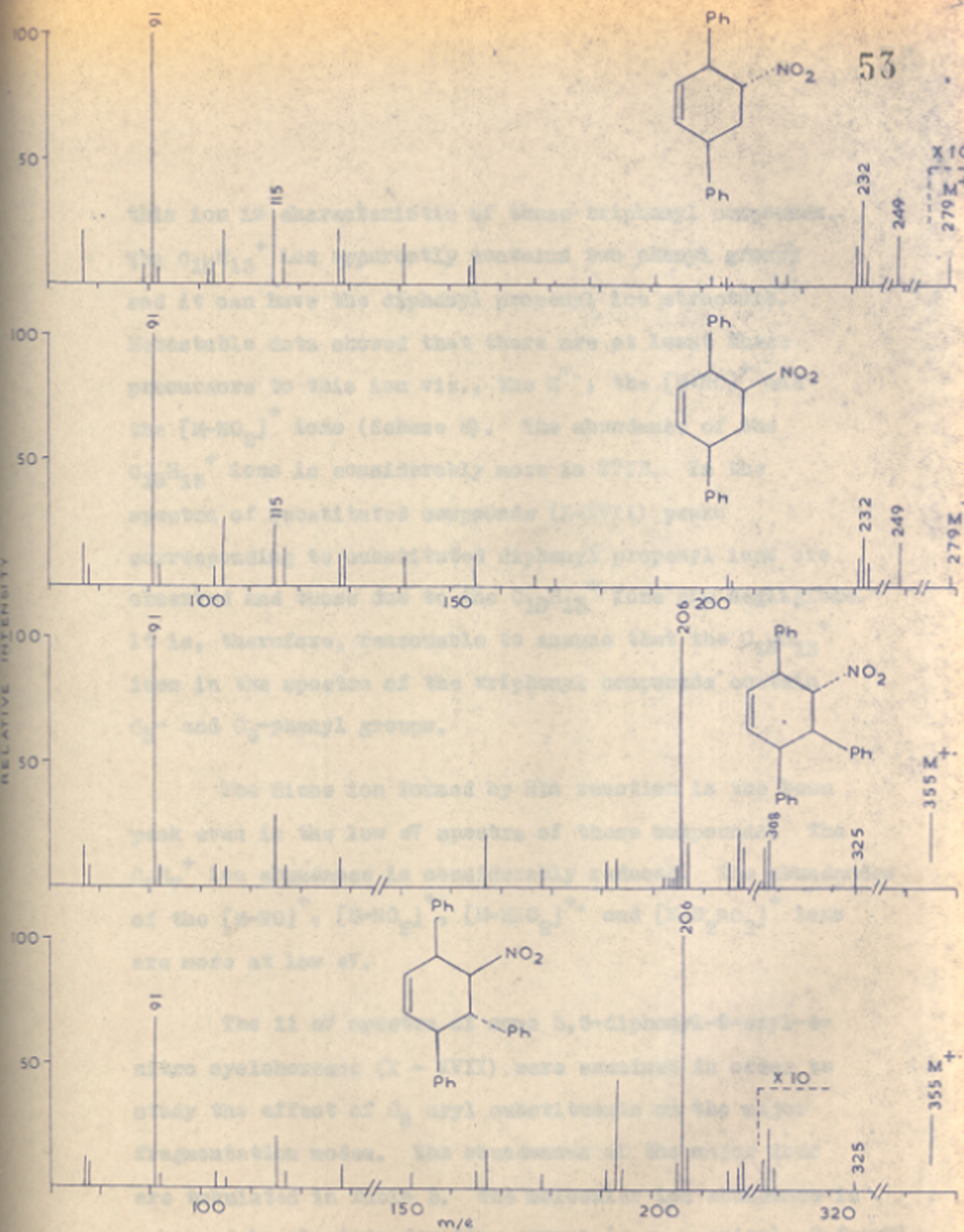
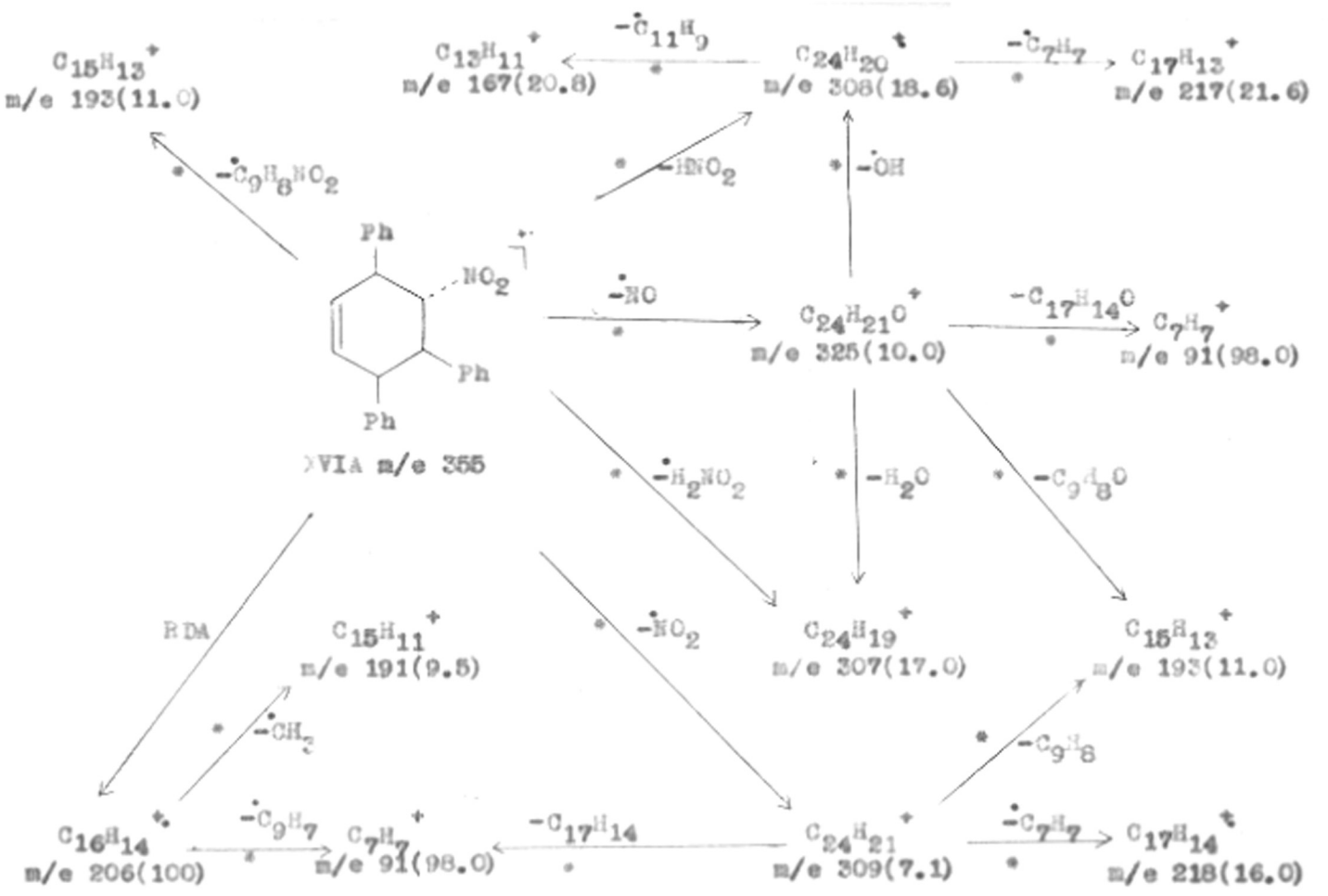

RELATIVE INTENSITY
100
50
91
115
232
249
279 M+
x 10
Ph
NO2
206
308
325
355 M+
m/e
100
150
200
320

FIG. 4

this ion is characteristic of these triphenyl compounds. The $C_{15}H_{13}^+$ ion apparently contains two phenyl groups and it can have the diphenyl propenyl ion structure. Metastable data showed that there are at least three precursors to this ion viz., the $M^{+\cdot}$, the $[M-NO]^+$ and the $[M-NO_2]^+$ ions (Scheme 6). The abundance of the $C_{15}H_{13}^+$ ions is considerably more in XVIB. In the spectra of substituted compounds (X-XVII) peaks corresponding to substituted diphenyl propenyl ions are observed and those due to the $C_{15}H_{13}^+$ ions are negligible. It is, therefore, reasonable to assume that the $C_{15}H_{13}^+$ ions in the spectra of the triphenyl compounds contain C_5- and C_6-phenyl groups.

The diene ion formed by RDA reaction is the base peak even in the low eV spectra of these compounds. The $C_7H_7^+$ ion abundance is considerably reduced. The abundances of the $[M-NO]^+$, $[M-NO_2]^+$, $[M-HNO_2]^{+\cdot}$ and $[M-H_2NO_2]^+$ ions are more at low eV.

The 11 eV spectra of some 3,6-diphenyl-5-aryl-4-nitro cyclohexenes (X - XVII) were examined in order to study the effect of C_5 aryl substituents on the major fragmentation modes. The abundances of the major ions are tabulated in Table 3. The molecular ion abundance is enhanced by electron donating groups (e.g. p-anisyl, 2-furyl).


C15H13+
m/e 193(11.0)
-C9H8NO2
C13H11+
m/e 167(20.8)
-C11H9
C24H20+
m/e 308(18.6)
-C7H7
C17H13+
m/e 217(21.6)
-HNO2
-OH
Ph
NO2
Ph
Ph
XVIA m/e 355
-NO
C24H21O+
m/e 325(10.0)
-C17H14O
C7H7+
m/e 91(98.0)
-H2NO2
-H2O
-C9H8O
RDA
C15H11+
m/e 191(9.5)
-NO2
C24H19+
m/e 307(17.0)
C15H13+
m/e 193(11.0)
-CH2
-C9H8
C16H14+.
m/e 206(100)
-C9H7
C7H7+
m/e 91(98.0)
-C17H14
C24H21+
m/e 309(7.1)
-C7H7
C17H14+
m/e 218(16.0)

SCHEME 6

TABLE – X

Relative intensities of the major peaks in the spectra of 3,6-diphenyl-5-aryl-4-nitro-Δ^1-cyclohexenes at 11 eV (as % base peak)

Compound (R)	$M^{+\cdot}$	$[M-NO]^+$	$[M-NO_2]^+$	$[M-HNO_2]^{+\cdot}$	$[M-H_2NO_2]^+$	RCH_2^+	$RC_7H_6^+$	$RC_9H_8^+$	Diene
XA (p-$MeOC_6H_4$)	4.2	0.2	0.9	1.7	0.8	7.6	2.8	3.5	100
XIA (2-Thienyl)	1.5	1.5	2.2	5.3	2.4	1.9	2.5	12.7	100
XIIA (p-MeC_6H_4)	1.0	11.5	3.9	13.0	14.4	3.2	0.8	2.0	100
XIIIA (2-Furyl)	5.3	2.7	4.4	14.5	2.5	3.2	7.2	47.0	100
XIVA (p-BrC_6H_4)	-	21.6	4.8	20.6	22.6	2.4	4.0	6.8	100
XVA (p-ClC_6H_4)	-	17.6	6.4	17.4	17.8	3.7	6.1	8.3	100
XVIA (C_6H_5)	-	27.5	10.5	33.0	33.0	7.2	9.9	11.7	100
XVIIA (p-CNC_6H_4)	-	40.0	29.5	92.0	57.0	1.5	7.4	54.0	100

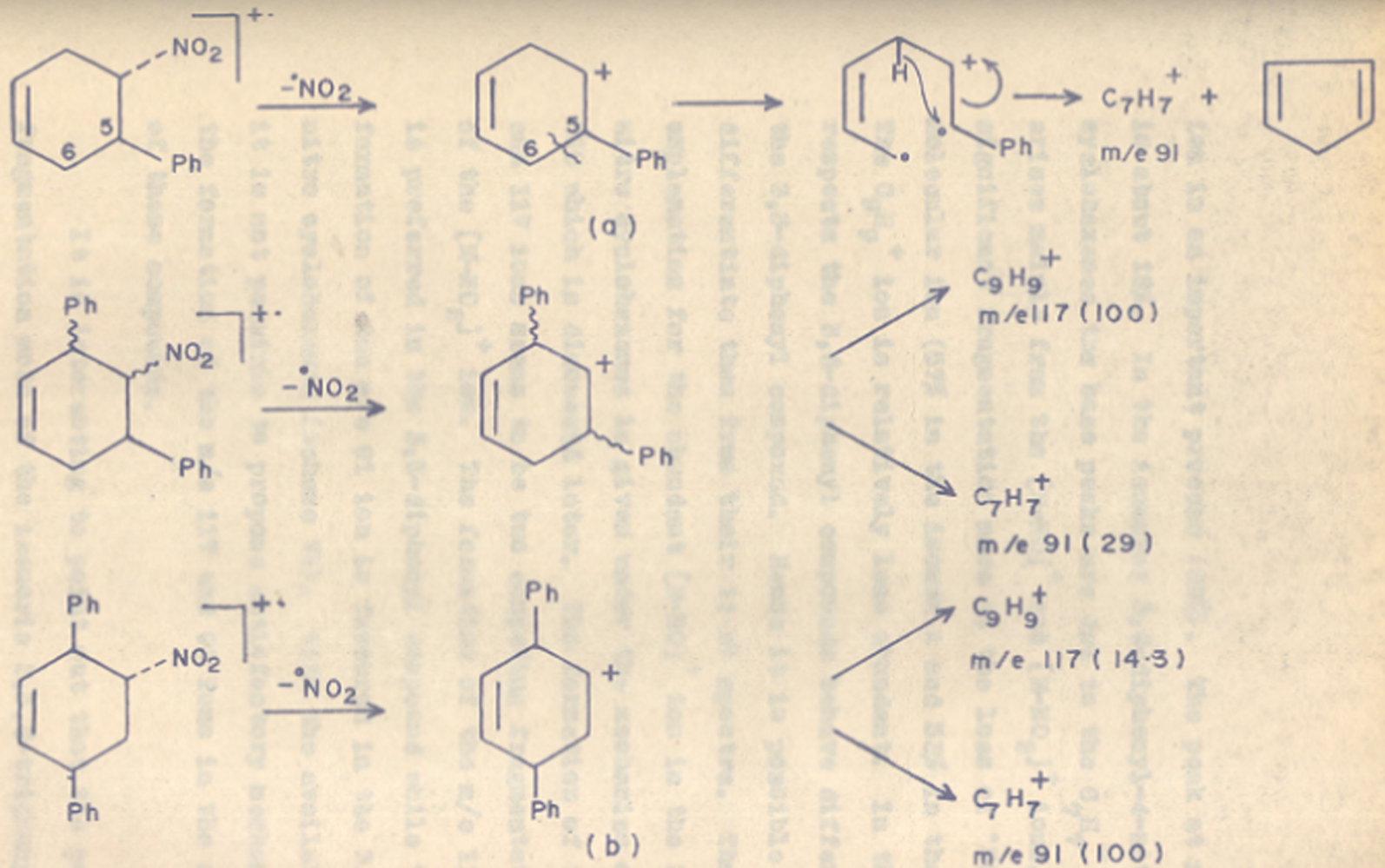
The base peaks in the spectra of all the compounds examined correspond to the diene ion. The abundance of the diene ion is increased by electron donating substituents on C_5, while these substituents are found to decrease the abundances of the $[M-NO]^+$, $[M-NO_2]^+$, $[M-HNO_2]^{+\cdot}$ and $[M-H_2NO_2]^+$ ions. Hence, these processes seem to compete with RDA reaction. The formation of RCH_2^+ ions is suppressed by electron attracting groups on C_5. Similar substituent effects were observed in the spectra of 5-aryl-4-nitro-Δ^1-cyclohexenes also.

2. Conclusion

From the above discussion it is clear that the introduction of phenyl groups in 4-nitro cyclohexene has significant effects in altering its fragmentation modes. A comparative study of the mass spectra of the compounds run at 11 eV has revealed the following points. In the parent compound the loss of $^{\cdot}NO$, $^{\cdot}NO_2$ and $^{\cdot}H_2NO_2$ compete with the rearrangement process leading to the loss of HNO_2. In the spectra of 3-phenyl-4-nitro-Δ^1-cyclohexene and 5-phenyl-4-nitro-Δ^1-cyclohexene the base peaks correspond to the rearrangement process leading to the expulsion of HNO_2. The loss of $^{\cdot}NO$, $^{\cdot}NO_2$ and $^{\cdot}H_2NO_2$ from the molecular ion are significantly less in the spectrum of the 3-phenyl-4-nitro cyclohexene compared with that in the spectra of

the parent and the 5-phenyl compounds. Peaks corresponding to the $C_7H_7^+$ ion are observed in the spectra of these monophenyl compounds. The abundances of the $C_7H_7^+$ ion were significantly different in the spectra of the 3-phenyl (5.1%) and 5-phenyl (54%) nitro cyclohexenes. It was found from metastable data that the m/e 91 ion in the spectra of these compounds come from the $[M-NO_2]^+$ ion. Hence it appears that the formation of the m/e 91 ion from the $[M-NO_2]^+$ ion is a preferred process in the 5-phenyl compound while it is a considerably less favoured process in the 3-phenyl compound. A possible mechanism is shown in Scheme 7a. Cleavage of the C_5-C_6 bond (β-to the double bond) followed by 1,3-hydrogen migration and charge migration to C_5 leads to the loss of neutral cyclopentadiene molecule resulting in the formation of $C_7H_7^+$ ion. A similar process is not favoured in 3-phenyl-4-nitro cyclohexene.

In the 3,5-diphenyl nitro cyclohexene the base peak corresponds to the formation of the m/e 117 ion. Unlike the parent and the monophenyl compounds loss of HNO_2 is not the major fragmentation mode (21%). There is a considerable reduction in the loss of $^{\cdot}NO_2$ and $^{\cdot}H_2NO_2$ from the molecular ion. The peak corresponding to the $[M-NO]^+$ ion is not significant. The formation of tropylium


NO2
-·NO2
Ph
(a)
H
C7H7+
m/e 91
C9H9+
m/e117 (100)
C7H7+
m/e 91 (29)
C9H9+
m/e 117 (14·3)
C7H7+
m/e 91 (100)
(b)

SCHEME 7

ion is an important process (29%). The peak at m/e 167 is about 18%. In the isomeric 3,6-diphenyl-4-nitro-Δ^1-cyclohexenes the base peaks are due to the $C_7H_7^+$ ion which arises mainly from the $[M-NO]^+$ and $[M-NO_2]^+$ ions. A significant fragmentation mode is the loss of $^{\bullet}NO$ from the molecular ion (57% in the isomer A and 53% in the isomer B). The $C_9H_9^+$ ion is relatively less abundant. In these three respects the 3,6-diphenyl compounds behave differently from the 3,5-diphenyl compound. Hence it is possible to differentiate them from their 11 eV spectra. The explanation for the abundant $[M-NO]^+$ ion in the 3,6-diphenyl nitro cyclohexenes is given under the mechanism of loss of $^{\bullet}NO$ which is discussed later. The formation of the m/e 91 and 117 ions seems to be two competing fragmentation modes of the $[M-NO_2]^+$ ion. The formation of the m/e 117 ion is preferred in the 3,5-diphenyl compound while the formation of the m/e 91 ion is favoured in the 3,6-diphenyl nitro cyclohexenes (Scheme 7b). With the available data it is not possible to propose satisfactory mechanisms for the formation of the m/e 117 and 91 ions in the spectra of these compounds.

It is interesting to point out that the preferred fragmentation mode of the isomeric 3,5,6-triphenyl-4-nitro-Δ^1-cyclohexenes is the formation of the diene ion by RDA reaction.

This fragmentation mode is practically absent in all the other compounds studied. The fragmentation mode leading to the loss of $^{\bullet}NO$ is a significant process. The other decomposition modes such as the loss of $^{\bullet}NO_2$, HNO_2 and $^{\bullet}H_2NO_2$ have different relative contributions.

The effect of the phenyl group in altering the fragmentation mode and in changing the relative abundances of ions can be rationalised on the basis of energetics. It is known that the phenyl group lowers the ionisation potential of a molecule and thereby changes the activation energies for the various competing fragmentation pathways. In the 70 eV spectra the differences are not as significant as those observed in the 11 eV spectra.

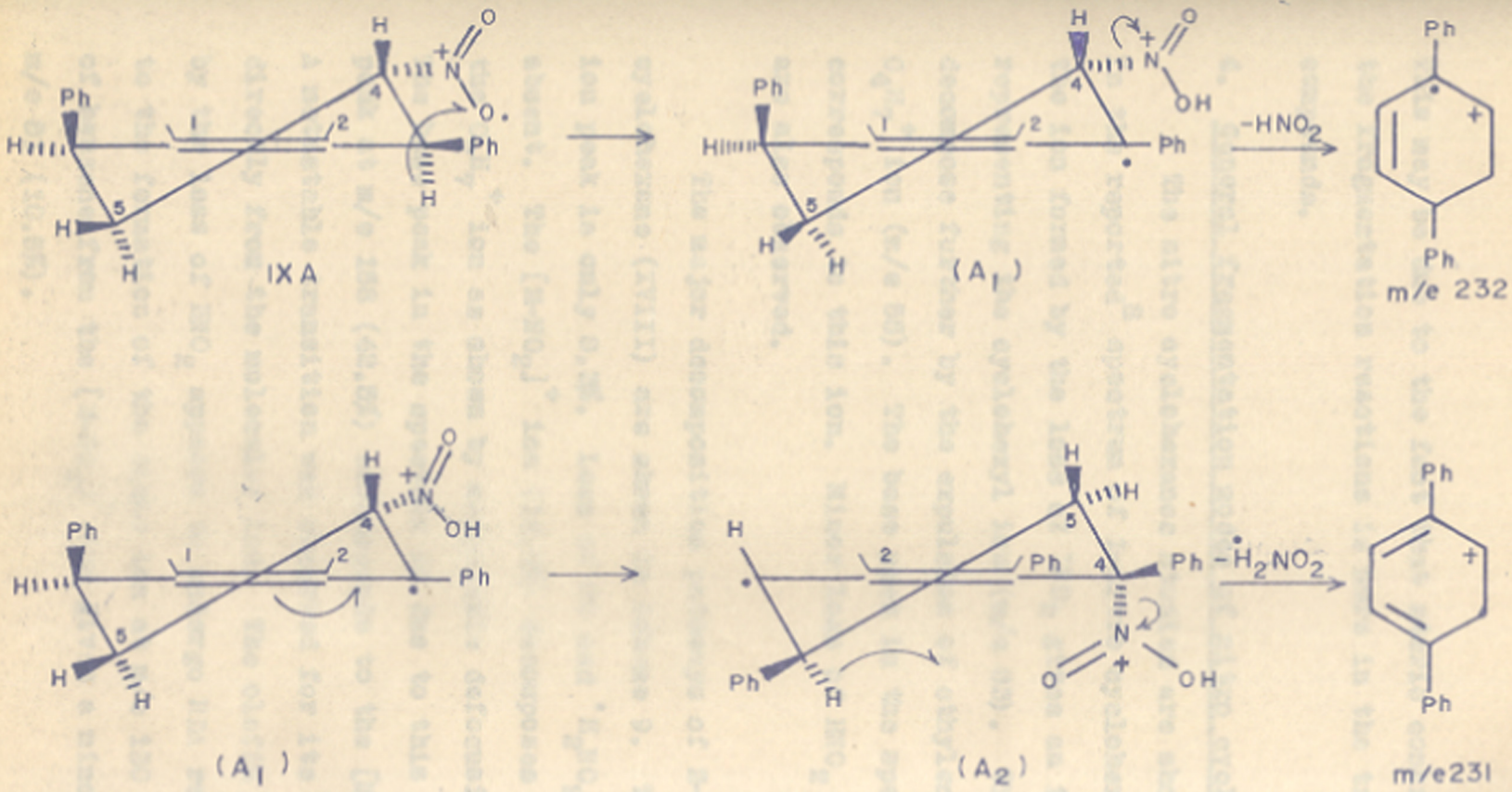
3. Steric effects on the fragmentation modes

The effect of stereochemistry on the fragmentation modes of 3,5,6-triphenyl-4-nitro-Δ^1-cyclohexenes has been reported[6,7]. Similar steric effects are observed in the 3,6-diphenyl-4-nitro-Δ^1-cyclohexenes also. The molecular ion abundance is considerably more in the isomer B. However, $[M-HNO_2]^{+\bullet}$ and $[M-H_2NO_2]^{+}$ ion abundances are remarkably less in the isomer B. Both the $[M-HNO_2]^{+\bullet}$ and $[M-H_2NO_2]^{+}$ ions are formed directly from the molecular ion and from the $[M-NO]^{+}$ ion by the loss of OH and H_2O

respectively. The proposed mechanism (Section A6) for the loss of $^{\cdot}NO$ from the molecular ions of the 3,6-diphenyl-4-nitro cyclohexenes involves ring opening. Hence, the stepwise formation of the $[M-HNO_2]^{+\cdot}$ and $[M-H_2NO_2]^{+}$ ions may not depend on the stereochemistry of the molecule. Therefore, the observed steric influence on the $[M-HNO_2]^{+\cdot}$ and $[M-H_2NO_2]^{+}$ ion abundances can be solely due to the direct expulsion of HNO_2 and $^{\cdot}H_2NO_2$ from the molecular ion. The direct elimination of HNO_2 from the molecular ion of 3,5,6-triphenyl-4-nitro cyclohexenes has been shown to be dependent on stereochemistry[7]. The spectra of the C_4- and C_5- deuterated analogues of XVIA and XVIB showed that the hydrogens attached to these carbon atoms are not lost to any significant extent. A 1,2-mechanism involving the C_3- hydrogen atom has been proposed for the loss of HNO_2 from the molecular ion of XVIA and XVIB[7]. A similar mechanism seems to operate in the diphenyl compounds (IXA and IXB). The <u>cis</u> configuration of the nitro group and the C_3- hydrogen atom are essential for the rearrangement process to operate. Hence, it is favoured in the isomer A where the C_3-hydrogen atom and the C_4-NO_2 group have the required stereochemistry while it is not a favoured process in the isomer B where the C_3-hydrogen atom and the C_4-NO_2 group are <u>trans</u> to each other.

Since both the $[M-HNO_2]^{+\cdot}$ and $[M-H_2NO_2]^{+}$ ion abundances show the same steric dependence it is possible that these two processes operate through a common rearranged intermediate A_1 (Scheme 8). The initial process appears to be the abstraction of the C_3-hydrogen atom by the nitro group resulting in the radical ion A_1. Cleavage of the C-N bond of this intermediate leads to the formation of the $[M-HNO_2]^{+\cdot}$ ion. Migration of the double bond to the C_2-C_3 position in conjugation with the C_3-phenyl group leads to the second intermediate A_2. Abstraction of the C_6-hydrogen by the $-\overset{\overset{O}{\|}}{N}-OH$ group via a six centred transition state followed by cleavage of the C-N bond leads to the loss of $^{\cdot}H_2NO_2$. Unlike in the 3,5,6-triphenyl nitro cyclohexenes the loss of $^{\cdot}NO$ in the 3,6-diphenyl nitro cyclohexenes is not affected by the stereochemistry of the molecule. It is clear from Table 1 that the other fragmentation modes of 3,6-diphenyl-4-nitro cyclohexenes are not influenced by stereochemistry to any significant extent.

A comparison of the spectra of the isomeric 3,6-diphenyl and 3,5,6-triphenyl nitro cyclohexenes (Table 1) shows that the stereochemical influence on the mass spectral behaviour is more in the triphenyl compounds than in the diphenyl nitro cyclohexenes.



SCHEME-8

This may be due to the fact that steric control over the fragmentation reactions is more in the triphenyl compounds.

4. General fragmentation modes of nitro cyclohexanes

The nitro cyclohexanes studied are shown in Fig. 1. In the reported[8] spectrum of 1-nitro cyclohexane (Fig.5) the ion formed by the loss of $^{\cdot}NO_2$ gives an intense peak, representing the cyclohexyl ion (m/e 83). This ion can decompose further by the expulsion of ethylene to give $C_4H_7^+$ ion (m/e 55). The base peak in the spectrum corresponds to this ion. Minor loss of HNO_2 and $^{\cdot}H_2NO_2$ are also observed.

The major decomposition pathways of 2-phenyl-1-nitro cyclohexane (XVIII) are shown in Scheme 9. The molecular ion peak is only 8.3%. Loss of $^{\cdot}NO$ and $^{\cdot}H_2NO_2$ are practically absent. The $[M-NO_2]^+$ ion (16.6%) decomposes mainly to form the $C_7H_7^+$ ion as shown by metastable defocusing data. The base peak in the spectrum is due to this ion. The peak at m/e 158 (42.5%) corresponds to the $[M-HNO_2]^{+\cdot}$ ion. A metastable transition was observed for its formation directly from the molecular ion. The olefin ion produced by the loss of HNO_2 appears to undergo RDA reaction leading to the formation of the diene ion at m/e 130 (8.7%). Loss of benzene from the $[M-NO_2]^+$ ion gives a minor peak at m/e 81 (10.5%).

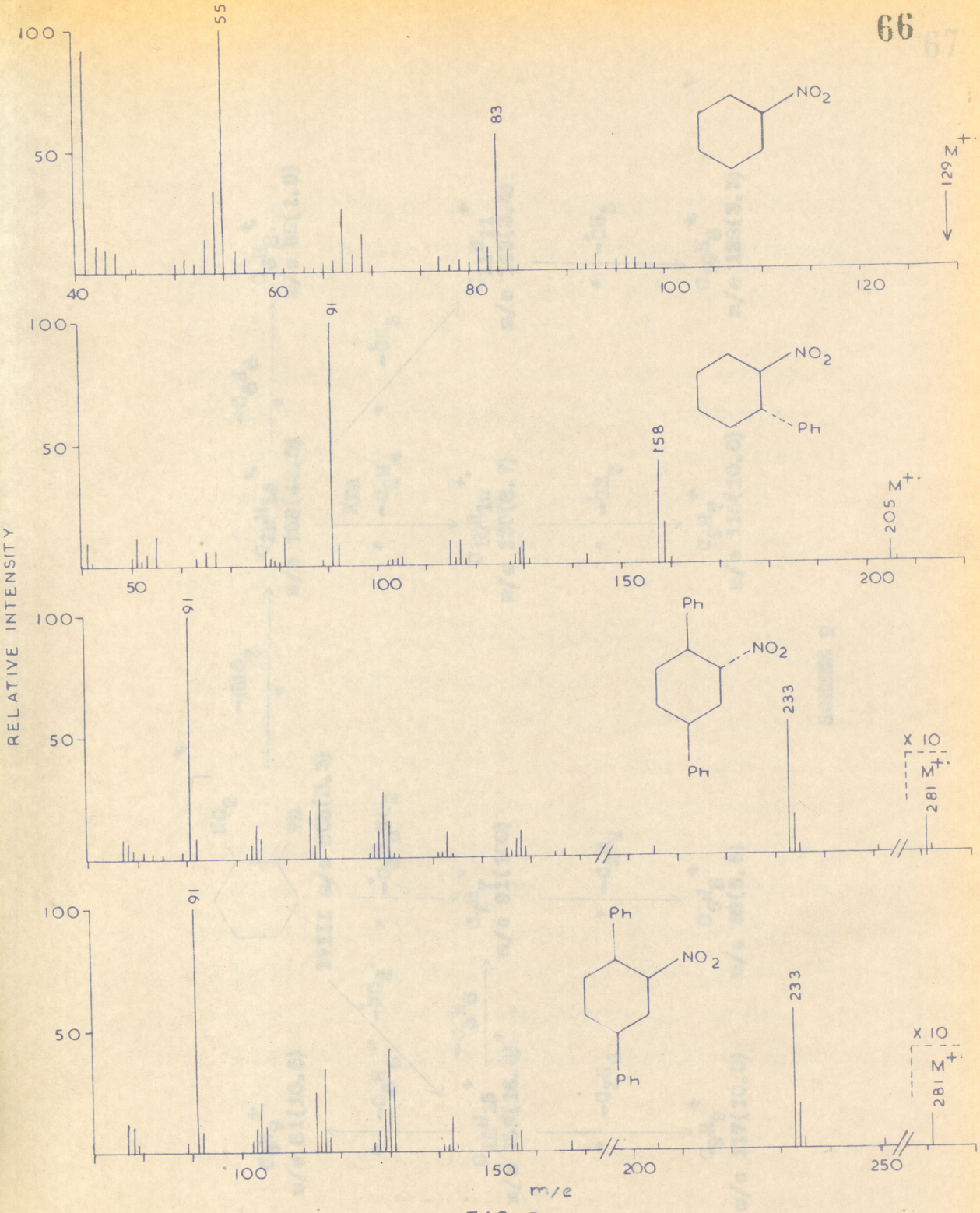
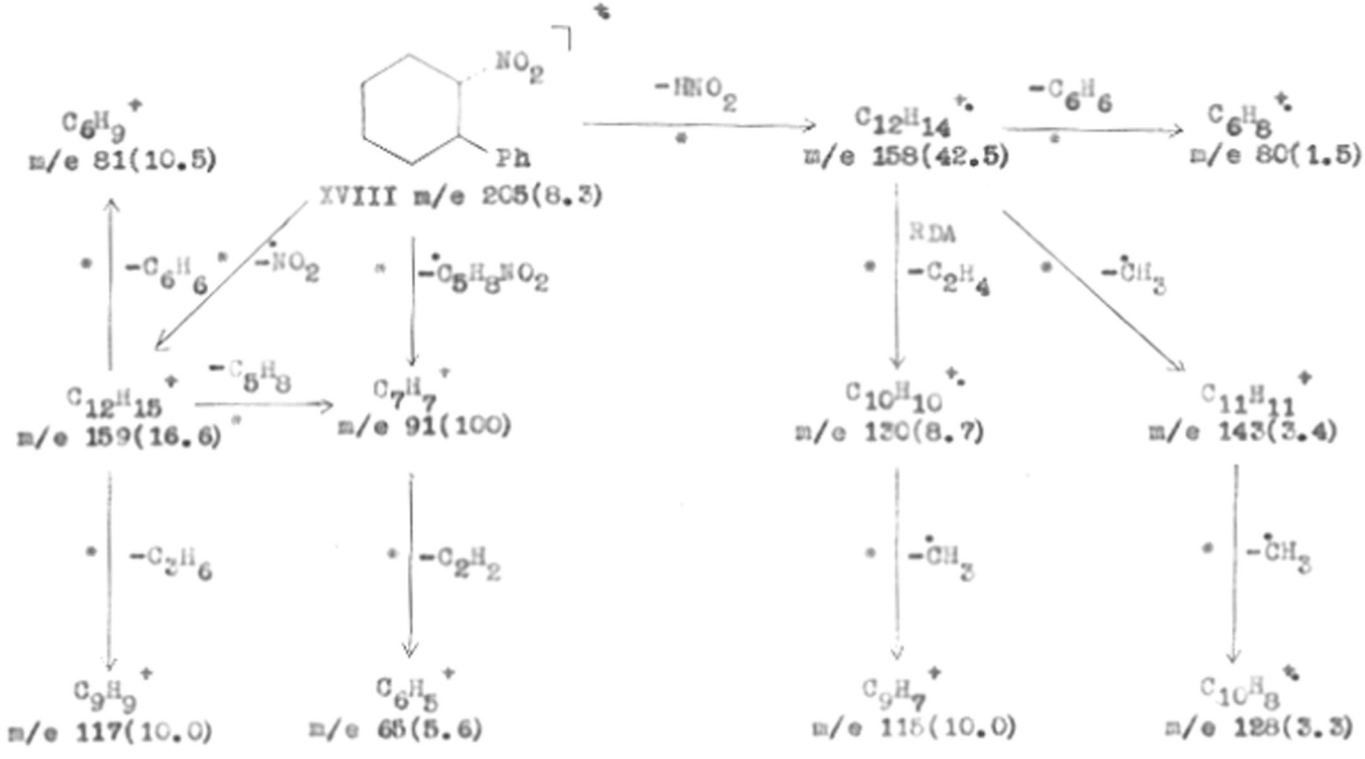

RELATIVE INTENSITY
100
50
55
83
129 M+·
NO2
40
60
80
100
120
91
158
205 M+·
Ph
50
100
150
200
233
x 10
281 M+·
m/e
250

FIG. 5


NO2
Ph
XVIII m/e 205(8.3)
-HNO2
C12H14+.
m/e 158(42.5)
-C6H6
C6H8+.
m/e 80(1.5)
C6H9+
m/e 81(10.5)
-C6H6
-NO2
-C5H8NO2
RDA
-C2H4
-CH3
C12H15+
m/e 159(16.6)
-C5H8
C7H7+
m/e 91(100)
C10H10+.
m/e 130(8.7)
C11H11+
m/e 143(3.4)
-C2H6
-C2H2
-CH3
-CH3
C9H9+
m/e 117(10.0)
C6H5+
m/e 65(5.6)
C9H7+
m/e 115(10.0)
C10H8+.
m/e 128(3.3)

SCHEME 9

2,6-Diphenyl-1-nitro cyclohexane (XIX) behaves exactly in the same way as 2-phenyl-1-nitro cyclohexane under electron impact. The $[M-NO]^+$ and $[M-H_2NO_2]^+$ ions are practically absent. $[M-NO_2]^+$ and $[M-HNO_2)^{+\cdot}$ ion intensities are comparable to those in the spectrum of 2-phenyl-1-nitro cyclohexane. The most important fragmentation process seems to be the formation of the m/e 91 ion. The m/e 206 ion (8.3%) is formed by RDA reaction of the $[M-HNO_2]^{+\cdot}$ ion as is evident from metastable data.

In the spectra of the 3,6-diphenyl-1-nitro cyclohexanes (XXA and XXB) a minor peak (2.4% and 2.6% respectively) corresponding to the $[M-NO]^+$ ion is observed. The $[M-NO_2]^+$ and $[M-HNO_2]^{+\cdot}$ ion abundances are considerably less than that in the spectrum of 2-phenyl-1-nitro cyclohexane. However, the $[M-H_2NO_2]^+$ ion is very significant (53.5% in XXA and 57% in XXB). Metastable transitions were observed for its formation from the molecular ion and from the $[M-NO]^+$ ion by the loss of H_2O. The $C_7H_7^+$ ion is the base peak in the spectra of both the isomers. There is no significant stereochemical effect in the fragmentation modes of the isomers.

It is interesting to note that the electron impact behaviour of 2,3,6-triphenyl-1-nitro cyclohexanes

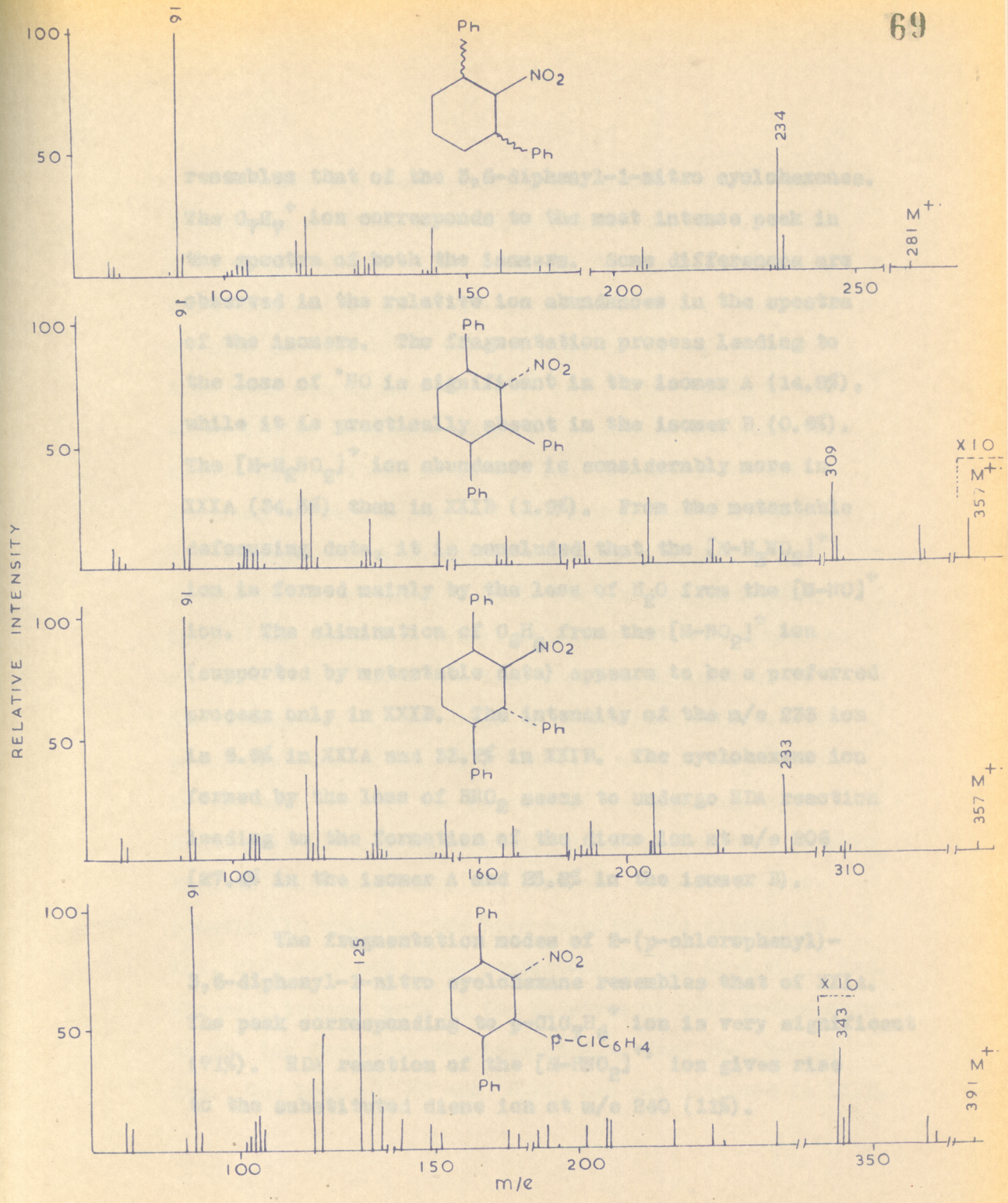

RELATIVE INTENSITY
100
50
91
Ph
NO2
Ph
234
281 M+
100
150
200
250
91
Ph
NO2
Ph
Ph
309
x 10
357 M+
91
Ph
NO2
Ph
Ph
233
357 M+
100
160
200
310
91
125
Ph
NO2
p-ClC6H4
Ph
x 10
343
391 M+
100
150
200
350
m/e

FIG. 6

resembles that of the 3,6-diphenyl-1-nitro cyclohexanes. The $C_7H_7^+$ ion corresponds to the most intense peak in the spectra of both the isomers. Some differences are observed in the relative ion abundances in the spectra of the isomers. The fragmentation process leading to the loss of $^{\cdot}NO$ is significant in the isomer A (14.8%), while it is practically absent in the isomer B (0.6%). The $[M-H_2NO_2]^+$ ion abundance is considerably more in XXIA (34.5%) than in XXIB (1.9%). From the metastable defocusing data, it is concluded that the $[M-H_2NO_2]^+$ ion is formed mainly by the loss of H_2O from the $[M-NO]^+$ ion. The elimination of C_6H_6 from the $[M-NO_2]^+$ ion (supported by metastable data) appears to be a preferred process only in XXIB. The intensity of the m/e 233 ion is 6.6% in XXIA and 33.2% in XXIB. The cyclohexene ion formed by the loss of HNO_2 seems to undergo RDA reaction leading to the formation of the diene ion at m/e 206 (27.4% in the isomer A and 25.8% in the isomer B).

The fragmentation modes of 2-(p-chlorophenyl)-3,6-diphenyl-1-nitro cyclohexane resembles that of XXIA. The peak corresponding to $p\text{-}ClC_7H_6^+$ ion is very significant (71%). RDA reaction of the $[M-HNO_2]^{+\cdot}$ ion gives rise to the substituted diene ion at m/e 240 (11%).

There are some striking differences in the ion abundances of these nitro cyclohexanes at low eV. The intensities of the major peaks in the spectra of these compounds run at 11 eV are given in Table 4. The most obvious difference is that in none of the spectra the base peak corresponds to $C_7H_7^+$ ion. Its abundance is considerably reduced. This can be due to the fact that simple cleavage processes are less preferred at low ionising voltage because of the energy requirements. The considerably less energy associated with the ions formed at low eV affects their further fragmentation. $C_7H_7^+$ ions which are formed mainly by the decomposition of the $[M-NO_2]^+$ ions are thus less significant at 11 eV. The abundances of the products of primary fragmentation processes such as $[M-NO]^+$, $[M-NO_2]^+$ and $[M-HNO_2]^{+\cdot}$ ion is the base peak in the spectra of 2-phenyl and 2,6-diphenyl-1-nitro cyclohexanes. It is interesting to note that in these compounds the loss of $^{\cdot}NO$ and H_2NO_2 are practically absent. The base peaks in the spectra of XXA, XXB, XXIA and XXIIA correspond to the $[M-H_2NO_2]^+$ ion. The most intense peak in the spectrum of XXIB corresponds to the ion formed by the loss of C_6H_6 from the $[M-NO_2]^+$ ion. The loss of $^{\cdot}NO$ and $^{\cdot}H_2NO_2$ are not favoured in XXIB.

Table - 6

Abundances of the major peaks in the spectra of nitro cyclohexanes at 11 eV (as % base peak)

Compound	$M^{+\cdot}$	$[M-HO]^+$	$[M-NO_2]^+$	$[M-HNO_2]^+$	$[M-H_2NO_2]^+$	$[(M-NO_2)-C_6H_6]^+$	$C_7H_7^+$	$C_9H_9^+$	$C_{13}H_{11}^+$	$C_{15}H_{13}^+$	m/e 130	m/e 206
XVIII	11.9	-	30.8	100	-	6.9	39.8	4.6	-	-	6.8	-
XIX	3.9	-	25.6	100	1.4	11.5	30.3	5.0	1.8	-	3.2	7.0
XXA	1.8	5.9	5.8	28.8	100	6.3	18.7	4.8	2.1	-	20.0	-
XXB	3.3	6.7	5.7	28.6	100	3.6	6.7	1.3	1.4	-	8.0	-
XXIA	0.5	46.0	7.4	30.0	100	14.1	31.0	16.0	19.0	8.8	2.1	49.0
XXIB	27.0	3.1	10.4	21.8	7.1	100	68.0	46.0	18.5	13.6	7.5	56.0
XXIIA	3.1	43.0	9.0	27.0	100	5.3	21.3 (m/e 125)	9.4	14.7 (m/e 201)	5.3 (m/e 227)	45.0 (m/e 240)	13.8

5. Conclusion

An examination of the 70 eV and 11 eV spectra of these nitro cyclohexanes has shown that the formation of the $C_7H_7^+$ ion is the most predominant process at 70 eV. The next important process seems to be the formation of the $[M-HNO_2]^{+\cdot}$ or $[M-H_2NO_2]^+$ ion. But at 11 eV the formation of the $[M-HNO_2]^{+\cdot}$ or $[M-H_2NO_2]^+$ ion takes precedence over the formation of the m/e 91 ion.

A comparison of the 11 eV spectra of the phenyl substituted nitro cyclohexanes and the corresponding nitro cyclohexenes has revealed some significant differences. The molecular ion abundances are slightly more in the saturated compounds. One of the outstanding observations is that in the 2-phenyl,2,6-diphenyl and 3,6-diphenyl nitro-cyclohexanes the fragmentation mode leading to the loss of $^{\cdot}NO$ is considerably reduced. The double bond appears to have some influence on this fragmentation mode. The mechanism is discussed later.

In the spectra of the 5-phenyl-4-nitro cyclohexene and its saturated analogue the most intense ion is the $[M-HNO_2]^{+\cdot}$. The base peaks in the spectra of the 3,5-diphenyl and 3,6-diphenyl nitro cyclohexenes correspond to the m/e 117 ion and m/e 91 ion respectively. In the corresponding saturated analogues these ions are less

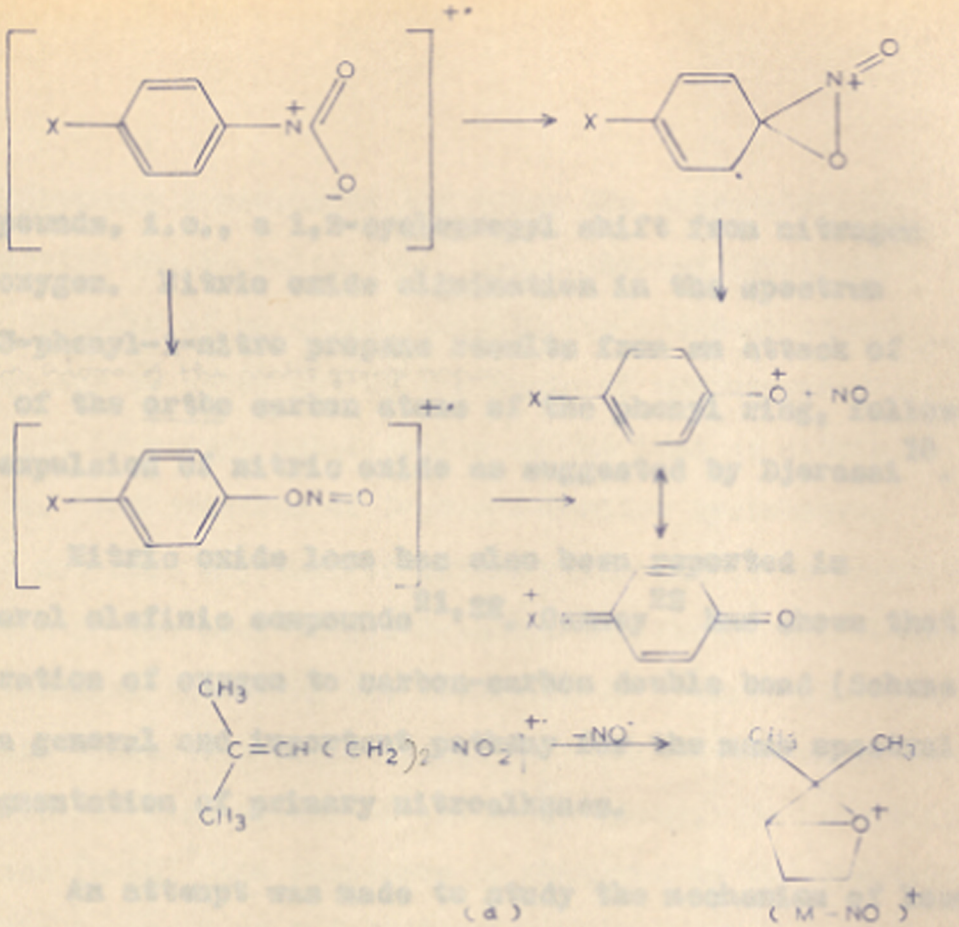
important. This shows that the rearrangement processes leading to the formation of the m/e 117 and m/e 91 ions are facilitated by the presence of a double bond in the cyclohexene ring. The most significant peak in the spectra of the saturated compounds correspond to the $[M-HNO_2]^{+\cdot}$ and $[M-H_2NO_2]^{+}$ ions. In the triphenyl nitro cyclohexenes the preferred process is the formation of the diene ion by RDA reaction. RDA fragmentation is a characteristic of the cyclohexene double bond. Hence, RDA reaction is not to be expected in the corresponding saturated compounds. The abundant diene ions (m/e 206) in the spectra of the triphenyl nitro cyclohexanes are due to the RDA reaction of the olefine ion produced by the loss of HNO_2 from the molecular ion. The base peaks in the spectra of the isomer A of the 2,3,6-triphenyl and 2-(p-chlorophenyl)-3,6-diphenyl nitro cyclohexanes are due to the $[M-H_2NO_2]^{+}$ ion. It is interesting to point out that the loss of C_6H_6 from the $[M-NO_2]^{+}$ ion is the most significant process in the spectrum of the isomer B of the 2,3,6-triphenyl compound.

The $[M-H_2NO_2]^{+}$ ion can come from any one of the following precursors, the $M^{+\cdot}$, $[M-NO]^{+}$, $[M-NO_2]^{+}$ and $[M-HNO_2]^{+\cdot}$. Metastable defocusing technique has shown that in the 3,6-diphenyl and the 3,5,6-triphenyl nitro

cyclohexanes it comes both from the $M^{+\cdot}$ and $[M-NO]^+$ ions. In the absence of additional information it is difficult to establish the mechanism of formation of $[M-H_2NO_2]^+$ ions.

6. Mechanism of loss of NO

Elimination of nitric oxide followed by loss of CO is a characteristic fragmentation mode of the aromatic nitro compounds[9,10]. Possible mechanisms for the loss of $^{\cdot}NO$ from the molecular ion of nitroarenes have been reviewed[11]. They include the *in situ* nitro-nitrite isomerism[10] and the rearrangement via a three membered ring intermediate[12] (Scheme 10a). Energy partitioning data on the elimination of nitric oxide has been used to obtain evidence for the three membered cyclic rearrangement[13]. The nitro-nitrite rearrangement is not observed for saturated aliphatic nitro compounds[15], as alkyl groups migrate with much more difficulty[16-18] than aryl groups[19] upon electron bombardment. Yet it has been reported[20] that loss of nitric oxide may occur from molecular ions, having the nitro group attached to a saturated carbon atom. Nitric oxide loss has been reported in the spectra of nitro cyclopropane[15,20] and 3-phenyl-1-nitro propane[19]. The loss of nitric oxide from the molecular ion of nitro cyclopropane could be explained in the same way as for aromatic nitro



SCHEME -10

compounds, i.e., a 1,2-cyclopropyl shift from nitrogen to oxygen. Nitric oxide elimination in the spectrum of 3-phenyl-1-nitro propane results from an attack of one of the oxygen atoms of the nitro group on one of the ortho carbon atoms of the phenyl ring, followed by expulsion of nitric oxide as suggested by Djerassi[15].

Nitric oxide loss has also been reported in several olefinic compounds[21,22]. Carney[22] has shown that migration of oxygen to carbon-carbon double bond (Scheme 10a) is a general and important pathway for the mass spectral fragmentation of primary nitroalkenes.

An attempt was made to study the mechanism of loss of nitric oxide in the nitro cyclohexenes studied with the help of the available data. Elimination of $^{\bullet}NO$ is a significant process only in the 3,6-diphenyl and the 3,5,6-triphenyl nitro cyclohexenes. Both the isomers of 3,6-diphenyl nitro cyclohexene give $[M-NO]^{+}$ ions of equal abundance while in the triphenyl compounds $[M-NO]^{+}$ ion is significant in the isomer A and negligible in the other isomer B. Two different mechanisms have been proposed for the loss of $^{\bullet}NO$ from the molecular ions of the 3,6-diphenyl and the 3,5,6-triphenyl nitro cyclohexenes.

Since the $[M-NO]^{+}$ ion abundance is negligible in 4-nitro cyclohexene, the monophenyl and 3,5-diphenyl nitro

cyclohexenes a mechanism involving the nitro-nitrite isomerism can be ruled out. The mechanism involving the transfer of an oxygen atom to the adjacent phenyl group can be ruled out on the basis of the observed effects of phenyl substitution on the loss of nitric oxide. The spectrum of 3-phenyl-4-nitro cyclohexene does not show any loss of nitric oxide and it is practically absent in the spectrum of 5-phenyl-4-nitro-Δ^1-cyclohexene. A mechanism involving the formation of a three-membered cyclic transition state should be expected to depend on the steric disposition of the nitro group. No reduction in the $[M-NO]^+$ ion abundance is observed in the spectrum of the isomer B of 3,6-diphenyl-4-nitro cyclohexene in which the nitro group and the two phenyl groups are on the same side of the ring. The $[M-NO]^+$ ion abundance is considerably reduced in the spectra of the corresponding saturated analogues. Similar effect on the loss of nitric oxide is observed on saturating the double bond of the parent, 5-phenyl and 3,5-diphenyl compounds. Hence, the loss of $^{\cdot}NO$ in these compounds involves double bond participation. Oxygen migration to the double bond as in the case of alkenes[22] appears to lead to the loss of $^{\cdot}NO$. The absence of any significant effect of stereochemistry on the loss of $^{\cdot}NO$ in the 3,6-diphenyl compounds suggests that the oxygen migration to the double bond is preceded

by ring opening β- to the double bond. There are two different ways of ring rupture: 1) cleavage of C_3-C_4 bond and 2) cleavage of C_5-C_6 bond. Cleavage of C_3-C_4 bond can be ruled out since α-cleavage in nitro alkanes is not a favourable process[15]. Hence, the loss of $^{\bullet}NO$ in the 3,6-diphenyl-4-nitro cyclohexenes involves rupture of C_5-C_6 bond followed by oxygen migration to the double bond (Scheme 10c). The observation that loss of $^{\bullet}NO$ is not completely suppressed on saturating the double bond in the 3,6-diphenyl nitro cyclohexenes, suggests that elimination of $^{\bullet}NO$ takes place via some other mechanism also. Oxygen transfer to the C_6-phenyl can take place in a concerted manner with prior ring opening.

A different mechanism seems to operate in the triphenyl compounds. Evidences have been obtained to rule out the other possible mechanisms. A mechanism involving oxygen migration to the adjacent phenyl group can be ruled out on the basis of the observation that loss of $^{\bullet}NO$ is not a significant process in 5-phenyl and 3,5-diphenyl nitro cyclohexenes. The possibility of oxygen migration to the double bond can also be ruled out since there is no reduction in the loss of $^{\bullet}NO$ in the corresponding saturated compounds. These observations lend further support to the mechanism involving a three-membered ring transition state proposed previously[6] (Scheme 10b).

The observed effects of stereochemistry and substituents on the C_5-phenyl support this mechanism. Electron attracting groups on C_5-phenyl increase the electron deficiency on C_4. This favours the interaction between C_4 and the lone pair of electrons of the oxygen atom of the nitro group. Loss of $^{\bullet}NO$ is favoured only when the nitro groups and the three phenyl groups are on opposite sides of the ring (isomer A). In the isomer B the C_3- and C_6- phenyl groups which are on the same side as the nitro group hinder the formation of the three-membered transition state.

B. Experimental

The samples were introduced through the direct inlet and volatilised at the lowest temperature possible. The spectra were checked for reproducibility. The metastable defocusing technique described by Barber and Elliott[23] was used. The high resolution mass measurements were made at a resolution of 10,000. The nitro cyclohexenes were synthesised according to known general procedures and their purity and identity were established by spectral and analytical methods. The NMR spectra were recorded on a Varian T-60 spectrometer. The melting points were determined on a hot block and are uncorrected.

Trans-1-Phenyl butadiene

It was prepared as described in literature[24]. A three-necked flask with a mercury-sealed stirrer, a reflux condenser with a $CaCl_2$ drying tube, a separatory funnel, a nitrogen inlet tube and a thermometer was used. 42.5 g of methyl magnesium iodide (0.26 mole), was prepared from 35.8 g of methyl iodide, 6.7 g magnesium turnings and 62.5 ml of absolute ether. It was cooled to below 10° by means of an ice-water bath. A solution of 33 g (0.25 mole) of pure cinnamaldehyde in 30 ml of absolute ether was added with stirring. The rate of addition was controlled so that the temperature remained below 10°. A slow stream of dry nitrogen was passed through the flask throughout the addition. The contents of the flask were transferred to a separatory funnel and the apparatus was reassembled without the drying tube and the nitrogen inlet tube. 88 ml of 30% sulfuric acid was placed in the flask. Without cooling but with efficient stirring, the ethereal solution of the cinnamaldehyde methyl magnesium iodide adduct was added rapidly to the acid. Gentle reflux was maintained for 20 minutes. The contents of the flask were immediately transferred to a separatory funnel, the lower aqueous layer was washed successively with 25 ml water, a mixture of 25 ml of 5%

aqueous sodium hydroxide solution and 25 ml water. Before the second washing 0.15 g of Nanox D was dissolved in the ether layer. The washed solution was dried over 10 g of anhydrous sodium sulfate for 1 hr. and then over 7 g of anhydrous potassium carbonate for 12 hrs. The ethereal solution was concentrated and again dried with 7 g of anhydrous potassium carbonate. The concentrated solution was filtered into a Claisen flask and distilled under reduced pressure in an atmosphere of nitrogen into a receiver containing 0.15 g of hydroquinone. The fraction distilling at 124-128°/15 mm was collected (18 g). It was dried over 2 g of anhydrous potassium carbonate and redistilled as before. The fraction boiling at 103°/10 mm was collected; yield 15.2 g.
Lit.[25], BP, 78-81°/8 mm.

4-Nitro-Δ^1-cyclohexene (I)

1.2 g of 1,3-butadiene, 0.73 g of nitroethylene and 0.05 g of hydroquinone were sealed in a thick-walled glass tube at -80° and heated at 110° for 24 hours. The tube was cooled to room temperature, and then further cooled in liquid air and opened. It was allowed to warm up to expel the excess butadiene. The contents of the tube were extracted with ether, dried over anhydrous sodium sulfate. The solvent was evaporated off and the product was distilled at reduced pressure. The fraction

boiling at 72-76/10 mm was collected (0.4 g). It was further purified by column chromatography on 30 g of silica gel. Elution with benzene: petroleum ether (1:1) gave pure 4-nitro cyclohexene (0.3 g).

Lit.[25], BP, 77°/10 mm.

NMR (CCl_4) τ 4.3 (bs, 2H, H-1 and H-2), 5.5 (m,1H,H-4), 7.35 (d, 2H, H_2-3), 7.77 (m, 4H, H_2-5 and H_2-6).

Analysis calculated for $C_6H_9NO_2$: N, 11.4%. Found: N, 11.5%.

3-Phenyl-4-nitro-Δ^1-cyclohexene (II)

0.5 g of 1-phenyl butadiene, 0.15 g of nitroethylene, 0.05 g of hydroquinone and 5 ml of benzene were sealed in a thick-walled glass tube at -80°. The tube was heated at 150° for 30 hrs. It was opened after cooling in liquid air and the product was taken up in benzene and chromatographed on 40 g of silica gel. Elution with petroleum ether gave 0.25 g of the unreacted diene. Elution with a mixture of equal volume of benzene and petroleum ether gave the product. It was crystallised from petroleum ether, colourless crystals, 0.15 g. MP, 60°.

NMR (CCl_4) τ 2.8 (s, 5H, aromatic protons), 4.2 (m, 2H, H-1 and H-2), 5.5 (m, 1H, H-4), 5.95 (m, 1H, H-3), 7.7 (m, 4H, H_2-5 and H_2-6).

Analysis calculated for $C_{12}H_{13}NO_2$: N, 6.8%

Found: N, 6.66%.

5-Phenyl-4-nitro-Δ^1-cyclohexene (III)

1 g of butadiene, 1 g of β-nitrostyrene, 0.05 g of hydroquinone and 1.5 ml of toluene were sealed in a thick-walled glass tube at -80° and heated at 110° for 50 hrs. The tube was then cooled in liquid air and was opened. The product was crystallised from methanol, colourless crystals, 0.75 g. MP, 102°. Lit.[26] 103°.
NMR (CCl_4) τ 2.82 (s, 5H, aromatic protons),
4.26 (s, 2H, H-1 and H-2), 5.18 (m, 1H, H-4),
6.62 (m, 1H, H-5), 7.25 (m, 2H, H_2-3), 7.6 (m, 2H, H_2-6).
Analysis calculated for $C_{12}H_{13}NO_2$: N, 6.8%.
Found: N, 6.65%.

5-(p-Tolyl)-4-nitro-Δ^1-cyclohexene (IV)

0.5 g of butadiene, 0.2 g of p-methyl-β-nitrostyrene[27], 0.025 g of hydroquinone and 1 ml of toluene were heated in a sealed tube at 115° for 50 hrs. The tube was cooled in liquid air and opened. The product was chromatographed on 30 g silica gel. Elution with petroleum ether gave the pure nitro cyclohexene. It was crystallised from petroleum ether, colourless crystals, 0.17 g, MP, 89°.
NMR (CCl_4) τ 3.1 (s, 4H, aromatic protons),
4.4 (s, 2H, H-1 and H-2), 5.25 (m, 1H, H-4),
6.75 (m, 1H, H-5), 7.3 (m, 2H, H_2-3),
7.7 (m, 5H, H_2-6 and CH_3)
Analysis calculated for $C_{13}H_{15}NO_2$: N, 6.5%.
Found: N, 6.6%.

5-(p-Chlorophenyl-4-nitro-Δ^1-cyclohexene (V)

0.5 g of butadiene, 0.1 g of p-chloro-β-nitrostyrene, 0.025 g of hydroquinone and 1 ml of toluene were heated in a sealed tube at 115° for 50 hrs. The tube was cooled in liquid air and then opened. The product was crystallised from methanol. Colourless crystals were obtained. 0.1 g, MP, 86°. Lit.[28], 88.5-89.5°.

NMR (CCl_4) τ 2.92 (m, 4H, aromatic protons), 4.3 (s, 2H, H-1 and H-2), 5.25 (m, 1H, H-4), 6.68 (m, 1H, H-5), 7.27 (m, 2H, H_2-3), 7.65 (m, 2H, H_2-6).

Analysis calculated for $C_{12}H_{12}ClNO_2$: N, 6.75%.

Found: N, 6.6%.

5-(p-Cyanophenyl)-4-nitro-Δ^1-cyclohexene (VI)

0.5 g of butadiene, 0.2 g of p-cyano-β-nitrostyrene[27], 0.025 g of hydroquinone and 1 ml of toluene were heated in a sealed tube at 115° for 50 hrs. The tube was cooled in liquid air and opened. The product was crystallised from methanol. Colourless crystals were obtained 0.25 g. MP, 130°.

NMR (CCl_4) τ 2.55 (m, 4H, aromatic protons), 4.2 (s, 2H, H-1 and H-2), 5.15 (m, 1H, H-4), 6.55 (m, 1H, H-5), 7.25 (m, 2H, H_2-3), 7.65 (m, 2H, H_2-6).

Analysis calculated for $C_{13}H_{12}N_2O_2$: N, 12.3%

Found: N, 12.33%.

5-(p-Nitrophenyl)-4-nitro-Δ^1-cyclohexene (VII)

0.5 g of butadiene, 0.2 g of p-nitro-β-nitrostyrene[27], 0.025 g of hydroquinone and 1 ml of toluene were heated in a sealed tube at 115° for 50 hrs. The tube was cooled in liquid air and opened. The product was crystallised from methanol, pale yellow crystals, 0.2 g.

MP, 148°. Lit.,[28] 138-9°.

NMR. ($CHCl_3$) τ 4.22 (s, 2H, H-1 and H-2) 5.05 (m, 1H, H-4), 6.47 (m, 1H, H-5), 7.17 (m, 2H, H_2-3), 7.55 (m, 2H, H_2-6).

Analysis calculated for $C_{12}H_{12}N_2O_4$: N, 11.3%

Found: N, 11.1%

3,5-Diphenyl-4-nitro-Δ^1-cyclohexene (VIII)

1 g of 1-phenyl butadiene, 0.5 g of β-nitrostyrene, 0.05 g of hydroquinone and 10 ml of o-dichlorobenzene were refluxed for 27 hrs. The solvent was removed by distillation under vacuum. TLC of the residue in benzene-petroleum ether (1:1) showed the presence of only one product. It was chromatographed on 50 g of silica gel. Elution with petroleum ether gave 0.35 g of unreacted diene. The Diels-Alder adduct was eluted with benzene-petroleum ether (1:1). It was crystallised from benzene-petroleum ether, colourless crystals, 0.55 g, MP, 164°.

Analysis calculated for $C_{18}H_{17}NO_2$: N, 5.04%.

Found: N, 4.84%.

Aromatization of the adduct with selenium gave m-diphenyl benzene. Hence, the adduct is 3,5-diphenyl-4-nitro-Δ^1-cyclohexene. It can exist in four stereoisomeric forms[29]. Attempts to separate the isomers were not successful.

Aromatization of the Diels-Alder adduct of 1-phenyl butadiene and β-nitrostyrene

0.25 g of the adduct was mixed with 0.025 g of selenium powder and heated in a salt bath at 230° for 30 minutes. The product was taken up in $CHCl_3$ and chromatographed on 20 g of silica gel. The white solid obtained when eluted with petroleum ether was crystallised from petroleum ether, colourless crystals, 0.03 g, MP, 89°. The physical constants, spectral and analytical data of the above product agreed with those of an authentic sample of m-diphenyl benzene prepared according to a reported procedure[30].

2-Phenyl-1-nitrocyclohexane (XVIII)

0.14 g of 5-phenyl-4-nitro-Δ^1-cyclohexene was hydrogenated using 0.01 g of PtO_2 catalyst in 20 ml of 1:1 ethyl acetate-glacial acetic acid. When the theoretical amount of hydrogen has been absorbed the reduction was stopped and the solvent was removed under vacuum. The product was crystallised from petroleum ether, colourless

crystals, 0.1 g, MP, 126-127°. Lit.[31] 124-125.5°.
NMR (CCl_4) τ 2.9 (s, 5H, aromatic protons),
5.47 (m, 1H, H-1), 6.7-8.9(m, 9H).
Analysis calculated for $C_{12}H_{15}NO_2$: N, 6.82%
Found: N, 6.98%.

2,6-Diphenyl-1-nitrocyclohexane (XIX)

0.1 g of 3,6-diphenyl-4-nitro cyclohexene was hydrogenated with 0.01 g PtO_2 catalyst as described before. The product was crystallised from glacial acetic acid, colourless crystals, 0.07 g. MP, 268°.
Analysis calculated for $C_{18}H_{19}NO_2$: N, 5.04%
Found: N, 4.9%.

3,6-Diphenyl-1-nitro-cyclohexanes (XXA) and (XXB)

0.1 g of the corresponding 3,6-diphenyl-4-nitro-Δ^1-cyclohexene was hydrogenated using 0.01 g of PtO_2 catalyst in 20 ml of 1:1 ethyl acetate - glacial acetic acid. When the reduction was over the solvent was removed under vacuum and the product was purified by preparative TLC in benzene-petroleum ether (1:1).
Yield 0.05 g.
Isomer A : MP, 66°.
NMR (CCl_4) τ 2.9 (m, 10H, aromatic protons),
5.1 (m, 1H, H-1), 6.4-8.3 (m, 8H).
Analysis calculated for $C_{18}H_{19}NO_2$: N, 5.04%
Found: N, 5.1%.

Isomer B : thick liquid

NMR (CCl_4) τ 2.8 (m, 10H, aromatic protons),

5.17 (m, 1H, H-1), 6.5-8.4 (m, 8H),

Analysis calculated for $C_{18}H_{19}NO_2$: N, 5.04%.

Found: N, 4.9%.

2,3,6-Triphenyl-1-nitro cyclohexane (XXIA and XXIB)

0.1 g of the corresponding 3,5,6-triphenyl-4-nitro-Δ^1-cyclohexene was hydrogenated using 0.01 g of PtO_2 catalyst as described before. The product was crystallised from benzene-petroleum ether.

Isomer A : Colourless crystals, 0.07 g.

MP, 168° Lit.,[32] 158°

NMR (CCl_4) τ 2.7 (m, 15H, aromatic protons),

4.6 (t, 1H, H-1), 6.2 (q, 1H, H-2), 6.6 (m, 2H, H-3 and H-6),

7.74 (m, 4H, H_2-4 and H_2-5).

Analysis calculated for $C_{24}H_{23}NO_2$: N, 3.93%

Found: 4.1%

Isomer B : colourless crystals, 0.07 g.

MP, 182°. Lit.,[32] 180°.

NMR (CCl_4) τ 2.6 (m, 15H, aromatic protons), 4.8 (q, 1H, H-1),

6.2 (t, 1H, H-2), 6.7 1H, H-3 merges with H-2, 7.3

(m, 1H, H-6), 7.95 (m, 4H, H_2-4 and H_2-5).

Analysis calculated for $C_{24}H_{23}NO_2$: N, 3.93%

Found: N, 3.8%.

3,6-Diphenyl-2-(p-chlorophenyl)-1-nitro cyclohexane (XXIIA)

0.1 g of the corresponding 3,6-diphenyl-5-(p-chlorophenyl)-4-nitro cyclohexene was hydrogenated as described before. The product was crystallised from benzene-petroleum ether, colourless crystals, 0.075 g, MP, 194°.

NMR (CCl_4) τ 3.15 (m, 14H, aromatic protons), 4.7 (t, 1H, H-1), 6.32 (q, 1H, H-3), 6.67 (m, 2H, H-3 and H-6), 7.8 (m, 4H, H_2-4 and H_2-5).

Analysis calculated for $C_{24}H_{22}ClNO_2$: N, 3.59%

Found: N, 3.5%.

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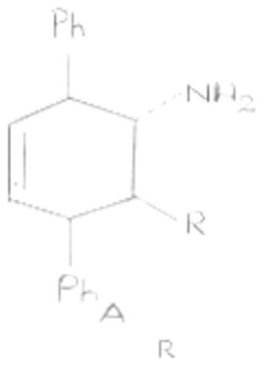
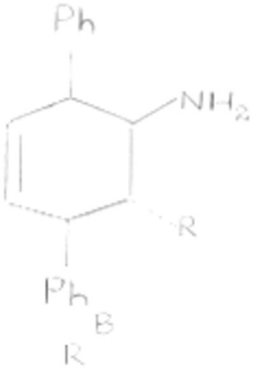
CHAPTER - III

UNIMOLECULAR ION DECOMPOSITIONS OF 3,6-DIPHENYL-5-ARYL-4-AMINO-Δ^1-CYCLOHEXENES UNDER DIFFERENT IONISING CONDITIONS

A. Present Work

The newer ionisation techniques such as CI, FI and FD are regarded as complementary techniques to EI. The present work was undertaken to compare the unimolecular ion decompositions and to study the fragmentation modes which compete with retro Diels-Alder reaction in some isomeric 3,6-diphenyl-5-aryl-4-amino-Δ^1-cyclohexenes under different ionising conditions. The pyrolytic reactions have also been studied. In the electron ionisation induced reactions both the decompositions taking place in the ion source and the first field-free region were examined. An attempt has been made to compare the behaviour of these amino cyclohexenes with their corresponding nitro analogues. The following compounds were examined in the present studies.





IA	p-$MeOC_6H_4$		
IIA	2-furyl	IIB	2-furyl
IIIA	p-MeC_6H_4	IIIB	p-MeC_6H_4
IVA	C_6H_5	IVB	C_6H_5
VA	p-ClC_6H_4	VB	p-ClC_6H_4
VIA	p-BrC_6H_4		
VIIA	p-CNC_6H_4		

1. Electron ionisation

i) Decompositions in the ion source

The molecular ion peak is not observed in the spectra of the amino compounds. The two major competing fragmentation modes operating from the molecular ions of the amino compounds are retro Diels-Alder reaction and the formation of the m/e 234 ion. Many of the other peaks in the spectra arise from the further fragmentation of these ions (Scheme 1, Fig.1-3).

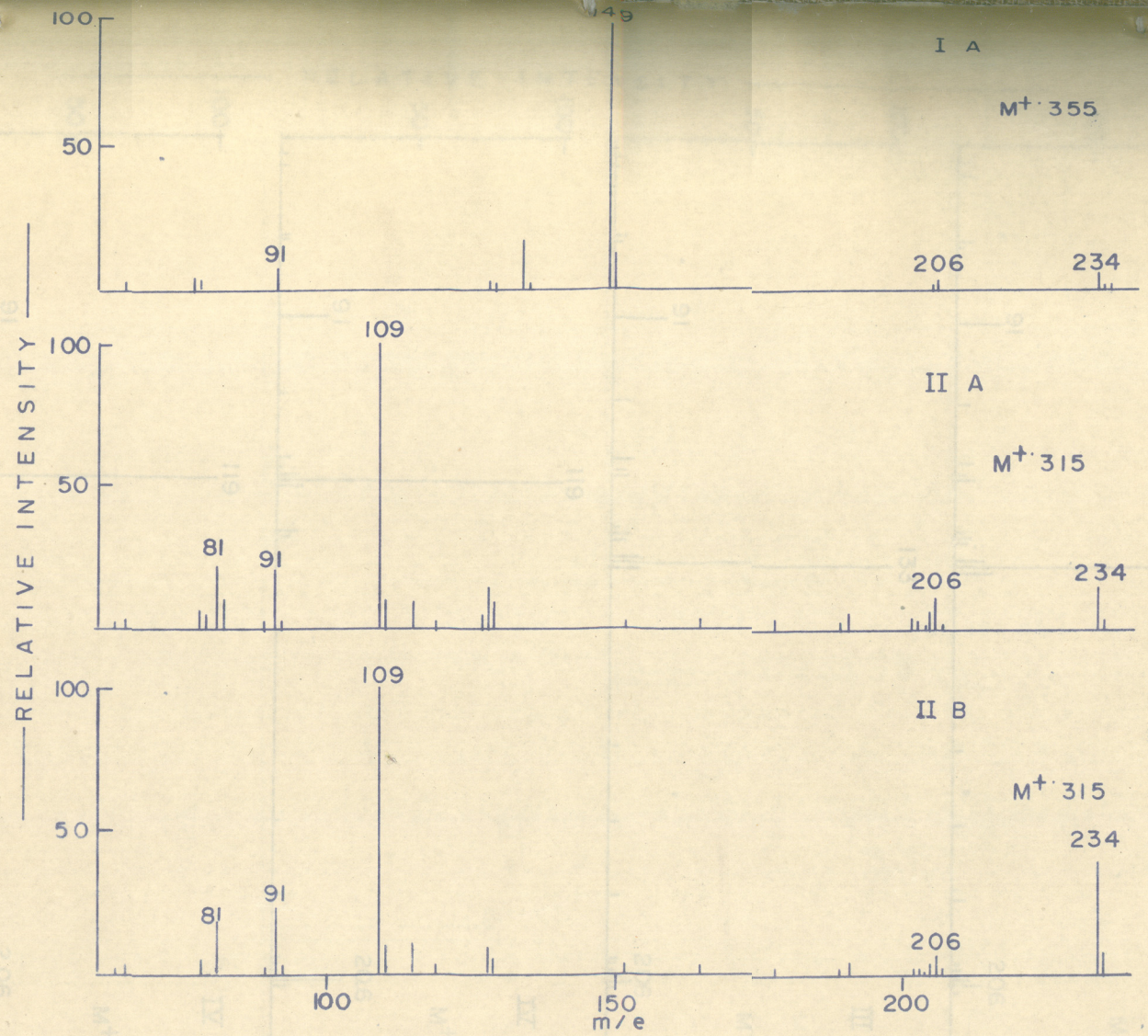

100
50
91
149
I A
M+· 355
206
234
RELATIVE INTENSITY
100
50
81
91
109
II A
M+· 315
206
234
100
50
81
91
109
II B
M+· 315
234
206
100
150
200
m/e

FIG I

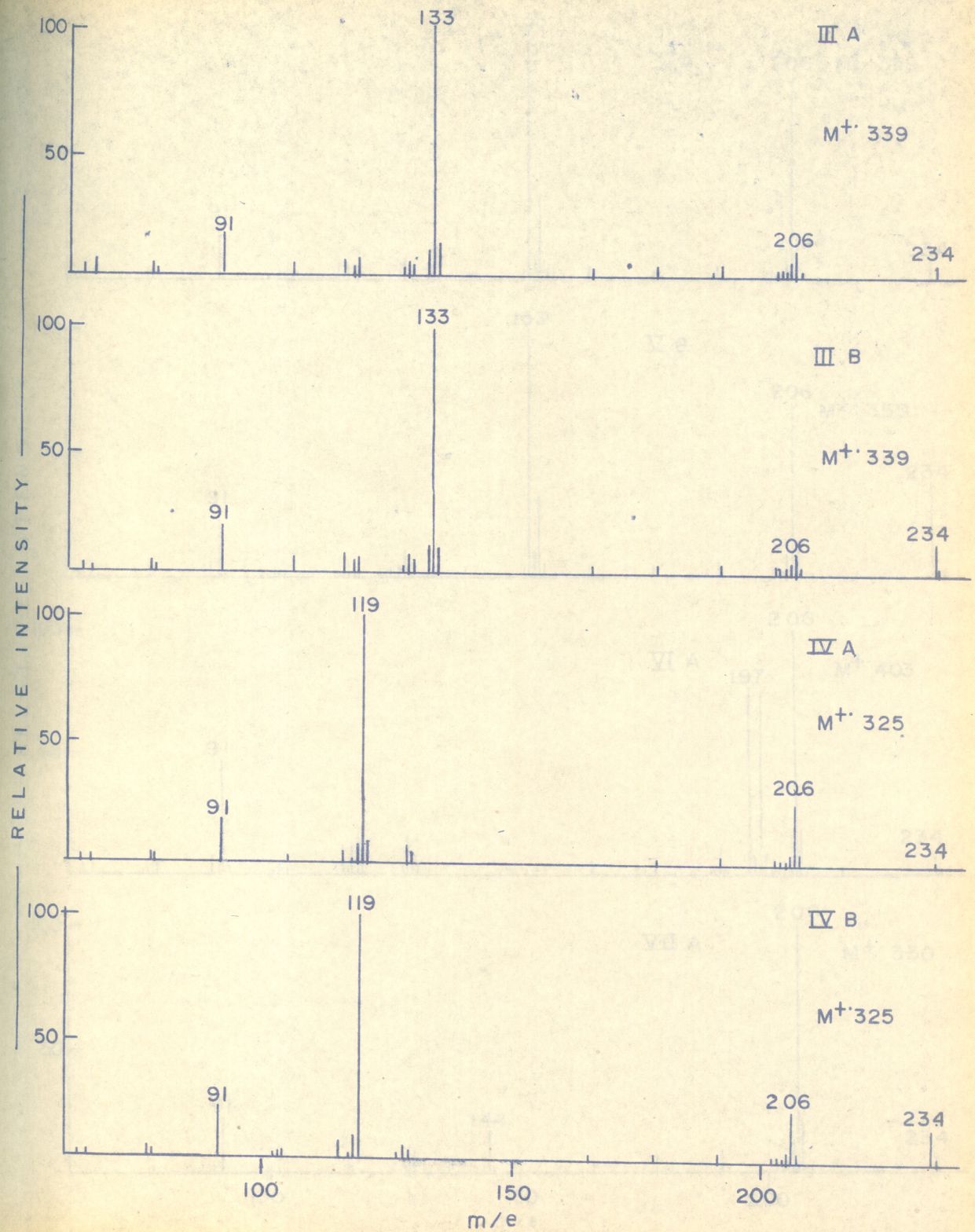

III A
M+· 339
133
91
206
234
III B
M+· 339
133
91
206
234
IV A
M+· 325
119
91
206
234
IV B
M+· 325
119
91
206
234
100
50
RELATIVE INTENSITY
100
150
200
m/e

FIG. 2

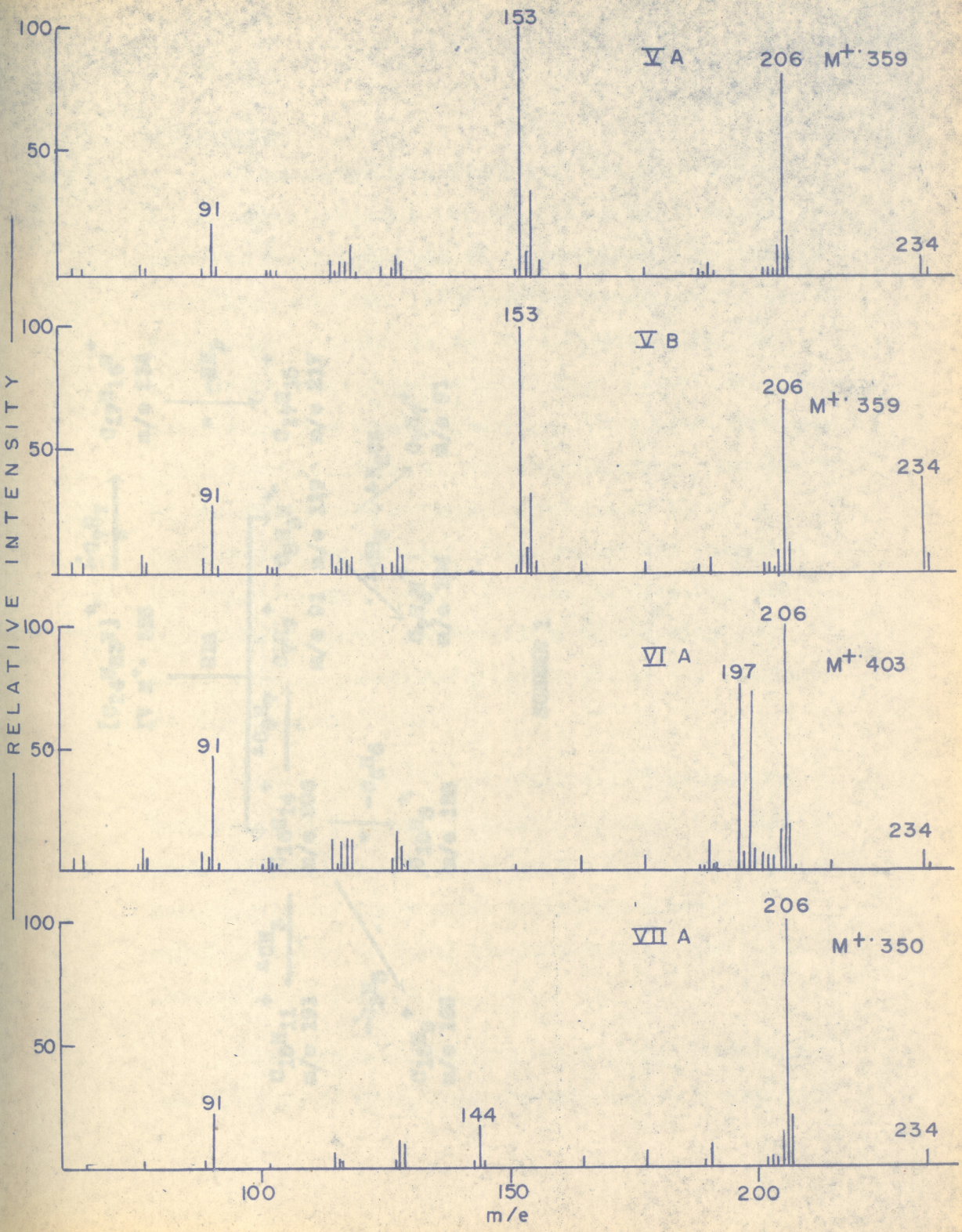
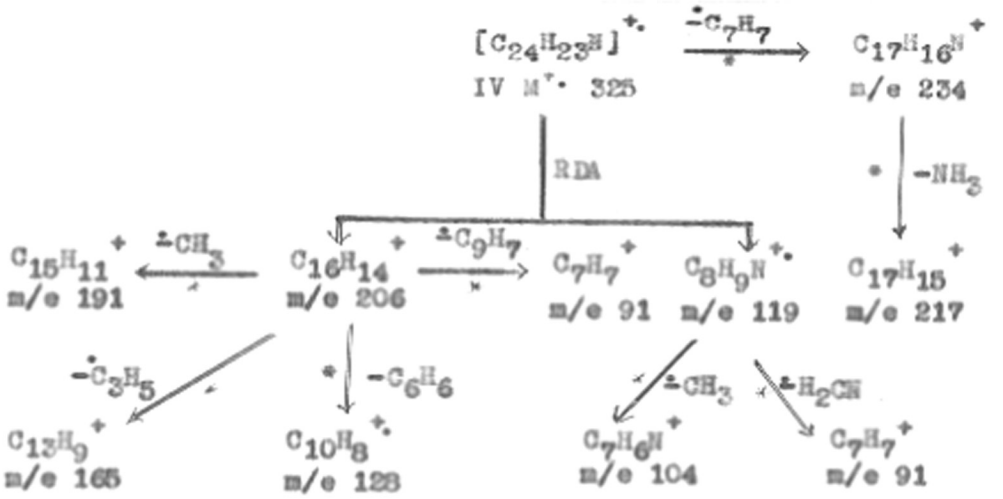

100
50
153
V A
206 M+· 359
91
234
100
50
153
V B
206
M+· 359
234
91
RELATIVE INTENSITY
100
50
206
VI A
197
M+· 403
91
234
100
50
206
VII A
M+· 350
91
144
234
100
150
200
m/e

FIG. 3


[C24H23N]+·
IV M+· 325
-C7H7·
C17H16N+
m/e 234
RDA
-NH3
C15H11+
m/e 191
-CH3·
C16H14+·
m/e 206
-C9H7·
C7H7+
m/e 91
C8H9N+·
m/e 119
C17H15+
m/e 217
-C3H5·
-C6H6
-CH3·
-H2CN
C13H9+
m/e 165
C10H8+·
m/e 128
C7H6N+
m/e 104
C7H7+
m/e 91

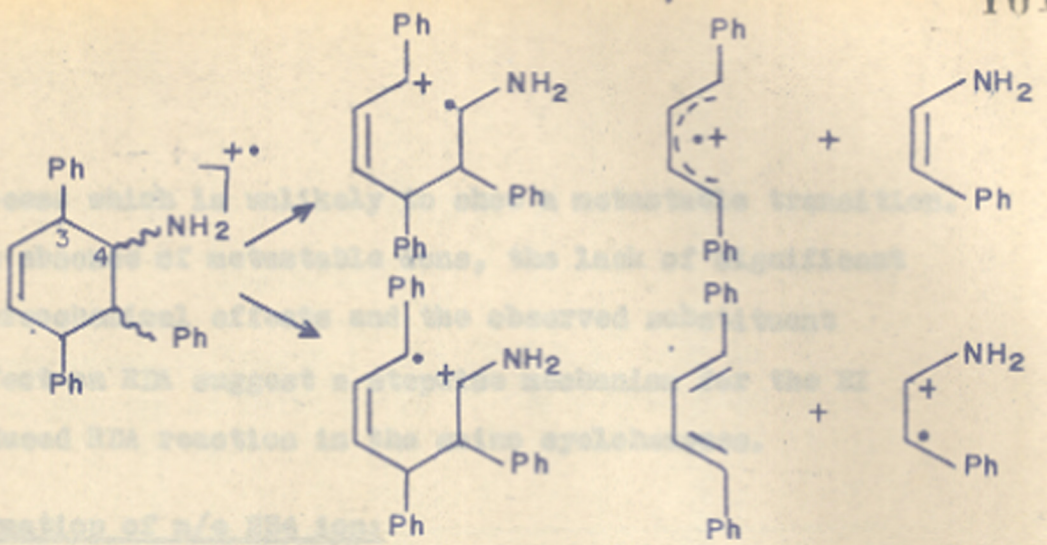
SCHEME 1

RDA reaction

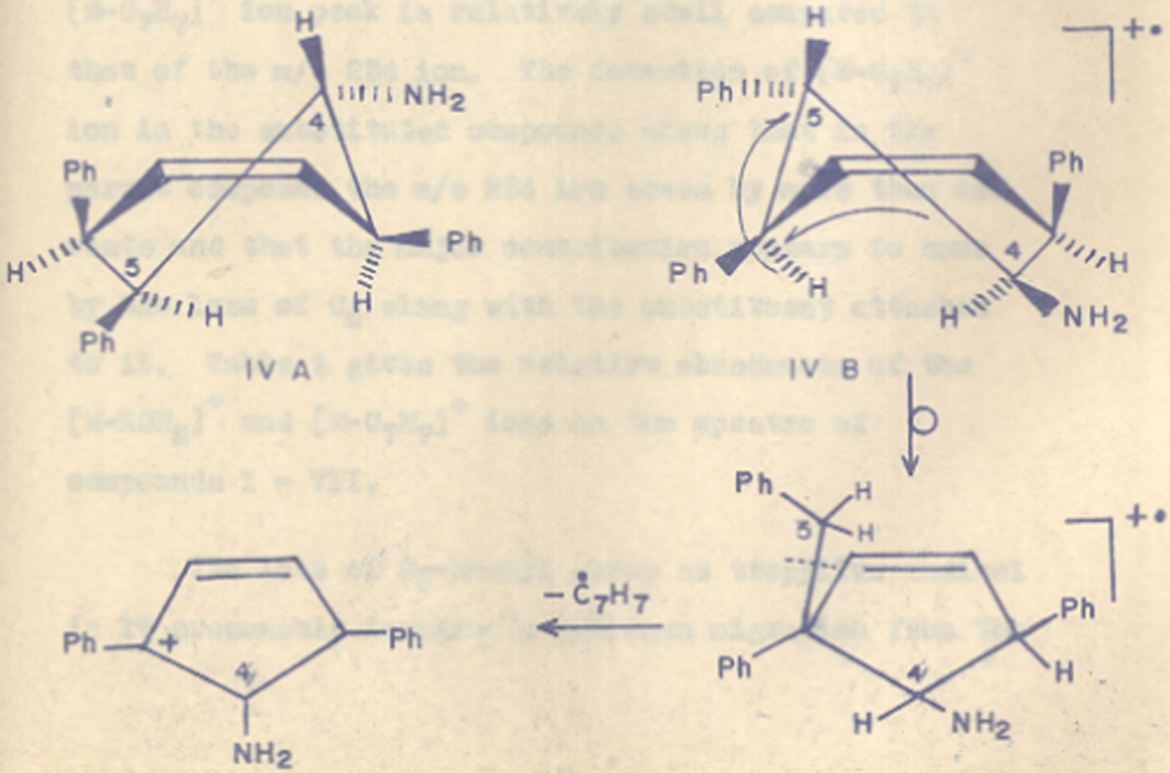
A characteristic feature of the RDA reaction in the amino compounds IVA and IVB is the formation of both the diene (25%) and the dienophile (100%) ions by competing processes. No metastable peaks were observed for the RDA reaction in the normal spectra and the metastable defocusing technique also did not show any transitions for these processes. There is no appreciable stereochemical effect on RDA fragmentation. The spectra of the substituted compounds showed that there is considerable substituent effect on the two competing RDA fragmentation modes. Electron withdrawing groups on C_5-phenyl favour the formation of the diene ion while electron releasing groups increase the abundance of the dienophile ions.

Both stepwise[1,2] and concerted[3,4] mechanisms have been put forward to explain RDA reaction. The observed relative abundances of the RDA fragmentations in the mass spectra of these amino cyclohexenes can be rationalised by assuming the formation of open chain intermediates (Scheme 2).

The charge-stabilising amino group can favour the cleavage of C_3-C_4 bond and this may be a very fast



SCHEME 2



SCHEME 3

process which is unlikely to show a metastable transition. The absence of metastable ions, the lack of significant stereochemical effects and the observed substituent effect on RDA suggest a stepwise mechanism for the EI induced RDA reaction in the amino cyclohexenes.

Formation of m/e 234 ion:

This fragment can result by the elimination of a tropylium radical from the molecular ion. In the spectra of IVA and IVB the C_3, C_5 or C_6-phenyl group can be involved in the process. The spectra of 5-aryl substituted derivatives showed peaks corresponding to both $[M-RCH_2]^+$ (m/e 234) and $[M-C_7H_7]^+$ ions. The $[M-C_7H_7]^+$ ion peak is relatively small compared to that of the m/e 234 ion. The formation of $[M-C_7H_7]^+$ ion in the substituted compounds shows that in the parent compound the m/e 234 ion comes by more than one route and that the major contribution appears to come by the loss of C_5 along with the substituent attached to it. Table 1 gives the relative abundances of the $[M-RCH_2]^+$ and $[M-C_7H_7]^+$ ions in the spectra of compounds I - VII.

The loss of C_5-phenyl group as tropylium radical in IV presumably involves a hydrogen migration from the

TABLE - 1

Abundances of $[M-RCH_2]^+$ and $[M-C_7H_7]^+$ ions in the spectra of I-VII at 70 eV (as % base peak).

Compound	$[M-RCH_2]^+$	$[M-C_7H_7]^+$
IA	6.2	0.3
IIA	14.2	-
IIB	39.0	-
IIIA	3.3	0.5
IIIB	13.0	0.7
IVA	2.4	2.4
IVB	14.0	14.0
VA	5.8	0.7
VB	37.0	1.7
VIA	7.4	1.0
VIIA	3.9	0.5

neighbouring carbon atoms to C_5. Both at 70 eV and 12 eV the ion at m/e 234 is more abundant in the isomer B. If the $^{\cdot}C_7H_7$ elimination involves a 1,2-hydrogen migration to C_5 the observed stereochemical effect could be explained. A 1,2-mechanism can operate by the transfer of either the C_4 or C_6 hydrogen. The C_4 hydrogen is axial in both the isomers and hence no difference in the behaviour of the isomers is expected. C_6 hydrogen is equatorial in IVA and axial in IVB. In IVA both the C_5 phenyl group and C_6 hydrogen are equatorial and hence the migration of C_6 hydrogen to C_5 may not be favoured. In IVB the equatorial axial orientation of the C_5 phenyl group and C_6-hydrogen are favourable for the hydrogen migration. A plausible mechanism for the loss of $^{\cdot}C_7H_7$ is shown in Scheme 3. The m/e 234 ion fragments mainly by the loss of NH_3.

Further fragmentation of the RDA fragments

Further fragmentation modes of the diene ion (m/e 206) were established (Scheme 1) by comparison with the mass spectra and from metastable defocusing data obtained from an authentic sample of 1,4-diphenyl butadiene. Eventhough there is no evidence to believe that the m/e 206 ion has the structure of 1,4-diphenyl butadiene it appears that there is some close similarity in their fragmentation reactions.

The further fragmentation modes of the dienophile ion (m/e 119) include the loss of $^{\bullet}CH_3$ and $^{\bullet}H_2CN$. Loss of $^{\bullet}H_2CN$ results in the formation of tropylium ion. Metastable transitions were observed for the above processes.

A comparison of the EI spectra of the amino cyclohexenes and the corresponding nitro cyclohexenes[5] shows that RDA reaction is the only common fragmentation mode of these two types of compounds. However, in the nitro compounds the positive charge is carried entirely by the π electron system of the diene whereas in the amino compounds the charge is shared between the diene and the dienophile fragments. There are two competing RDA reactions operating in the amino cyclohexenes. It is well known that compared with the amino group, the nitro group is a poor charge-stabilizing moiety. In the transition state of the RDA reaction the charge distribution could be expected to be different in the nitro and the amino compounds. It may be localised almost entirely in the diene part of the molecule in the nitro compounds while in the amino compounds the charge distribution may be more on the dienophile part.

Loss of $^{\bullet}NO$, $^{\bullet}NO_2$, HNO_2, $^{\bullet}H_2NO_2$, formation of m/e 193 and m/e 167 ions are some of the other major fragmentation pathways operating in the nitro compounds.

Similar decomposition routes are not operating in the spectra of the amino compounds. Only the loss of tropylium radical from the molecular ion competes with RDA reaction in the amino compounds. Thus RDA reaction seems to be more facile in the amino cyclohexenes.

ii) Decompositions in the first field-free region

The IKE technique was used to study the metastable transitions taking place in the first field-free region. The observations were supported by metastable defocusing data. The IKE spectra of all the amino cyclohexenes were recorded by scanning the electric sector voltage. An analysis of the IKE spectra of IVA and IVB (Fig. 4) has shown that only the peak 'F' corresponds to a metastable transition of the molecular ion ($325^{+\cdot} \rightarrow 234^{+} + {}^{\cdot}91$). It was found that there is some significant difference in the intensity of this peak in the spectra of the isomers. It is considerably more intense in IVB than in IVA. This may be due to the fact that the loss of ${}^{\cdot}C_7H_7$ is favoured in the isomer B. Similar steric effects were observed on the formation of m/e 234 ion in the electron impact spectra also. Hence, the stereochemical requirements for the formation of the m/e 234 ion in the first field-free region are similar to that in the ion source. All the other peaks in the IKE spectra of IVA and IVB correspond to the metastable

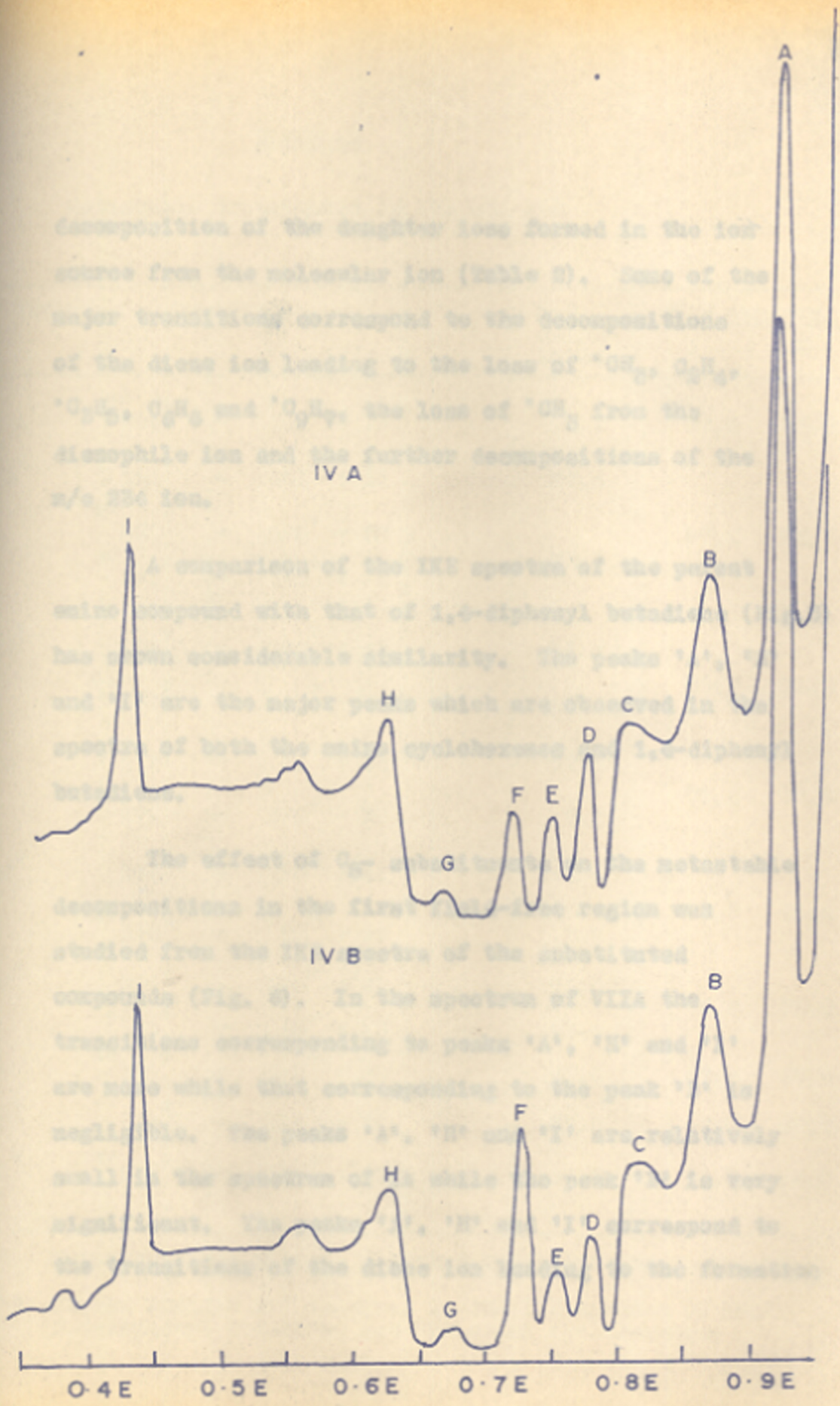


FIG. 4.

decomposition of the daughter ions formed in the ion source from the molecular ion (Table 2). Some of the major transitions correspond to the decompositions of the diene ion leading to the loss of $^{\cdot}CH_3$, C_2H_4, $^{\cdot}C_3H_5$, C_6H_6 and $^{\cdot}C_9H_7$, the loss of $^{\cdot}CH_3$ from the dienophile ion and the further decompositions of the m/e 234 ion.

A comparison of the IKE spectra of the parent amino compound with that of 1,4-diphenyl butadiene (Fig.5) has shown considerable similarity. The peaks 'A', 'H' and 'I' are the major peaks which are observed in the spectra of both the amino cyclohexenes and 1,4-diphenyl butadiene.

The effect of C_5- substituents on the metastable decompositions in the first field-free region was studied from the IKE spectra of the substituted compounds (Fig. 6). In the spectrum of VIIA the transitions corresponding to peaks 'A', 'H' and 'I' are more while that corresponding to the peak 'B' is negligible. The peaks 'A', 'H' and 'I' are relatively small in the spectrum of IA while the peak 'B' is very significant. The peaks 'A', 'H' and 'I' correspond to the transitions of the diene ion leading to the formation

TABLE -2

Metastable transitions in IVA and IVB

Peak	Transition	% E calculated	% E observed A	% E observed B
A*	$^{**}206^{+\cdot} \rightarrow 191^{+} + \cdot 15$	92.7	92.5	92.5
B*	$119^{+\cdot} \rightarrow 104^{+} + \cdot 15$	87.4		
	$^{**}206^{+\cdot} \rightarrow 178^{+} + 28$)	86.4	87.2	86.7
	$^{**}191^{+} \rightarrow 165^{+} + 26$)			
C*	$234^{+} \rightarrow 191^{+} + 43$	81.6	81.2	81.6
	$^{**}206^{+\cdot} \rightarrow 165^{+} + \cdot 41$	80.1		
D	$117^{+} \rightarrow 91^{+} + 26$	77.8	78.2	77.6
	$^{**}178^{+\cdot} \rightarrow 139^{+} + \cdot 39$	78.1		
E*	$234^{+} \rightarrow 178^{+} + 56$	76.0	75.7	75.4
	$^{**}115^{+} \rightarrow 89^{+} + 26$	77.2		
F*	$325^{+\cdot} \rightarrow 234^{+} + \cdot 91$	72.0	72.6	72.6
	$^{**}91^{+} \rightarrow 65^{+} + 26$	71.4		
G	$^{**}191^{+} \rightarrow 128^{+\cdot} + \cdot 63$	67.0	67.4	67.4
H*	$^{**}206^{+\cdot} \rightarrow 128^{+\cdot} + 78$	62.2	63.5	62.7
I*	$^{**}206^{+\cdot} \rightarrow 91^{+} + \cdot 115$	44.2	44.1	44.5

* Metastable transitions observed by defocusing technique.

** Common transitions observed in the IKE spectra of both 1,4-diphenyl butadiene and the amino cyclohexenes.

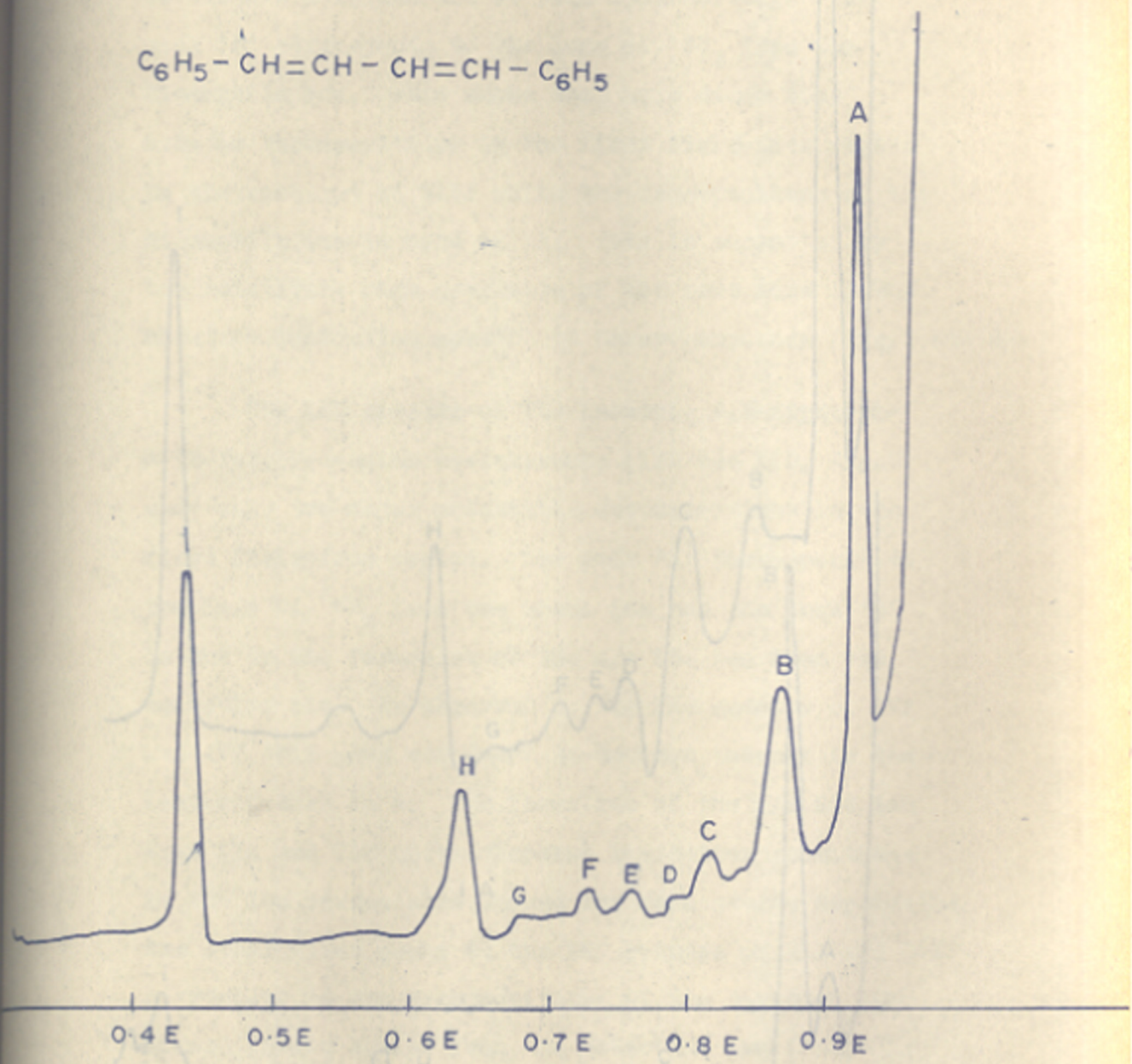


FIG. 5

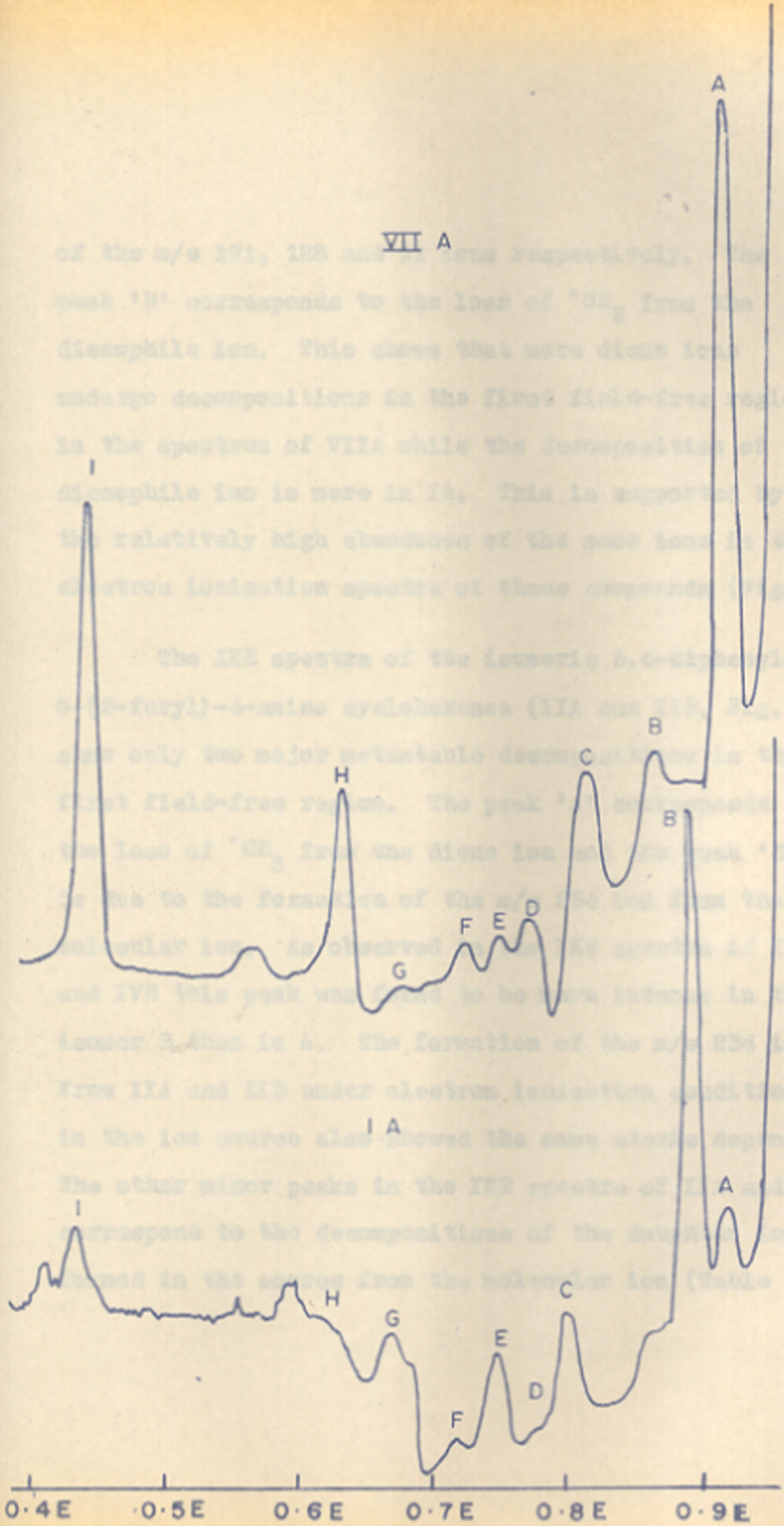


FIG. 6

of the m/e 191, 128 and 91 ions respectively. The peak 'B' corresponds to the loss of $^{\cdot}CH_3$ from the dienophile ion. This shows that more diene ions undergo decompositions in the first field-free region in the spectrum of VIIA while the decomposition of the dienophile ion is more in IA. This is supported by the relatively high abundance of the same ions in the electron ionisation spectra of these compounds (Fig.1 and 3).

The IKE spectra of the isomeric 3,6-diphenyl-5-(2-furyl)-4-amino cyclohexenes (IIA and IIB, Fig.7) show only two major metastable decompositions in the first field-free region. The peak 'A' corresponds to the loss of $^{\cdot}CH_3$ from the diene ion and the peak 'B' is due to the formation of the m/e 234 ion from the molecular ion. As observed in the IKE spectra of IVA and IVB this peak was found to be more intense in the isomer B than in A. The formation of the m/e 234 ion from IIA and IIB under electron ionisation conditions in the ion source also showed the same steric dependence. The other minor peaks in the IKE spectra of IIA and IIB correspond to the decompositions of the daughter ions formed in the source from the molecular ion (Table 3).

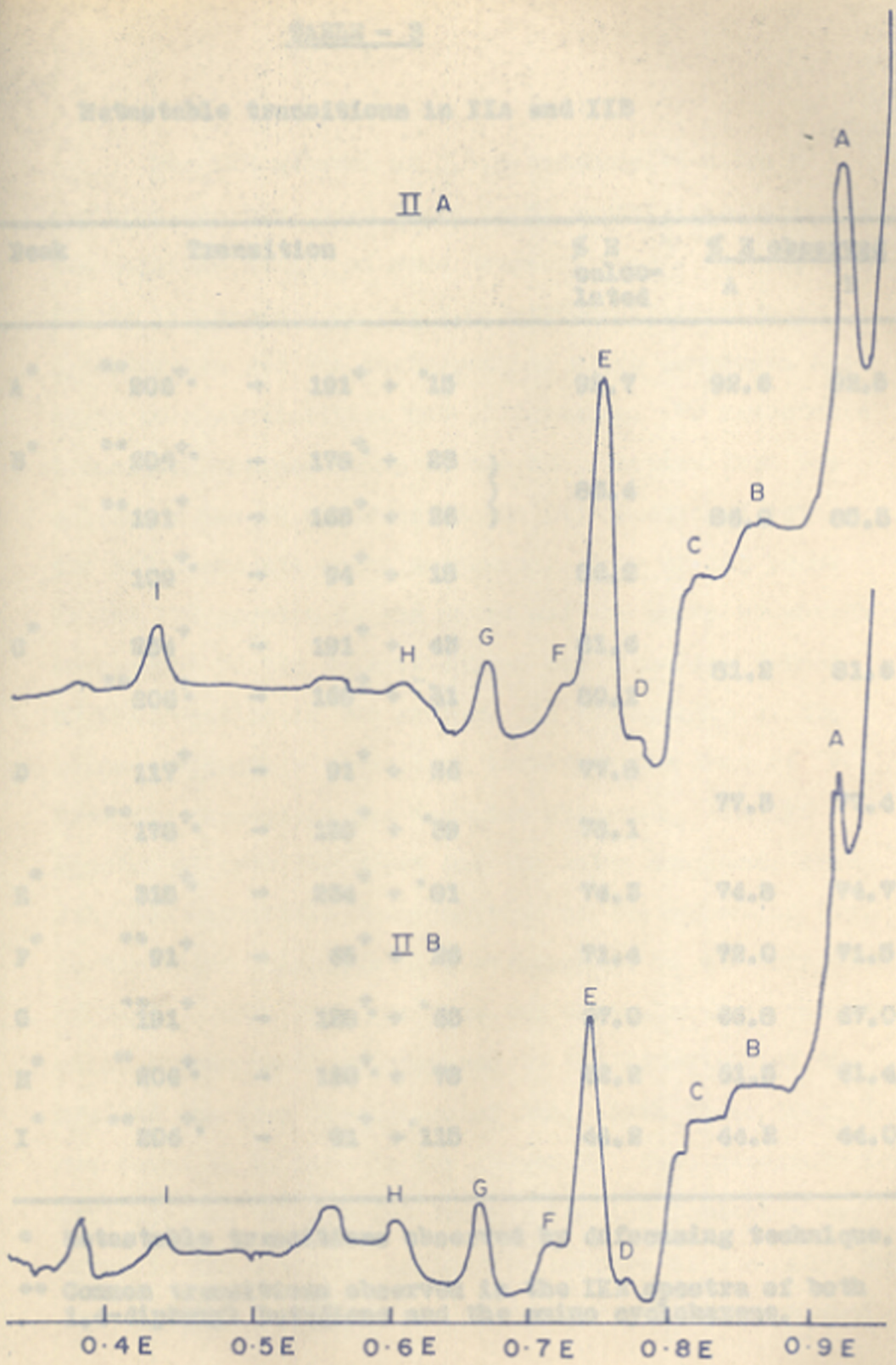


FIG. 7

TABLE - 3

Metastable transitions in IIA and IIB

Peak	Transition			% E calculated	% E observed A	% E observed B
A*	**206$^{+\cdot}$	→	191^{+} + 15	92.7	92.6	92.5
B*	**206$^{+\cdot}$	→	178$^{+\cdot}$ + 28	86.4	86.0	85.5
	**191^{+}	→	165^{+} + 26			
	109$^{+\cdot}$	→	94^{+} + 15	86.2		
C*	234^{+}	→	191^{+} + 43	81.6	81.2	81.6
	**206$^{+\cdot}$	→	165^{+} + 41	80.1		
D	117^{+}	→	91^{+} + 26	77.8	77.5	77.4
	**178$^{+\cdot}$	→	139^{+} + 39	78.1		
E*	315$^{+\cdot}$	→	234^{+} + 81	74.3	74.8	74.7
F*	**91^{+}	→	65^{+} + 26	71.4	72.0	71.5
G	**191^{+}	→	128$^{+\cdot}$ + 63	67.0	66.8	67.0
H*	**206$^{+\cdot}$	→	128$^{+\cdot}$ + 78	62.2	61.5	61.4
I*	**206$^{+\cdot}$	→	91^{+} + 115	44.2	44.2	44.0

* Metastable transitions observed by defocusing technique.

** Common transitions observed in the IKE spectra of both 1,4-diphenyl butadiene and the amino cyclohexene.

The IKE spectra of 3,5,6-triphenyl-4-nitro Δ^1 cyclohexenes have been found to be useful in establishing the multiple origin of some fragment ions[6]. A comparison of the IKE spectra of the 3,5,6-triphenyl-4-amino Δ^1 cyclohexenes and the corresponding nitro compounds has shown some similarities and differences. No metastable transition corresponding to the RDA reaction from the molecular ion is observed in the IKE spectra of both the nitro and the amino compounds. Many of the peaks in the IKE spectra of the nitro and the amino compounds correspond to the transitions of the diene ion formed by RDA reaction in the source. In the spectra of the amino compounds a transition involving the loss of $^{\cdot}CH_3$ from the dienophile ion was also observed. The IKE spectra of both the nitro and the amino compounds show only one metastable decomposition of the molecular ion. In the nitro compounds this corresponds to the formation of $C_{15}H_{13}^{+}$ (m/e 193) ion from the molecular ion. In the amino compounds it corresponds to the formation of the m/e 234 ion from the molecular ion. Both these transitions are found to be more in the isomer B. Same stereochemical influence on the m/e 193 and m/e 234 ion formation was found in the electron ionisation spectra of the nitro and the amino compounds. This shows that the stereochemical

requirements for the formation of these ions are the same in the source and in the first field-free region. Apart from the decompositions of the molecular ion and the diene ion the transitions taking place in the first field-free region in the spectra of the nitro compounds include those corresponding to the formation of the m/e 193 ion from the $M^{+\cdot}$, $[M-NO]^+$ and $[M-NO_2]^+$ ions and also the formation of tropylium ions from the $[M-NO]^+$ and $[M-NO_2]^+$ ions. Transitions other than those involving the molecular ion and the RDA reaction products observed in the IKE spectra of the amino compounds include the formation of the m/e 191 and 178 ions from the m/e 234 ion.

2. Chemical ionisation *

Among the newer ionisation techniques FI and FD spectra are relatively simple. Abundant molecular ions are generally observed. The overall sensitivity is comparatively low and the analysis is subject to considerable operational complexity. CI mass spectrometry is characterised by high sensitivity, operational

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* The author is thankful to Dr. H.M. Fales, N.I.H., Bathesda, USA, for the CI spectra.

simplicity, easy interpretation and a remarkable degree of flexibility by use of different reactant gases. CI mass spectra can be interpreted by assuming that the reactant ions attack specific sites in a molecule and that these isomeric ions, protonated at different sites, decompose to give specific products[7].

The methane CI mass spectra of the 3,5,6-triphenyl-4-amino-Δ^1-cyclohexenes (IVA and IVB) were recorded. The $[M+H]^+$ ions at m/e 326 correspond to the base peaks in the spectra of both IVA and IVB (Figure 8). This is to be expected since the double bond[8], the amino function[9] and the phenyl group[10] are all favourable sites for protonation in the molecule. The $[M+H]^+$ ion is more intense in IVB. This can be explained on the basis of the stereochemistry of the molecule. In IVA all the three phenyl groups are on the same side while in IVB only two phenyl groups are on one side and the third phenyl group and the amino group are on the other side and hence the $[M+H]^+$ ion of IVB is stabler than that of IVA. A small peak corresponding to the $M^{+\cdot}$ ion is also observed in IVB. This can be formed by charge exchange reactions of minor ions in the methane plasma[9]. Abundant $[M + C_2H_5]^+$ and $[M + C_3H_5]^+$ ions are observed in the CI mass spectra of IVA and IVB.

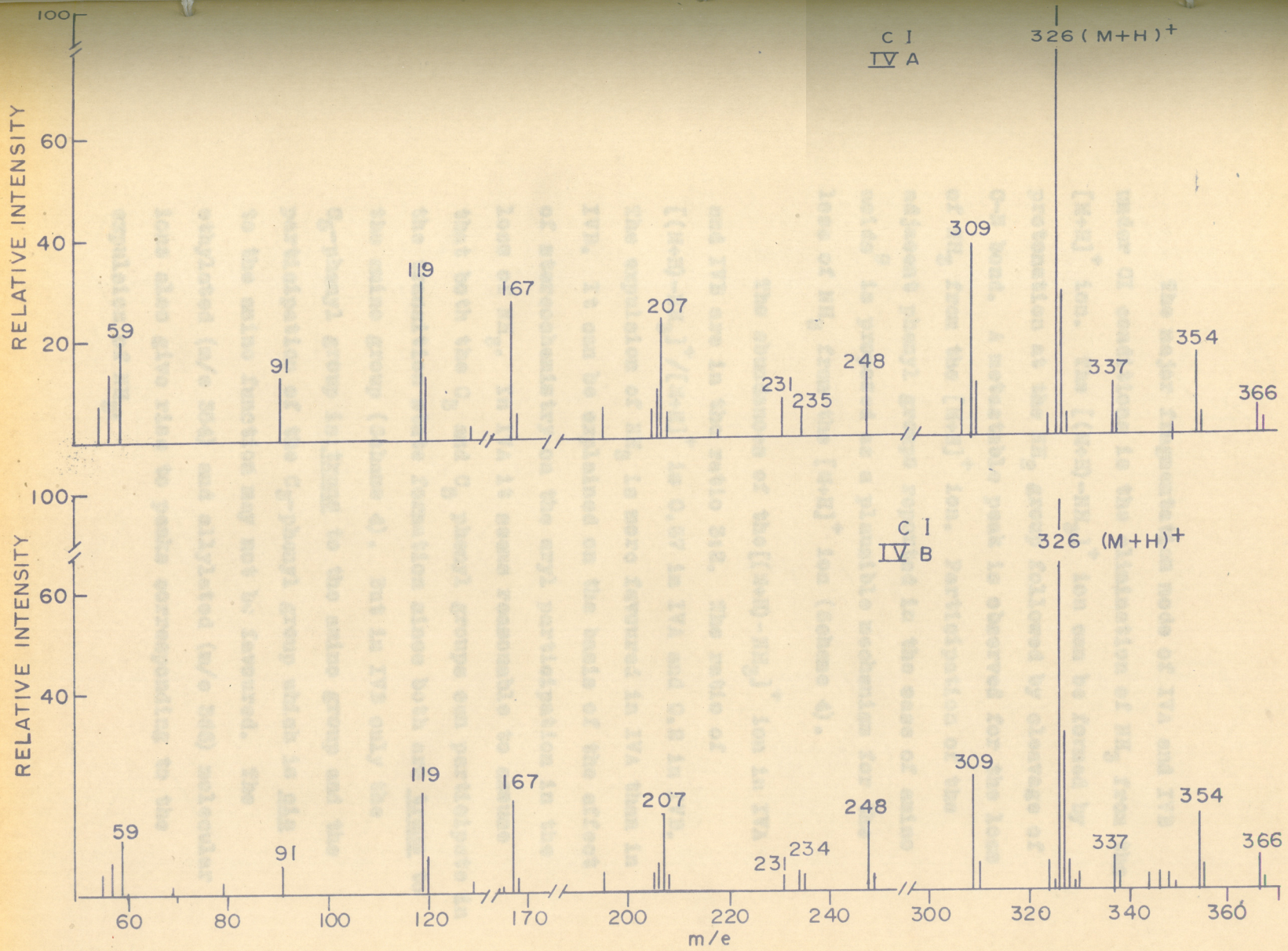
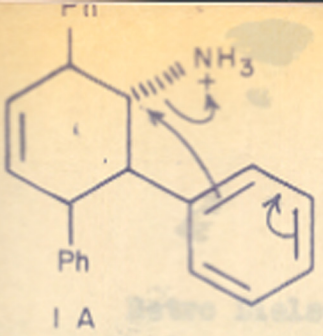

C I
IV A
326 (M+H)+
RELATIVE INTENSITY
100
60
40
20
59
91
119
167
207
231
235
248
309
337
354
366
C I
IV B
326 (M+H)+
RELATIVE INTENSITY
100
60
40
59
91
119
167
207
231
234
248
309
337
354
366
60
80
100
120
170
200
220
240
300
320
340
360
m/e

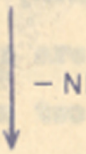
FIG. 8

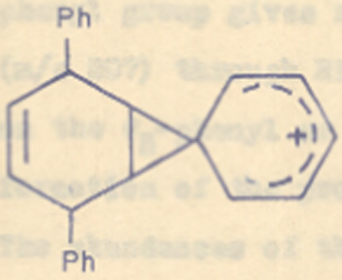
The major fragmentation mode of IVA and IVB under CI conditions is the elimination of NH_3 from the $[M+H]^+$ ion. The $[(M+H)-NH_3]^+$ ion can be formed by protonation at the NH_2 group followed by cleavage of C-N bond. A metastable peak is observed for the loss of NH_3 from the $[M+H]^+$ ion. Participation of the adjacent phenyl groups reported in the case of amino acids[9] is proposed as a plausible mechanism for the loss of NH_3 from the $[M+H]^+$ ion (Scheme 4).

The abundances of the $[(M+H)-NH_3]^+$ ion in IVA and IVB are in the ratio 3:2. The ratio of $[(M+H)-NH_3]^+/[M+H]^+$ is 0.37 in IVA and 0.2 in IVB. The expulsion of NH_3 is more favoured in IVA than in IVB. It can be explained on the basis of the effect of stereochemistry on the aryl participation in the loss of NH_3. In IVA it seems reasonable to assume that both the C_3 and C_5 phenyl groups can participate in the transition state formation since both are trans to the amino group (Scheme 4). But in IVB only the C_5-phenyl group is trans to the amino group and the participation of the C_3-phenyl group which is cis to the amino function may not be favoured. The ethylated (m/e 354) and allylated (m/e 366) molecular ions also give rise to peaks corresponding to the expulsion of NH_3.

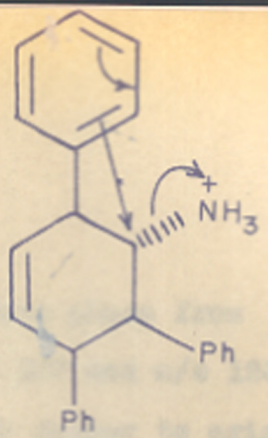


I A

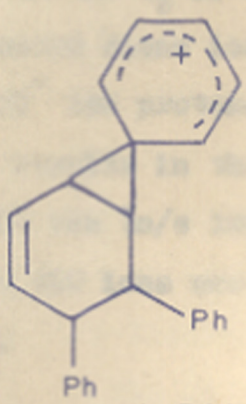




m/e 309

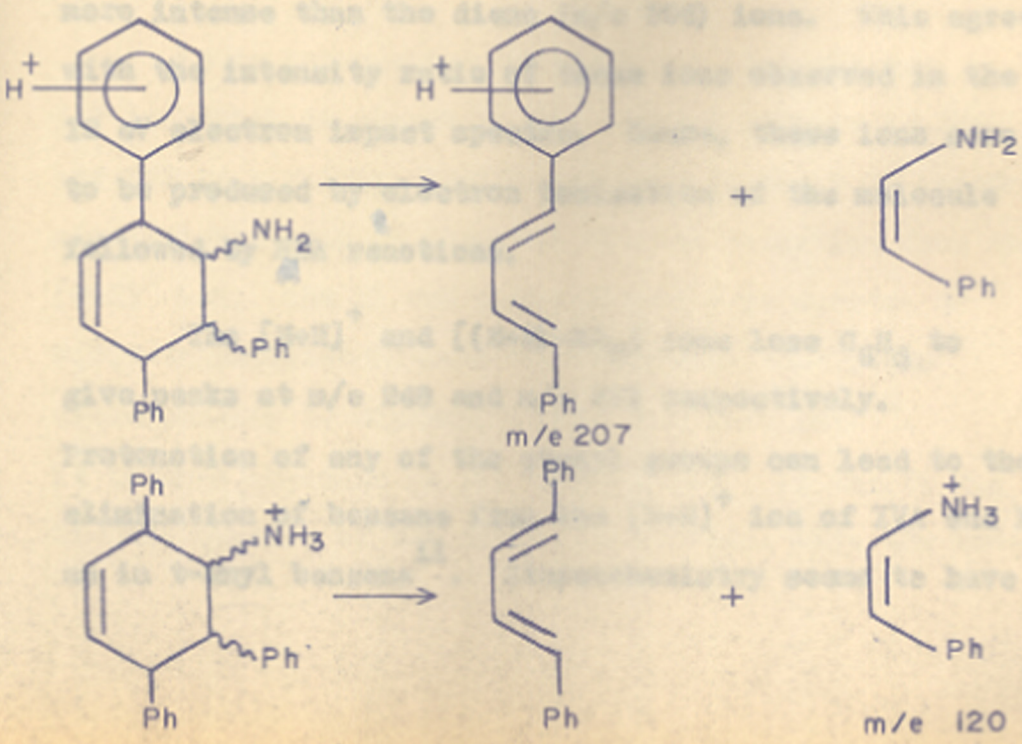


I A



m/e 309

SCHEME 4



SCHEME 5

Retro Diels-Alder reaction takes place from the $(M+H)^+$ ions. Since both the m/e 207 and m/e 120 ions are observed in the spectra they appear to arise from two different $[M+H]^+$ (Scheme 5). The $[M+H]^+$ ion in which protonation has taken place on the C_3 or C_6-phenyl group gives rise to the protonated diene ion (m/e 207) through RDA reaction. $[M+H]^+$ ion protonated on the C_5-phenyl or on the NH_2 group results in the formation of the protonated dienophile ion (m/e 120). The abundances of the m/e 207 and m/e 120 ions are in the ratio 2:1 in both the isomers.

Significant peaks are also observed at m/e 206 and m/e 119 corresponding to the unprotonated diene and dienophile ions. The m/e 119 ion is about three times more intense than the diene (m/e 206) ions. This agrees with the intensity ratio of these ions observed in the 12 eV electron impact spectra. Hence, these ions seem to be produced by electron ionisation of the molecule followed by RDA reactions.

The $[M+H]^+$ and $[(M+H)-NH_3]$ ions lose C_6H_6 to give peaks at m/e 248 and m/e 231 respectively. Protonation of any of the phenyl groups can lead to the elimination of benzene from the $[M+H]^+$ ion of IVA and IVB as in t-amyl benzene[11]. Stereochemistry seems to have

no effect on benzene elimination. Minor peaks due to loss of $^{\cdot}C_7H_7$ from $[M+H]^+$ and $[(M+H)-NH_3]^+$ ions are also observed.

Another route for the decomposition of the amino cyclohexenes under CI conditions is the formation of $C_7H_7^+$ ions. Metastable peak evidence was obtained for its formation from the $[M+H]^+$ ion. This ion is more abundant in IVA than in IVB. In the CI mass spectra of amino acids such as phenyl alanine protonation of the carboxyl or amino function followed by α, β-fission leads to the formation of $C_7H_7^+$ ions[9]. In the CI spectrum of benzyl acetate it has been suggested to come from ring protonated $[M+H]^+$ ions[12]. In the amino cyclohexenes both the mechanisms may be operating.

It is interesting to point out that the m/e 167 ion which is absent in the EI mass spectra of IVA and IVB is a fairly significant peak in their CI spectra. A metastable peak is observed for its formation from the $[M+H]^+$ ion. The EI and isobutane CI mass spectra of 3,5,6-triphenyl-4-nitro-Δ^1-cyclohexenes show peaks corresponding to diphenyl methyl ion (m/e 167)[13]. It is more abundant in IVA than in IVB. In the EI and CI mass spectra of the nitro cyclohexenes also the same

stereochemical effects are observed. Hence, it may be reasonable to assume that the formation of the m/e 167 ion in the CI mass spectra of IVA and IVB may involve 1,2- and 1,4-phenyl migration as in the nitro cyclohexenes.

In the CI mass spectra of 3,5,6-triphenyl-4-nitro-Δ^1-cyclohexenes recorded using isobutane as the reagent gas the $(M+H)^+$ ions are very minor peaks. But in the methane CI mass spectra of the amino cyclohexenes IVA and IVB, the $[M+H]^+$ ions correspond to the base peaks in the spectra. This reflects the greater ability of the amino group to stabilise the positive charge compared to the nitro group. Fairly abundant $[M + t\text{-butyl}]^+$ ions are observed in the CI mass spectra of the nitro compounds. Ethylated and allylated molecular ions are observed in the CI mass spectra of IVA and IVB.

The $[M+H]^+$ ions of the nitro compounds readily lose nitrous acid to give a strong peak at m/e 309. The amino compounds lose NH_3 from the $[M+H]^+$ ion under CI conditions to give rise to a peak at m/e 309. The m/e 309 ion fragments by the loss of a neutral molecule of benzene. This results in the formation of the m/e 231 ion.

The diphenyl methyl ion (m/e 167) is fairly abundant in both the nitro and the amino compounds. It is

one of the predominant processes in the CI mass spectra of the nitro compounds while in the case of the amino compounds it is of lesser importance.

An important difference between the CI mass spectra of the nitro and the amino compounds is the absence of RDA reaction in the nitro compounds. The CI mass spectra of the amino compounds show peaks corresponding to the protonated diene as well as the protonated dienephile ions. However, the loss of neutral molecules which help the $[M+H]^+$ ion to retain its even-electron character in the fragments, compete successfully with RDA reaction.

3. Field desorption *

It is not uncommon for a molecular ion to be undetectable in electron impact spectrum yet observable in field ionisation spectrum. Variation in the method of introduction of the sample to the FI source widens the applicability of this technique[14]. Field desorption mass spectrometry is a modification of the FI technique[15].

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* The author is grateful to Prof. Dr. H.D. Beckey, Institute fur Physikalische Chemie, Bonn, Germany, for the FD spectra.

One of the important aspects of the field desorption technique is the use of a field anode for achieving sufficiently high ion currents. Since the emitter micro-needles present a relatively large surface, sufficient organic solid material can be deposited on the field anode to obtain mass spectra. The organic material which is to be analysed can be deposited by dipping the field anode in a solution of that particular compound. The amount of substance which adheres to the field anode depends on the concentration of the solution. To make the organic molecules mobile so that the substance can diffuse along the shanks of the micro needles on the field anode into the emission region one need supply only the heat of surface diffusion.

In addition to the increase in the relative molecular ion intensities and the decrease in the thermal decomposition of the sample, the FD technique has the advantage of an increase in sensitivity as compared with the FI technique. An adsorbed amount of a sample of 10^{-6} to 10^{-9} g is sufficient for an FD mass spectrum. However, the FD technique is naturally restricted to substances having relatively low volatilities.

It is a general observation that FD mass spectra display enhanced intensities of the $M^{+\cdot}$ or $[M+H]^+$ ions as compared to EI mass spectra. This is the most significant difference between the two ionisation modes. With respect to the high intensities of the $[M+H]^+$ ions obtained FD shares the advantages of CI and complements EI mass spectra where primary ionisation of molecules in the gas phase results in odd-electron molecular ions. There are two main reasons for the high molecular ion intensities. (1) The smaller energy transferred during the ionisation process in the high field[15] and (2) the samples are applied to the emitter from a solution using the emitter dipping technique and hence ionisation and desorption of the adsorbed molecules can be performed with minimal thermal stress[16].

FD technique has been successfully used for determining the molecular weight of submicrogram quantities of unprotected compounds with high polarity, such as sugars[17], amino acids[18], peptides[19] and salts[20]. Protonation of heteroatom (in line with their proton affinity) leads to direct bond ruptures in the sample molecules yielding easily intelligible and valuable

structure information. In other words FD spectra complement EI spectra.

The FD spectra of the amino compounds (IVA and IVB) were examined in order to study their behaviour and to compare with the behaviour under other ionising conditions. A characteristic feature of the FD spectra is the very intense molecular ion peaks. The molecular ion is more abundant in IVB. This is understandable on the basis of the stereochemistry of the molecule. The only fragmentation mode observed in the FD spectra of IVA and IVB is the RDA reaction. Both the diene and the dienophile ions are observed (Table 4).

The FD spectra of the corresponding nitro cyclohexenes have been studied[5]. Intense parent peaks (more in the isomer B) are observed. The other peaks in their FD spectra correspond to the metastable transitions:-

$$M^{+\cdot} \rightarrow [M-HNO]^{+} \qquad (1)$$

$$M^{+\cdot} \rightarrow [M-HNO_2]^{+\cdot} \qquad (2)$$

$$M^{+\cdot} \rightarrow m/e\ 193 \qquad (3)$$

$$M^{+\cdot} \rightarrow m/e\ 206 \qquad (4)$$

TABLE - 4

FD spectral data of IVA and IVB

	IVA	IVB
m/e 325	100	100
m/e 206	35	20
m/e 119	40	9

Transitions (1) and (2) are significant only in the isomer A of the nitro compounds, while the transitions (3) and (4) are insignificant in the isomer A.

Except the RDA reaction all other fragmentation modes of the nitro compounds are absent in the FD spectra of the amino cyclohexenes. Of all the other fragmentation modes RDA reaction appears to have the minimum activation energy.

4. Pyrolysis

Since unimolecular reactions are so prominent in the gas phase decomposition of organic molecules, they have received much theoretical and experimental attention. There is an extensive review of thermal unimolecular reactions of hydrocarbons[21]. A thermal unimolecular reaction is a consequence of an occasional molecule acquiring enough energy to undergo chemical change as a result of collision with other molecules in its environment. In principle, the reactivity of the molecular ion, as represented in a mass spectrum, can be used to directly deduce the reactivity of the same molecule in photolytic or thermal processes[22]. The results of the comparison of mass spectral and thermochemical investigations have often been striking[23-27].

However, a qualitative guide to the relationship between mass spectral reactions and unimolecular thermal processes has yet to be fully developed. In mass spectrometry cation and cation radicals are the final products whereas the corresponding pyrolytic processes yield radicals or neutral molecules[28].

Simple molecular theory[29] and the quasi-equilibrium theory of mass spectra[30] suggest that a molecule and its first excited state should have very similar geometries to the corresponding radical cations.

The energy distributions are substantially different for mass spectral, thermochemical and photochemical systems. Thermal processes tend to proceed from one well on a potential surface to another by the path which maximizes the energy separation between the ground state and first excited state surface. The driving force for ground state and excited state mass spectral reactions is essentially the same as for the neutral analogues. The differences in the time scale for mass spectral reaction, pyrolysis and photolysis are not nearly as significant as it might first appear, because these reactions are generally fast with reference to the experimental time scale. Only major, singly

charged ions have to be considered for predicting thermal or photochemical reactivity.

The qualitative correlation of mass spectral and thermochemical reaction for methyl phenanthrenes was remarkably high[22]. The five major fragment ions in the mass spectra were related to more than 90% of the pyrolysis products in more than two-thirds of the runs.

Cyclohexene decomposes in the neighbourhood of 800°K in a first order reaction, the primary products being ethylene and butadiene[31].

It was concluded that in the absence of any catalyst cyclohexene undergoes retro Diels-Alder reaction readily than dehydrogenation to benzene. In the presence of 5% Pt-alumina catalyst on pyrolysis at 280°C cyclohexene undergoes aromatization giving rise to benzene (100%)[32].

The pyrolytic behaviour of the 3,5,6-triphenyl-4-amino-Δ^1-cyclohexenes was studied for comparison with the behaviour under electron impact. RDA reaction is the major fragmentation mode in the electron impact

spectra both at 70 eV and at lower eVs. Hence, one would expect the thermal behaviour of these compounds to be analogous to the electron-impact induced behaviour and look for the diene formed by RDA reaction[22].

The 3,5,6-triphenyl-4-amino-Δ^1-cyclohexenes were pyrolysed by passing the vapour through a glass tube maintained at 400°C at reduced pressure in an atmosphere of nitrogen. A complex pyrolytic mixture was obtained. The major component of the mixture was found to be 1,4-diphenyl butadiene by GLC and by comparison with an authentic sample (Table 5). Preliminary efforts to separate and identify other pyrolytic products were not very successful. No traces of m-diphenyl benzene, p-diphenyl benzene or 1,2,4-triphenyl benzene could be detected in the pyrolytic mixture by GLC. This clearly shows that aromatization is not favoured in this system and like cyclohexene the triphenyl amino analogues also undergo RDA reaction on pyrolysis. The result agrees with the prediction based on their electron impact behaviour. The isomers (IVA and IVB) behave more or less in the same way.

A comparison of the thermal behaviour of the amino compounds with that of the corresponding nitro compounds[5]

TABLE -5

Percentage composition of the components in the pyrolytic mixture of IVA and IVB (from GLC data).

Component	Percentage	
	IVA	IVB
I	5.7	6.6
II	13.7	18.1
1,4-Diphenyl butadiene	79.0	72.2

would be interesting. The major pyrolytic decomposition product of 3,5,6-triphenyl-4-nitro-Δ^1-cyclohexenes is 1,2,4-triphenyl benzene formed by aromatization of the cyclohexene ring. Traces of 1,4-diphenyl butadiene, m-diphenyl benzene and p-diphenyl benzene are also obtained. The difference in the pyrolytic behaviour of the amino compounds is striking. RDA reaction is the most favoured pathway in the amino compounds whereas aromatization is the preferred reaction in the nitro compounds.

5. Conclusion

A comparison of the major fragmentation modes of the amino cyclohexenes (IVA and IVB) under EI, CI, FD and pyrolytic conditions has shown that RDA is a favoured decomposition mode under these conditions. The base peak in the electron impact spectrum is due to the dienophile ion formed by RDA reaction. No metastable transitions were observed for the RDA reaction and it seems to be unaffected by the stereochemistry of the molecule. These and the significant influence of substituents on the RDA fragmentation abundances suggest that the RDA process in the amino cyclohexene is a stepwise process. The only reaction which competes with RDA reaction under EI condition is the formation of the m/e 234 ion.

But this process gives rise only to minor peaks in the spectra whereas under CI condition the loss of neutral molecule effectively competes with the RDA reaction. $[M+H]^+$ ions give rise to the most intense peaks in the CI spectra and loss of ammonia from $[M+H]^+$ ion is a favoured process. In the FD spectra the molecular ion is the base peak. The only fragment ions observed are due to RDA reaction products. The pyrolytic behaviour of these compounds is similar to that observed under electron impact conditions.

B. Experimental

The samples were introduced through the direct inlet system and vaporised at temperatures ranging from 120°C to 180°C. The beam monitor reading was steady during recording. All the spectra were checked for reproducibility.

A CEC 21-110B mass spectrometer was modified to carry out metastable defocusing work and ion kinetic energy measurements. The metastable defocusing technique described by Elliott and Barber[33] was used.

The output from the beam monitor was connected to a Varian recorder to measure the IKE spectra. The chart speed of the recorder was 2" per minute. The electric sector voltage was scanned from 400 volts to 0 volts by motor driven scan. The constancy of the motor driven scan and the chart speed allowed the measurements of the IKE voltages to an accuracy of $\pm$ 2 volts. These voltages were again checked using a volt meter. Each IKE spectrum was run at least thrice to check the reproducibility.

The samples were introduced through the direct inlet and vaporised at the minimum temperature. The total beam monitor reading was adjusted to 10^{-10} ampere range and before recording the IKE spectra the selector switch was brought to the 10^{-12} ampere range. This allowed sufficient sensitivity to record the IKE spectrum. The main electric sector voltage (400 volts) and the various voltages at which ~~signal~~ peaks in the IKE spectrum appear were measured and the % E values determined. From these % E values found, an attempt was made to characterise the metastable transitions by referring to the "Table of ion energies for metastable transitions"[34].

Satisfactory agreement was found between the calculated and observed $\frac{m}{e}$ values. The metastable transitions indicated by these measurements were checked by metastable defocusing technique.

The 3,6-diphenyl-5-aryl-4-amino-Δ^1-cyclohexenes were prepared by the reduction of the corresponding nitro cyclohexenes according to a reported procedure[35]. The melting points were determined in a sulfuric acid bath and they are uncorrected. The NMR spectra were recorded on a Varian T-60 instrument.

3,5,6-Triphenyl-4-amino-Δ^1-cyclohexene (IVA and IVB)

Isomer A: 18 g of the corresponding isomer of 3,5,6-triphenyl-4-nitro cyclohexene dissolved in 150 ml of glacial acetic acid was added to a stirred suspension of 12 g of metallic tin in 30 ml glacial acetic acid heated on a water bath. After the addition (30 minutes) the stirring and heating was continued for 1.5 hrs more. The reaction mixture was filtered and the filtrate cooled and basified with 10 N sodium hydroxide solution. It was extracted with $CHCl_3$ and washed with distilled water. Constant boiling hydrobromic acid (48%) was added to the concentrated $CHCl_3$ extract with stirring until the

aqueous layer was acidic to litmus. The separated amine hydrobromide was collected in a Buchner funnel, washed with distilled water and dried in a vacuum desiccator (17 g). It was washed with benzene to remove the unreacted nitro compound. The residue was suspended in $CHCl_3$ and the free amine was precipitated by adding ammonia solution. The $CHCl_3$ layer was separated, washed with distilled water and dried over anhydrous sodium sulfate and the solvent was removed. The product (11 g) was chromatographed on 400 g silica gel. Elution with chloroform : methanol (19:1) gave the pure amine. It was crystallised from ether-petroleum ether, colourless crystals, 7.3 g. M.P, 142°. Lit.[35] 140°.

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

Analysis calculated for $C_{24}H_{23}N$: N, 4.3.
Found: N, 4.5%

Isomer B: 14.4 g of the corresponding nitro cyclohexene dissolved in 120 ml glacial acetic acid was reduced with 9.6 g of tin in 24 ml of glacial acetic acid. It was worked up in the same way described for IVA and was crystallised from ether-petroleum ether, colourless

crystals, 6.0 g.

MP, 110°. Lit.[35] 110°.

NMR ($CDCl_3$) τ 2.8 (m, 15H, aromatic protons), 4.0 (s, 2H, H-1 and H-2), 6.3 (m, 3H), 7.4 (t, 1H, H-5), 9.4 (s, 2H, NH_2).

Analysis calculated for $C_{24}H_{23}N$: N, 4.3.

Found: N, 4.11%

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

0.5 g of the corresponding nitro cyclohexene was reduced with 0.4 g of metallic tin in glacial acetic acid. It was worked up as described above. Isomer A was crystallised from petroleum ether, colourless crystals, 0.22 g. MP, 84°.

NMR (CCl_4) τ 2.6-3.7 (m, 14H, aromatic protons), 4.2 (s, 2H, H-1 and H-2), 6.6 (m, 4H), 7.8 (s, 3H, CH_3), 9.2 (s, 2H, NH_2).

Analysis calculated for $C_{25}H_{25}N$: N, 3.2.

Found: N, 3.18%

Isomer B was crystallised from petroleum ether, colourless crystals, 0.25 g. MP, 94°.

NMR (CCl_4) τ 2.95 (m, 14H, aromatic protons), 4.05 (s, 2H, H-1 and H-2), 6.45 (m, 3H), 7.49 (t, 1H, H-5), 7.78 (s, 3H, CH_3), 9.48 (s, 2H, NH_2).

Analysis calculated for $C_{25}H_{25}N$: N, 3.2

Found: N, 3.1%

3,6-Diphenyl-5(p-chlorophenyl)-4-amino-Δ^1-cyclohexenes (VA and VB)

Isomer A: 2 g of the corresponding nitro cyclohexene dissolved in 15 ml of glacial acetic acid was reduced with 1.4 g of tin in 3 ml glacial acetic acid. The usual work up followed by crystallisation from petroleum ether gave 0.8 g of VA, colourless crystals, MP, 92°.

NMR (CCl_4) τ 3.1 (m, 14H, aromatic protons), 4.18 (s, 2H, H-1 and H-2), 6.55 (m, 4H), 9.34 (s, 2H, NH_2).

Analysis calculated for $C_{24}H_{22}ClN$: N, 3.89

Found: N, 3.64%

Isomer B: Reduction of 0.5 g of the corresponding nitro cyclohexene with 0.4 g of tin in 5 ml of glacial acetic acid as described before gave 0.3 g of VB, colourless crystals (crystallised from petroleum ether) MP, 143°.

NMR (CCl_4) τ 2.9 (m, 14H, aromatic protons), 4.05 (s, 2H, H-1 and H-2), 6.4 (m, 3H), 7.47 (t, 1H, H-5), 9.66 (s, 2H, NH_2).

Analysis calculated for $C_{24}H_{22}ClN$: N, 3.89.

Found: N, 3.74%

3,6-Diphenyl-5(2-furyl)-4-amino-Δ^1-cyclohexene (IIA and IIB)

0.3 g of the corresponding nitro cyclohexene was reduced with 0.2 g of tin as described for IVA. The product was crystallised from petroleum ether.

Isomer A: Yield, 0.1 gm. MP, 112.5°.

NMR (CCl_4) τ 2.88-3.23 (m, 11H), 3.94 (q, 1H), 4.15 (s, 2H, H-1 and H-2), 4.44 (d, 1H), 6.45 (m, 4H), 9.2 (s, 2H, NH_2).

Analysis calculated for $C_{22}H_{22}NO$: N, 4.4.

Found: N, 4.54%

Isomer B: Yield, 0.1 g. MP, 119°.

NMR (CCl_4), τ 2.8 (m, 11H), 3.86 (q, 1H), 3.97 (s, 2H, H-1 and H-2), 4.32 (d, 1H), 6.3 (m, 3H), 7.4 (t, 1H, H-5), 9.42 (s, 2H, NH_2).

Analysis calculated for $C_{22}H_{21}NO$: N, 4.4.

Found: N, 4.51%

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

0.5 g of the nitro cyclohexene was reduced with 0.4 g of tin in glacial acetic acid (5 ml) and worked up as described for IVA. It was crystallised from petroleum ether, colourless crystals, 0.25 g. MP, 116°.

NMR (CCl_4) τ 3.15 (m, 14H, aromatic protons),
4.15 (s, 2H, H-1 and H-2), 6.55 (m, 4H),
9.35 (s, 2H, NH_2).
Analysis calculated for $C_{24}H_{22}BrN$: N, 3.5
Found: N, 3.67%

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

Reduction of 0.5 g of the corresponding nitro cyclohexene with 0.4 g tin in 5 ml glacial acetic acid gave 0.26 g of VIIA, colourless crystals. (crystallised from ether-petroleum ether), MP, 106°.
NMR (CCl_4) τ 2.95 (m, 14H, aromatic protons),
4.1 (s, 2H, H-1 and H-2), 6.55 (m, 4H), 9.35 (s, 2H, NH_2).
Analysis calculated for $C_{25}H_{22}N_2$: N, 8.0.
Found: N, 7.91%

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

0.5 g of the corresponding nitro cyclohexene was reduced with 0.4 g of tin in 5 ml glacial acetic acid. The usual work up followed by crystallisation from petroleum ether gave 0.3 g of IA as colourless crystals. MP, 118°.
NMR (CCl_4) τ 2.9 (m, 10H, aromatic protons),
3.5 (s, 4H, 5-p-anisyl), 4.1 (s, 2H, H-1 and H-2),
6.28 (s, 3H, OCH_3), 6.55 (m, 4H), 9.38 (s, 2H, NH_2)
Analysis calculated for $C_{25}H_{25}NO$: N, 3.94.
Found: N, 4.08%

Pyrolysis

The pyrolysis of the amino cyclohexenes was done in an apparatus as shown in Fig.9. The apparatus was assembled and 0.5 g of 3,5,6-triphenyl-4-amino-Δ^1-cyclohexene was taken in a glass sample boat and introduced into the glass tube. Dry nitrogen gas was passed through the apparatus and it was evacuated by connecting it to a vacuum pump. The nitrogen flow was adjusted so that the pressure inside the apparatus was 5 mm.

The furnace was switched on and when the temperature (measured by the thermocouple) reached 400°C the sample was heated by means of the heating tape in such a way that the sample was vaporised completely in half-an-hour and passed through the pyrolysis zone. The products were collected in liquid nitrogen traps. The pyrolysis was stopped after half-an-hour. The liquid nitrogen traps were allowed to come to room temperature and the products taken up in chloroform. It weighed 0.45 g. It was found to be a complex mixture by TLC (silica gel, 1:1 benzene-petroleum ether). The mixture was analysed by GLC (SE-30, 20%, 245°C) and found to contain three major

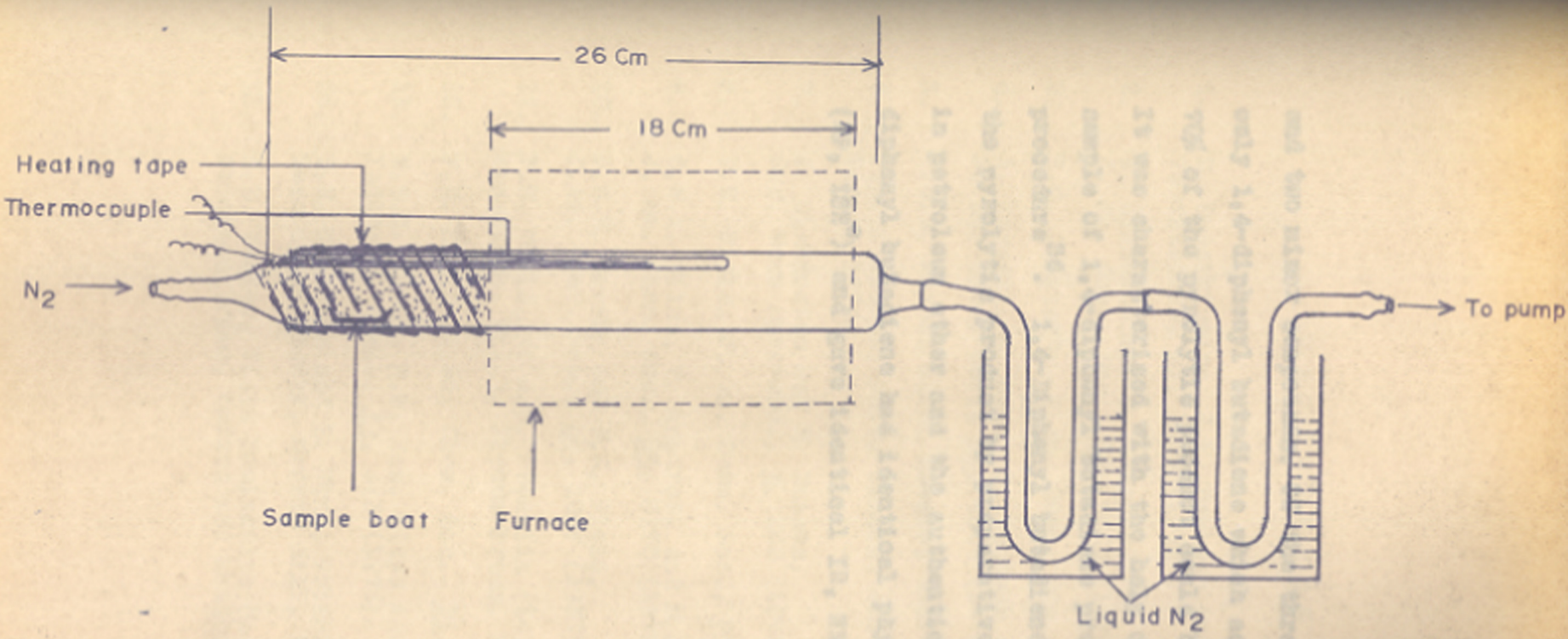
26 Cm
18 Cm
Heating tape
Thermocouple
N_2
To pump
Sample boat
Furnace
Liquid N_2

FIG. 9

and two minor compounds. Of the three major components only 1,4-diphenyl butadiene which accounted for nearly 70% of the pyrolytic product could be identified. It was characterised with the help of an authentic sample of 1,4-diphenyl butadiene prepared by a reported procedure[36]. 1,4-Diphenyl butadiene isolated from the pyrolytic product by preparative TLC on silica gel in petroleum ether and the authentic sample of 1,4-diphenyl butadiene had identical physical characteristics (MP, 152°) and gave identical IR, NMR and mass spectra.

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CHAPTER - IV

STUDIES ON SUBSTITUENT EFFECTS ON MOLECULAR AND FRAGMENT IONS

A. Present Work

It is well known[1] that a substituent can alter the fragmentation of an organic compound by changing (i) the energy distribution p(E) of the molecular ion, (ii) the activation energy (AE) of the possible fragmentation paths, (iii) the rate constants k(E) of the competing unimolecular reactions leading to the fragment ions, and (iv) the successive decompositions of the primary fragment ions.

These effects are reflected in the abundances of molecular and daughter ions. Many attempts have been made to correlate fragment ion abundances[2,3], metastable ion abundances[4,5], ionisation potential[6-10], appearance potential[3,11,12] and activation energy[3,11,13-16] with substituent constants. A substituent can either decrease or increase the ionisation potential of a molecule with respect to the unsubstituted molecule[6].

It can alter the fraction of the decomposing and the non-decomposing molecular ions. These factors will determine the relative abundances of the molecular ions in the spectrum of a substituted compound with respect to the unsubstituted compound. In the present work this aspect has been studied with the help of many substituted acetophenone ketals.

One of the important structural informations provided by the mass spectrum of a compound is the molecular weight. Since it is well known that a substituent can alter the ionisation potential of the molecule one would expect that the introduction of a substituent which lowers the ionisation potential of the molecule should result in the formation of relatively more abundant ions than the unsubstituted compound or a compound which contains a substituent that increases the ionisation potential of the molecule. The spectra of acetophenone ketal run at 18 eV and 70 eV do not show the molecular ion peak. The present work was undertaken to study the effect of both electron donating and electron withdrawing substituents on the relative abundances of the molecular ions. As expected, it was observed that an electron donating substituent enhances the molecular ion abundance.

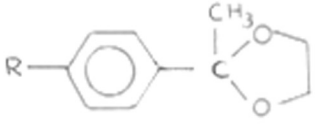
In competing simple cleavage processes it has been reported that the ratio of the relative abundances of the daughter ions represents the ratio of the rate constants for two reactions[17-20]. This approach has been extended to study the effect of substituents on the two competing reactions, viz., the retro Diels-Alder reaction and the loss of $^{\cdot}NO_2$ in 3,6-diphenyl-5-aryl-4-nitro-Δ^1-cyclohexenes. The logarithm of the ratio of the abundances of the diene and the $[M-NO_2]^+$ ions was plotted against substituent constants. Correlations were obtained both at 70 eV and at low eV for Hammett's σ and Brown's σ^+ constants.

This approach has also been extended to study the effect of substituents on two competing fragmentation modes which operate in 3,6-diphenyl-5-aryl-4-amino-Δ^1-cyclohexenes. The logarithm of the ratio $[diene]^{+\cdot}/[dienophile]^{+\cdot}$ was plotted against the ionising voltage and also Brown's σ^+ constants. Considerable energy and substituent effects were observed. The results support the assumption that in competing RDA fragmentation modes the ratio of the relative abundances of the diene and the dienophile ions indicate the ratio of the relative rate constants.

1. Substituent effects on molecular ion abundance

An electron donating substituent (e.g., OMe, OH) has been known to decrease the ionisation potential and an electron withdrawing substituent (e.g., CN, NO_2) increases the ionisation potential relative to that of the unsubstituted compound.[6] The halogens have a sort of marginal effect of either slightly decreasing or increasing the ionisation potential of the molecule. These effects have been rationalised on the basis of electrostatic polarization concept and dipole moment[8]. It has been shown by Howe and Williams[21] that in the mass spectra where the molecular ion abundance is negligible owing to very rapid unimolecular decay of all parent ions, the molecular weight may be determined for a suitable derivative having a very low ionisation potential. The mass spectra of ethylene acetals containing remote phenyl or p-anisyl substituents were examined. The results showed that the p-methoxy group increases the molecular ion abundance as expected. Correlations of log $[M]^{+\cdot}$ expressed as percentage of total ionisation with substituent constants have been reported for acetophenones[3]. It was shown that electron releasing substituents which have a pronounced effect in lowering the molecular ionisation potential lead

to an increased molecular ion abundance while electron withdrawing substituents give rise to a decreased molecular ion abundance. The present work was undertaken in order to further substantiate these facts. The following acetophenone ethylene ketals were prepared. These compounds were selected because the mass spectrum of the parent acetophenone ethylene ketal shows only an insignificant peak corresponding to the molecular ion. The spectra were recorded at 18 eV (Figure 1 and 2).



Compound	I	II	III	IV	V	VI	VII	VIII
R	OCH_3	OH	Br	Cl	F	H	CN	NO_2

The major fragmentation modes operating in these ketals are (1) loss of $^{\bullet}CH_3$ and $^{\bullet}CH_3O$ (2) formation of $C_7H_5O^+$, $C_4H_7O_2^+$ and $C_6H_5^+$ ions (Scheme 1).

The genesis of these fragment ions has been established from high resolution and metastable data. In the spectra of all the compounds the base peak corresponds to the $[M-CH_3]^+$ ion.

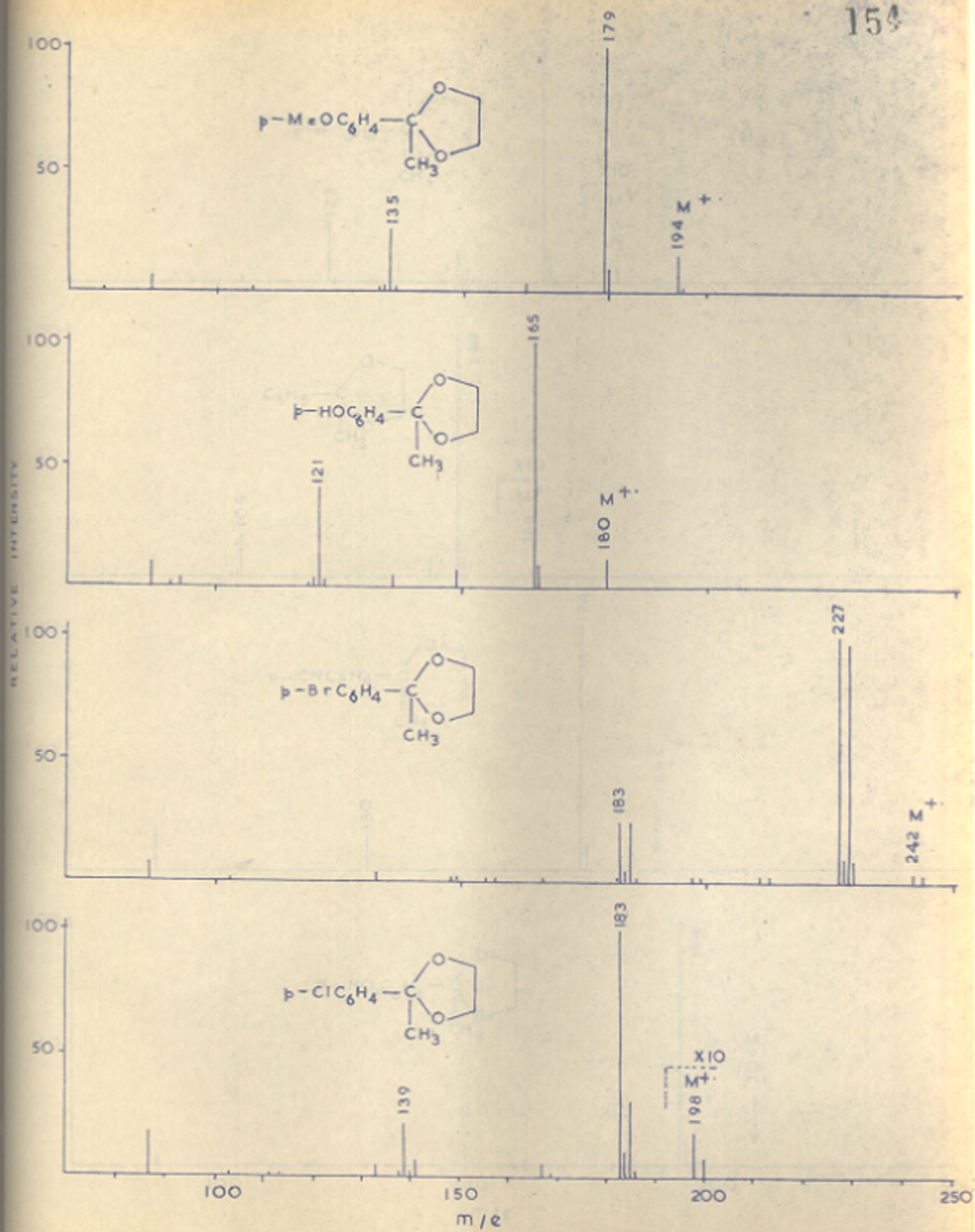

100
50
p-MeOC6H4-C
CH3
179
135
194 M+
100
50
p-HOC6H4-C
CH3
165
121
180 M+
100
50
p-BrC6H4-C
CH3
227
183
242 M+
100
50
p-ClC6H4-C
CH3
183
X10
M+
198
139
100
150
200
250
m/e
RELATIVE INTENSITY

FIG - 1

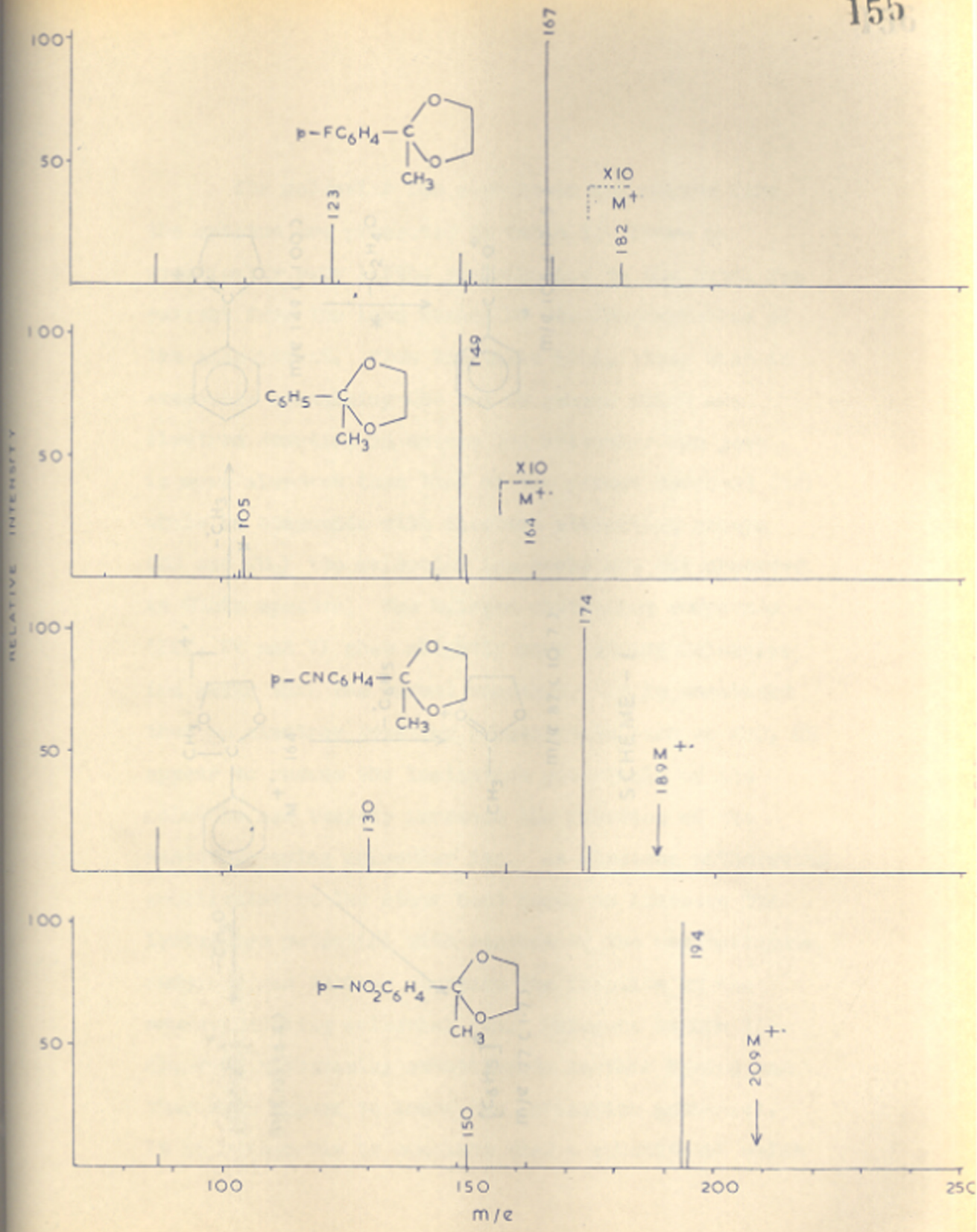
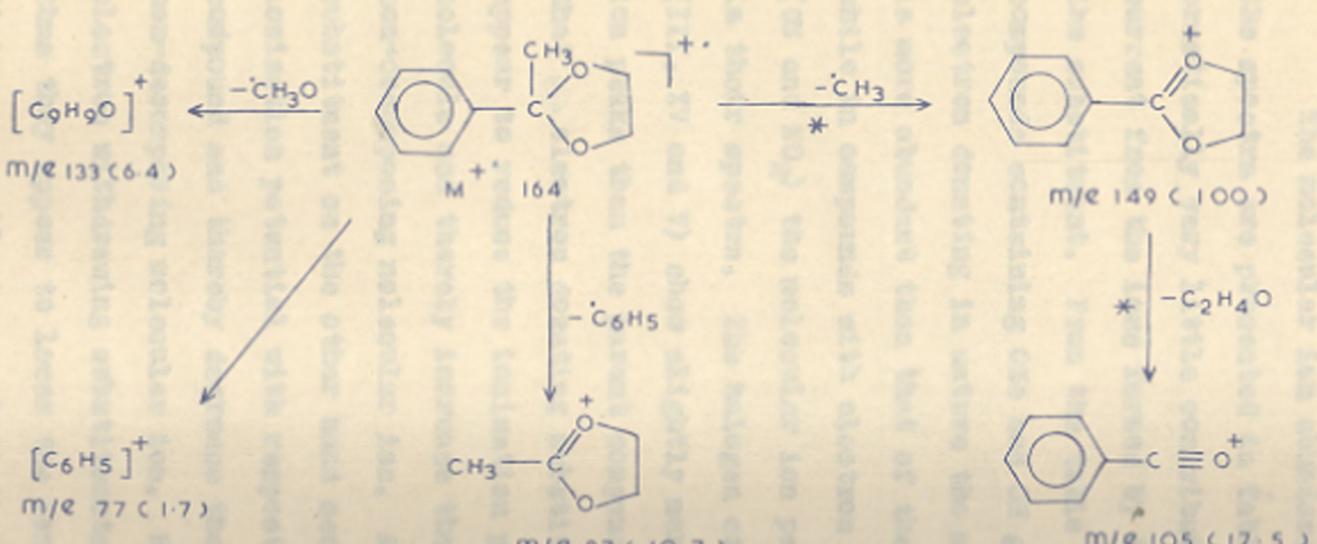

100
50
p-FC6H4-C
CH3
167
123
X10
M+
182
100
50
C6H5-C
CH3
149
105
X10
M+
164
100
50
p-CNC6H4-C
CH3
174
130
189 M+
100
50
p-NO2C6H4-C
CH3
194
150
209 M+
100
150
200
250
m/e
RELATIVE INTENSITY

FIG - 2


[C9H9O]+
m/e 133 (6·4)
-·CH3O
CH3
C
O
O
+·
M+· 164
-·CH3
*
m/e 149 (100)
-·C6H5
*
-C2H4O
[C6H5]+
m/e 77 (1·7)
CH3
C
O
O
+
m/e 87 (10·7)
C ≡ O+
m/e 105 (17·5)

SCHEME – I

The molecular ion abundances calculated from the spectra are presented in Table 1. There is practically very little contribution to the total ion current from the ions formed by the fragmentation of the substituent. From the table it is clear that in compounds containing OMe and OH groups which are electron donating in nature the molecular ion peak is more abundant than that of the parent compound (VI) while in compounds with electron attracting groups (CN and NO_2) the molecular ion peaks are not observed in their spectra. The halogen containing compounds (III, IV and V) show slightly more intense molecular ion peaks than the parent compound. It is concluded that the electron donating substituents such as MeO, OH appear to reduce the ionisation potentials of the molecule and thereby increase the fraction of the non-decomposing molecular ion. An electron withdrawing substituent on the other hand seems to increase the ionisation potential with respect to the unsubstituted compound and thereby decrease the fraction of the non-decomposing molecular ion. Halogens behave like electron withdrawing substituents in this system and thus they appear to lower the ionisation potential. It is reasonable to conclude that a substituent which

TABLE - 1

Molecular ion abundances in substituted acetophenone ketals

Compound (R)	Relative abundance of $M^{+\cdot}$ as % of base peak	Relative abundance of $M^{+\cdot}$ as % of total ionisation (% Σ_{40})
I (OMe)	15.8	8.3
II (OH)	12.4	6.1
III (Br)	8.3	2.7
IV (Cl)	2.7	1.3
V (F)	0.9	0.6
VI (H)	0.3	0.2
VII (CN)	-	-
VIII (NO_2)	-	-

lowers the ionisation potential increases the molecular ion abundance.

An attempt was made to study the substituent effects on the loss of $^{\bullet}CH_3$ and $^{\bullet}RC_6H_4$ from the molecular ion. The log Z/Z_o ($Z = A_R^+ / M_R^+$) were calculated from the 18 eV spectra of these ketals for the loss of $^{\bullet}CH_3$ and $^{\bullet}RC_6H_4$ from the $M^{+\bullet}$ and plotted against substituent constants. No correlation was observed with either Hammett σ constants[22] or Brown's σ^+ constants[23].

Application of the modified treatment of Chin and Harrison[3] leads one to look for linear correlation for $\frac{[A]^+}{[M_o]^+(1-f)}$ vs σ or σ^+. Plots of this type were obtained for the loss of $^{\bullet}CH_3$ and $^{\bullet}RC_6H_4$ from the M^+ (Figure 3). For the two simple cleavage processes (loss of $^{\bullet}CH_3$ and $^{\bullet}RC_6H_4$) the slopes of the correlations have the same sign. The slopes of these plots are expected to have opposite signs[24] for a major pair of competing reactions.

2. <u>Substituent effects on competing fragmentation modes</u>

Substituent effects on ion abundances of simple cleavage and rearrangement processes of unimolecular ion decompositions have been studied by many workers.

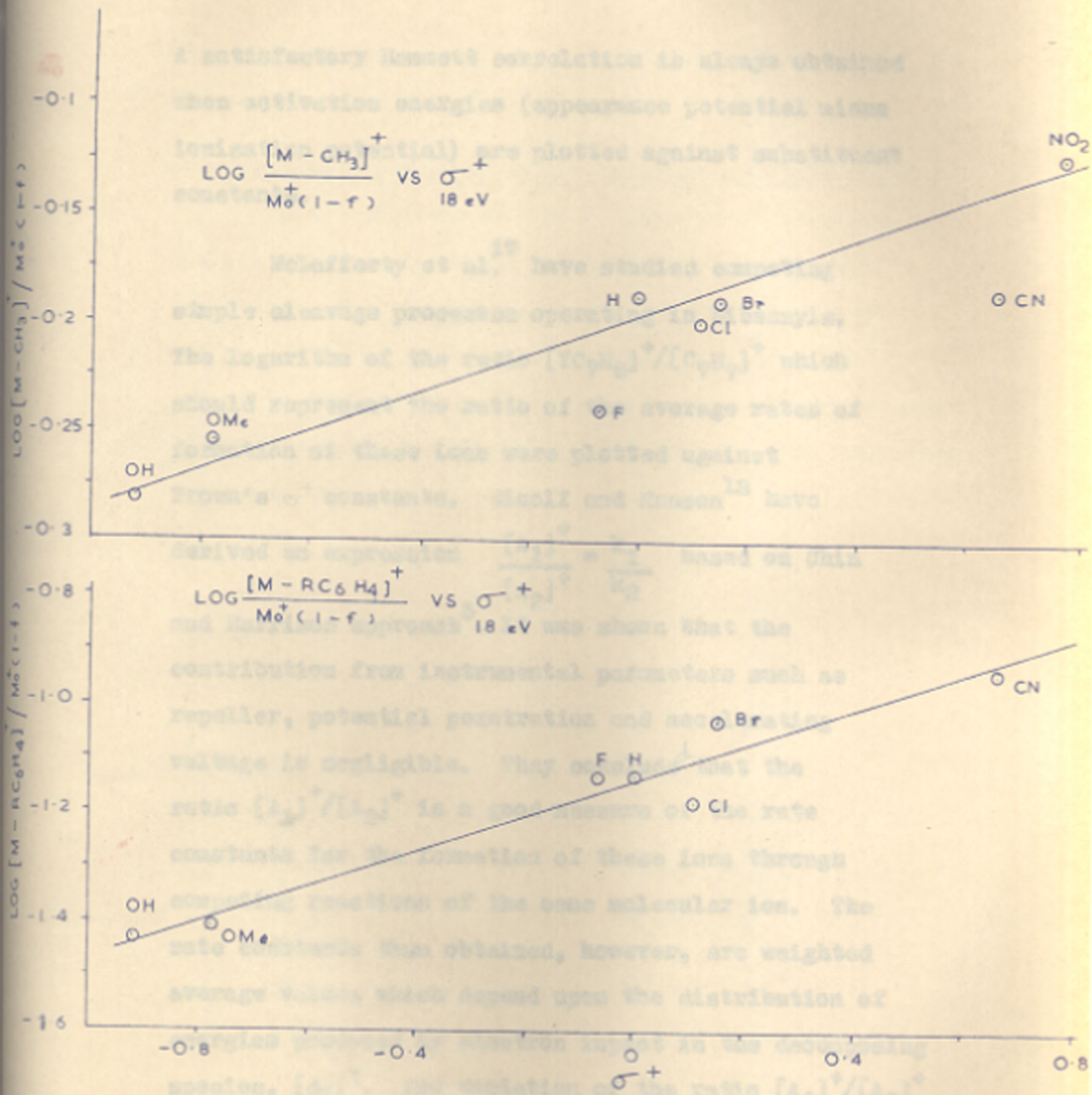

LOG [M − CH3]+ / Mo+(1−f)
LOG [M − CH3]+ / Mo+(1−f)
VS σ+ 18 eV
-0·1
-0·15
-0·2
-0·25
-0·3
NO2
H
Br
Cl
CN
F
OMe
OH
LOG [M − RC6H4]+ / Mo+(1−f)
LOG [M − RC6H4]+ / Mo+(1−f)
VS σ+ 18 eV
-0·8
-1·0
-1·2
-1·4
-1·6
CN
Br
F
H
Cl
OH
OMe
-0·8
-0·4
0·4
0·8
σ+

FIG. - 3

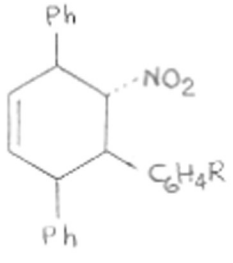
A satisfactory Hammett correlation is always obtained when activation energies (appearance potential minus ionisation potential) are plotted against substituent constants.

McLafferty et al.[17] have studied competing simple cleavage processes operating in bibenzyls. The logarithm of the ratio $[YC_7H_6]^+/[C_7H_7]^+$ which should represent the ratio of the average rates of formation of these ions were plotted against Brown's σ^+ constants. Sinolf and Munson[18] have derived an expression $\frac{[A_1]^+}{[A_2]^+} = \frac{k_1}{k_2}$ based on Chin and Harrison approach[3]. It was shown that the contribution from instrumental parameters such as repeller, potential penetration and accelerating voltage is negligible. They concluded that the ratio $[A_1]^+/[A_2]^+$ is a good measure of the rate constants for the formation of these ions through competing reactions of the same molecular ion. The rate constants thus obtained, however, are weighted average values which depend upon the distribution of energies produced by electron impact in the decomposing species, $[d_M]^+$. Any variation of the ratio $[A_1]^+/[A_2]^+$

with the ionising energy or substituent results from the variation of the rate constant.

i) Substituent effects on RDA reaction and loss of $^{\cdot}NO_2$

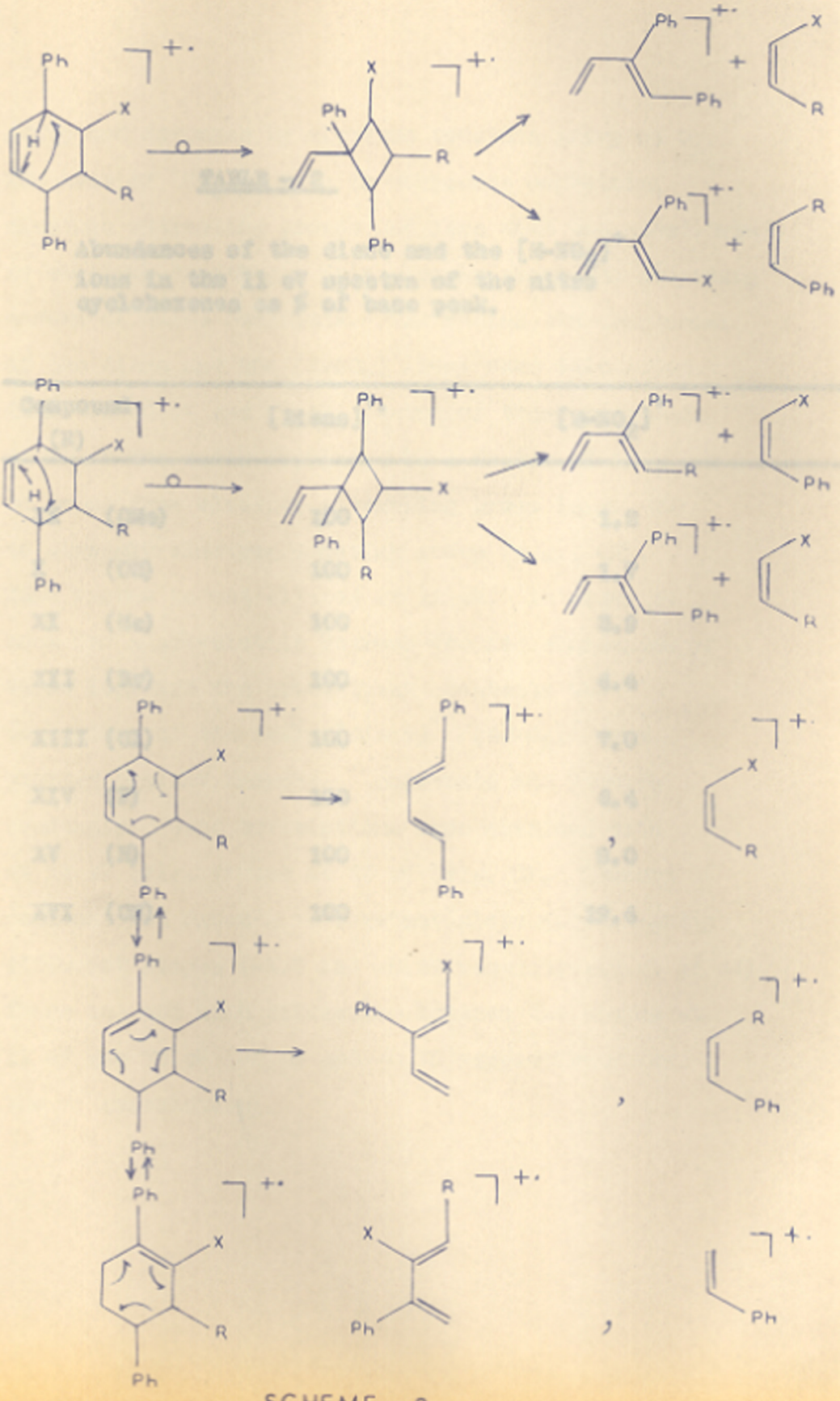
In 3,6-diphenyl-5-aryl-4-nitro-Δ^1-cyclohexenes the RDA reaction leads to the formation of only the diene ion. The dienophile ion is absent. At low eV the loss of $^{\cdot}NO_2$ from the molecular ion is a major competing fragmentation mode. The further decompositions of these primary fragments are negligible. The following compounds were examined.



	R		R
IX	p-CH_3O	XIII	p-Cl
X	p-HO	XIV	p-F
XI	p-CH_3	XV	H
XII	p-Br	XVI	p-CN

In order to study the substituent effects on the competing processes it has to be ascertained that the diene ion arises only by RDA decomposition. It has been reported that in tetralin a hydrogen transfer process can give rise to a product similar to that formed by the RDA decomposition[25,26]. Double bond migration similar to that in cyclohexenes[27] is also possible. If these processes operate in the nitro cyclohexenes more than one substituted diene ions will be observed in the spectra (Scheme 2). Even in the 70 eV spectra these additional peaks were insignificant. The spectra recorded at different temperatures were reproducible and showed very little difference in the relative intensities of the diene and the $[M-NO_2]^+$ ions. This shows that there is no significant contribution from pyrolysis towards the diene and the $[M-NO_2]^+$ ion formation. Hence, it is reasonable to assume that the diene and the $[M-NO_2]^+$ ions observed in the spectra of the nitro compounds are formed entirely by electron impact induced reactions.

The abundances of the diene and the $[M-NO_2]^+$ ions in the 11 eV spectra of these nitro cyclohexenes are given in Table 2. From the table it is evident that RDA reaction is inhibited by electron attracting



SCHEME - 2

TABLE - 2

Abundances of the diene and the $[M-NO_2]^+$ ions in the 11 eV spectra of the nitro cyclohexenes as % of base peak.

Compound (R)	$[Diene]^{+\cdot}$	$[M-NO_2]^+$
IX (OMe)	100	1.2
X (OH)	100	1.7
XI (Me)	100	3.9
XII (Br)	100	4.4
XIII (Cl)	100	7.0
XIV (F)	100	6.4
XV (H)	100	8.0
XVI (CN)	100	19.4

group and favoured by electron donating group on C_5. The loss of $^{\cdot}NO_2$ is more in compounds containing electron attracting groups and less when the substituent is electron donating. This clearly shows the competing nature of these reactions. The ratios of the abundances of the diene and the $[M-NO_2]^+$ ions were calculated from the 70 eV and 11 eV spectra of these compounds. At 70 eV the ratio increases by a factor of 16 on going from electron attracting group (e.g., CN) to strongly electron donating group (e.g., OH). This factor is not altered at 11 eV. In order to look for a correlation between the ion abundances of these ions and the substituent constants the logarithms of the ratio $[diene]^{+\cdot}/[M-NO_2]^+$ were plotted against Hammett σ constants and Brown's σ^+ constants. Good correlations were obtained both at 11 eV (Fig. 4) and at 70 eV (Fig. 5). Hammett σ constant and Brown's σ^+ constant plots gave slightly different slopes (-1.0 and -0.69 respectively at 11 eV). There was not much difference between the slopes at 11 eV and 70 eV (-0.69 and -0.75 respectively for the σ^+ correlation).

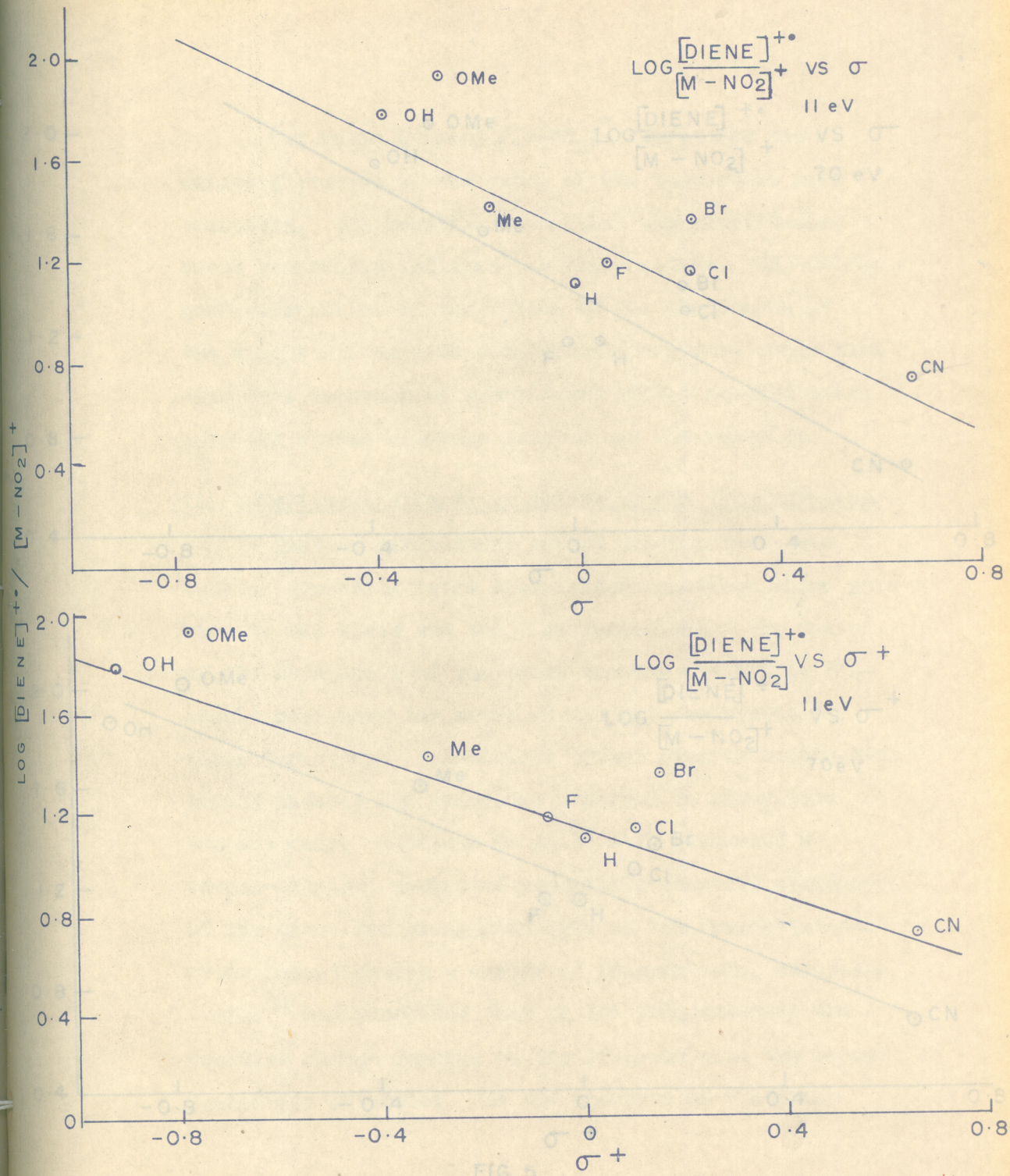

LOG [DIENE]+• / [M − NO2]+
2·0
1·6
1·2
0·8
0·4
OMe
OH
Me
Br
F
Cl
H
CN
−0·8
−0·4
0
0·4
0·8
σ
LOG [DIENE]+• / [M − NO2]+ VS σ
11 eV
LOG [DIENE]+• / [M − NO2]+
2·0
1·6
1·2
0·8
0·4
0
OMe
OH
Me
Br
F
Cl
H
CN
−0·8
−0·4
0
0·4
0·8
σ+
LOG [DIENE]+• / [M − NO2] VS σ+
11 eV

FIG. 4

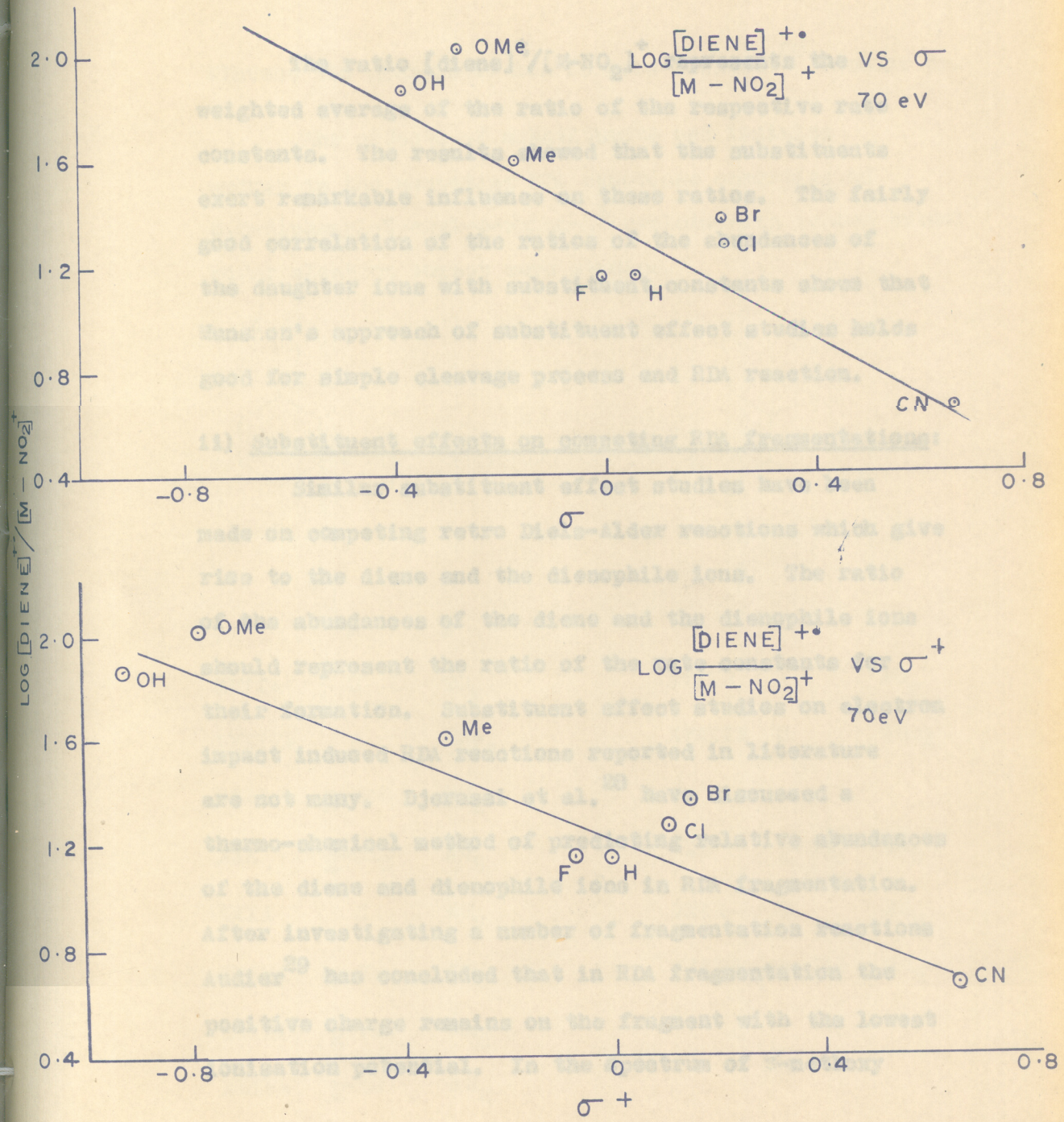

LOG [DIENE]+• / [M − NO2]+
2·0
1·6
1·2
0·8
0·4
−0·8
−0·4
0
0·4
0·8
σ
OMe
OH
Me
Br
Cl
F
H
CN
LOG [DIENE]+• / [M − NO2]+ VS σ
70 eV
LOG [DIENE]+• / [M − NO2]+
2·0
1·6
1·2
0·8
0·4
−0·8
−0·4
0
0·4
0·8
σ+
OMe
OH
Me
Br
Cl
F
H
CN
LOG [DIENE]+• / [M − NO2]+ VS σ+
70eV

FIG.5

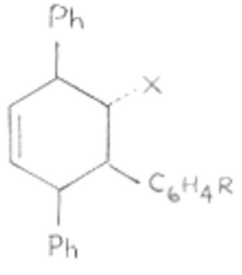
The ratio $[diene]^{+\cdot}/[M-NO_2]^{+}$ represents the weighted average of the ratio of the respective rate constants. The results showed that the substituents exert remarkable influence on these ratios. The fairly good correlation of the ratios of the abundances of the daughter ions with substituent constants shows that Hunsdiecker's approach of substituent effect studies holds good for simple cleavage process and RDA reaction.

ii) Substituent effects on competing RDA fragmentations:

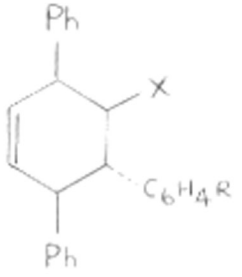
Similar substituent effect studies have been made on competing retro Diels-Alder reactions which give rise to the diene and the dienophile ions. The ratio of the abundances of the diene and the dienophile ions should represent the ratio of the rate constants for their formation. Substituent effect studies on electron impact induced RDA reactions reported in literature are not many. Djerassi et al.[28] have discussed a thermo-chemical method of predicting relative abundances of the diene and dienophile ions in RDA fragmentation. After investigating a number of fragmentation reactions Audier[29] has concluded that in RDA fragmentation the positive charge remains on the fragment with the lowest ionisation potential. In the spectrum of 3'-methoxy

flavane the dienophile ion is more abundant[30] (Scheme 3).

The effects of substituents and ionising energy on the competing RDA reactions operating in 3,6-diphenyl-5-aryl-4-amino-Δ^1-cyclohexenes (shown below) under electron impact were studied.



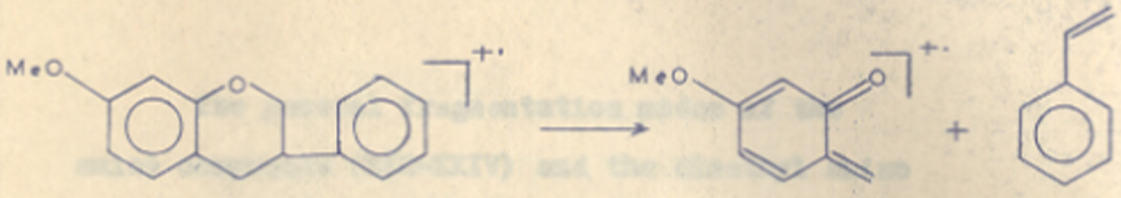
A



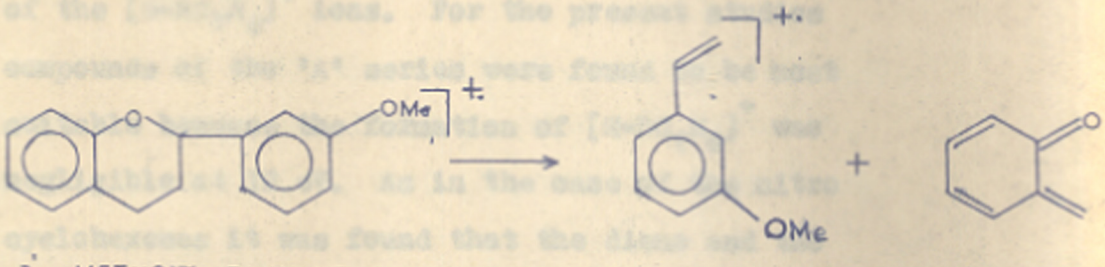
B

	R	X
XVIIA	H	NO_2
XVIIIA	H	NMe_2
XIXA	p-MeO	NH_2
XXA	p-CH_3	NH_2
XXIA	H	NH_2
XXIIA	p-Cl	NH_2
XXIIIA	p-Br	NH_2
XXIVA	p-CN	NH_2

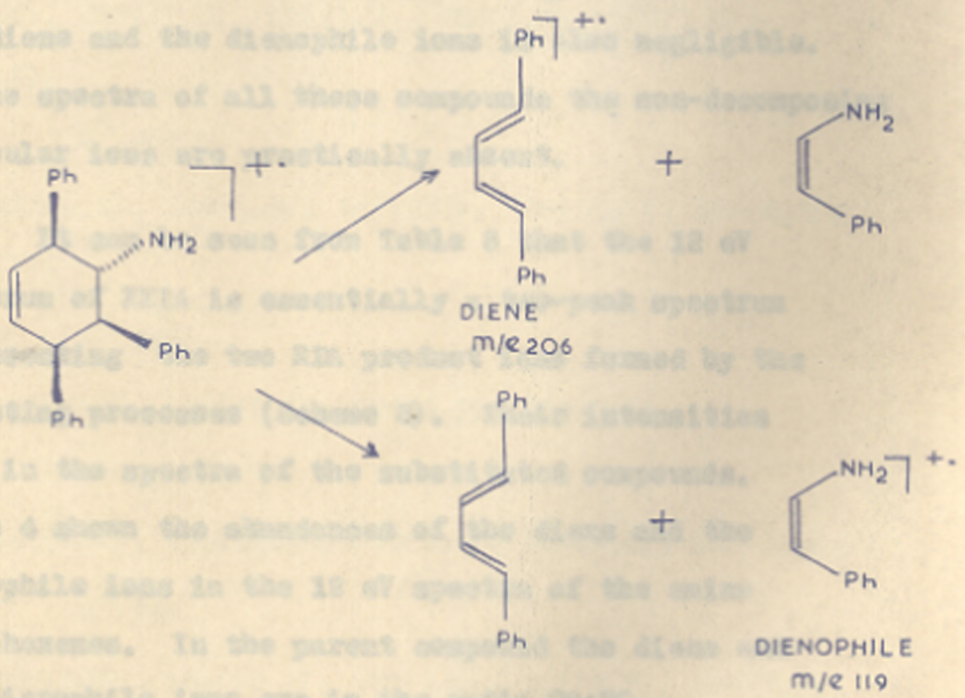
	R	X
XVIIB	H	NO_2
XVIIIB	H	NMe_2
XXB	p-CH_3	NH_2
XXIB	H	NH_2
XXIIB	p-Cl	NH_2



7 – METHOXY ISOFLAVANE



3 – METHOXY FLAVANE



DIENE
m/e 206

DIENOPHILE
m/e 119

SCHEME – 3

The general fragmentation modes of the amino compounds (XIX-XXIV) and the dimethyl amino compounds (XVIII) at 12 eV include the competing RDA fragmentation processes and the fragmentation of the $[M-RC_7H_6]^+$ ions. For the present studies compounds of the 'A' series were found to be most suitable because the formation of $[M-RC_7H_6]^+$ was negligible at 12 eV. As in the case of the nitro cyclohexenes it was found that the diene and the dienophile ions arise only by electron impact induced RDA reaction. Subsequent fragmentation of the diene and the dienophile ions is also negligible. In the spectra of all these compounds the non-decomposing molecular ions are practically absent.

It can be seen from Table 3 that the 12 eV spectrum of XXIA is essentially a two-peak spectrum representing the two RDA product ions formed by the competing processes (Scheme 3). Their intensities vary in the spectra of the substituted compounds. Table 4 shows the abundances of the diene and the dienophile ions in the 12 eV spectra of the amino cyclohexenes. In the parent compound the diene and the dienophile ions are in the ratio 28:70.

TABLE - 3

Mass spectra of the substituted cyclohexenes at 12 eV.*

XVIIA $M^{+\cdot}$ 355

91(4.2), 167(6.2), 193(11.2), 194(2.0), 205(2.0), 206(100), 207(19.2), 208(3.3), 218(5.0), 307(43.0), 308(39.6), 309(11.2), 310(2.0), 325(39.6), 326(10.8).

XVIIB $M^{+\cdot}$ 355

91(0.7), 167(2.3), 193(54.0), 194(9.2), 205(2.0), 206(100), 207(17.0), 208(1.5), 307(1.8), 308(1.5), 325(1.0).

XVIIA $M^{+\cdot}$ 353

132(4.9), 146(1.6), 147(100), 148(12.5), 206(2.3), 262(1.3).

XVIIIB $M^{+\cdot}$ 353

147(100), 148(12.5), 206(0.3), 262(0.6).

XIXA $M^{+\cdot}$ 355

149(100), 150(11.2), 206(0.9), 234(4.6), 235(1.0).

XXA $M^{+\cdot}$ 339

133(100), 134(12.2), 178(1.1), 206(3.7), 234(1.2).

TABLE - 3 (Continued)

XXB $M^{+\cdot}$ 239

133(100), 134(11.7), 206(3.1), 234(6.2).

XXIA $M^{+\cdot}$ 325

119(100), 120(9.1), 206(27.2), 207(4.5), 234(1.2).

XXIB $M^{+\cdot}$ 325

119(100), 120(8.0), 206(29.0), 207(4.8), 234(12.0), 235(2.0).

XXIIA $M^{+\cdot}$ 359

153(92.0), 154(7.1), 155(30.5), 156(2.7), 206(100), 207(17.3), 234(4.5).

XXIIB $M^{+\cdot}$ 359

153(100), 154(9.3), 155(33.0), 156(3.3), 206(100), 207(19.3), 234(49.0), 235(9.3).

XXIIIA $M^{+\cdot}$ 403

91(1.9), 197(56.0), 198(5.0), 199(53.0), 200(5.3), 206(100), 207(17.5), 234(5.0).

XIVA $M^{+\cdot}$ 350

91(1.5), 144(3.7), 145(1.0), 206(100), 207(16.5), 208(1.5), 234(2.0).

---

* The figures in parantheses indicate the relative abundance.

TABLE - 4

Abundances of the diene and the dienophile ions in the spectra of the amino cyclohexenes at 12 eV.

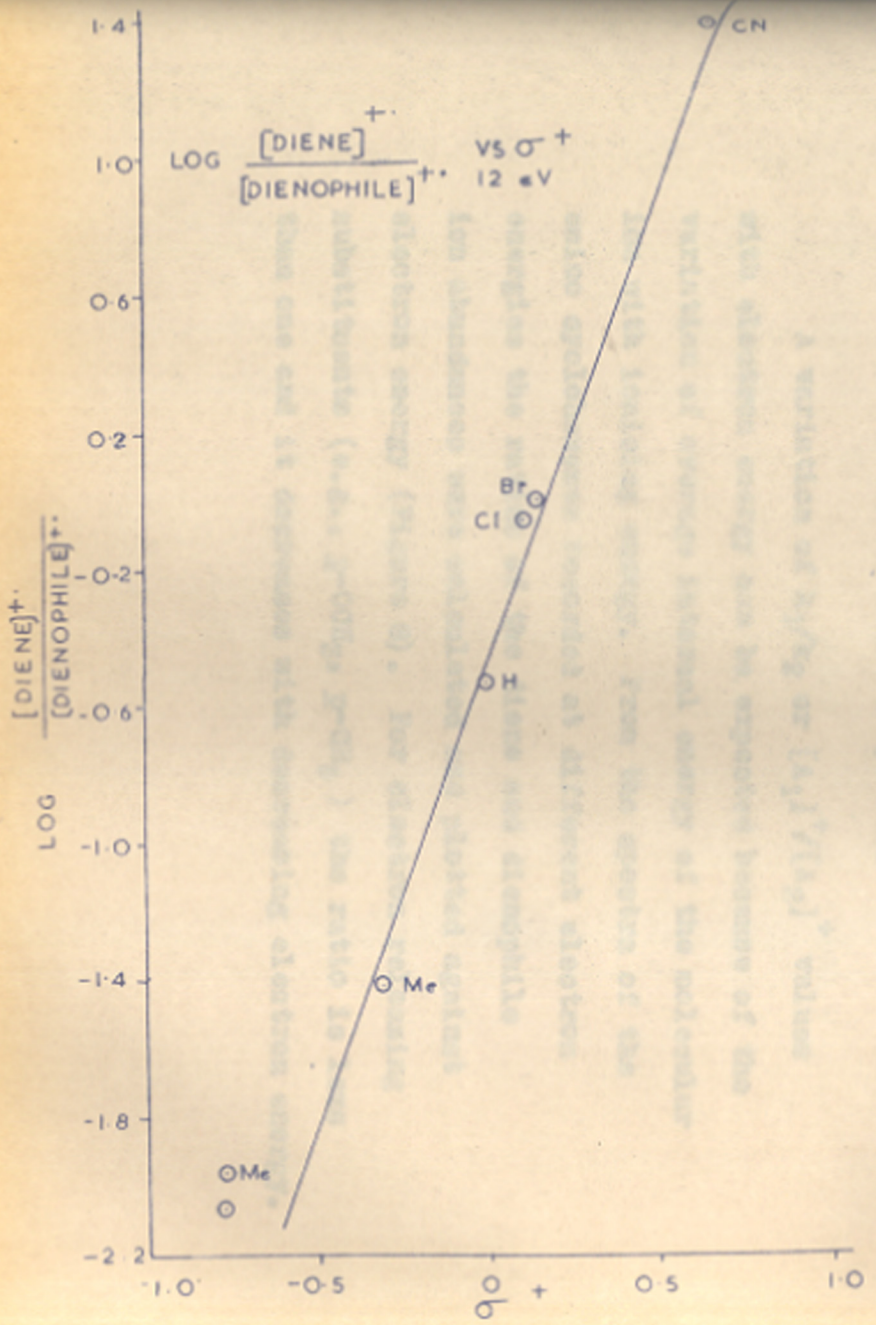
Compound (R)	(Diene)$^{+\cdot}$ % Σ_{40}	[Dienophile]$^{+}$ % Σ_{40}
XIXA (p-CH_3O)	0.8	93.4
XXA (p-CH_3)	3.6	94.5
XXIA (H)	28.2	70.3
XXIIA (p-Cl)	45.8	52.0
XXIIIA (p-Br)	47.2	48.8
XXIVA (p-CN)	92.7	3.7

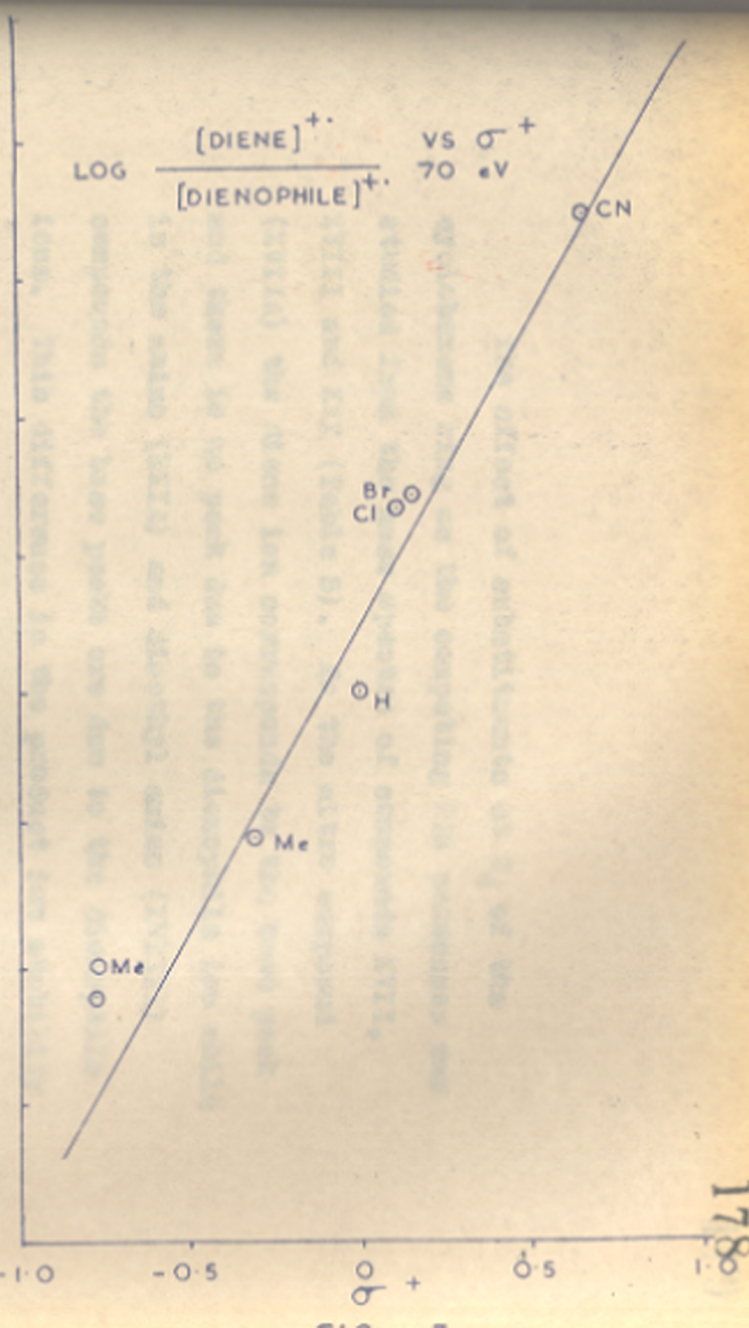
Electron donating groups (e.g., CH_3O, CH_2) increase the abundance of the dienophile ion while in compounds containing Cl or Br the ratio is almost 1:1 and in the cyano compound the diene ion is more abundant than the dienophile ion. The table clearly shows that there is considerable substituent effect on the two competing RDA reactions giving rise to the diene and the dienophile ions. This can be rationalised on the basis of the effect of the substituent on the charge distribution within the decomposing molecular ions in the transition state. With electron donating substituents the charge appears to be localised more on the dienophile part of the molecule while with electron attracting groups the charge appears to be localised more on the diene part. In the chloro and the bromo compounds the charge distribution in the diene and the dienophile parts of the molecule seems to be more or less equal. In this system the halogens behave like electron attracting groups increasing the abundance of the diene ions relative to that in the parent compound.

These observations can also be rationalised on the basis of Stevenson's rule[31]. When a decomposition results in two fragments more charge will be carried

by that fragment which has the lower ionisation potential. Electron donating groups (e.g., OMe) are known to decrease the ionisation potential of a molecule and hence more of the dienophile ion is seen in the spectra of compounds containing electron donating groups at C_5.

Since no molecular ions were observed in the spectra it was not possible to study the substituent effects on ion abundances of the individual competing RDA processes. The ratios of the diene and the dienophile ions were calculated (from the 12 eV spectra). One would expect a fairly good correlation when log $[diene]^{+\cdot}/[dienophile]^{+\cdot}$ are plotted against substituent constants. Figures 6 and 7 show the correlation of log $[diene]^{+\cdot}/[dienophile]^{+\cdot}$ with Brown's σ^{+} constants. A satisfactory correlation is obtained both at 12 eV (Figure 6) and at 70 eV (Figure 7) thereby showing that ion abundances of the diene and the dienophile fragments obey the Hammett equation. The slope increases from + 1.8 at 70 eV to + 2.7 at 12 eV. This effect is expected since differences in activation energy will have greater effect when the total energy of the molecular ion is lower.


LOG [DIENE]+· / [DIENOPHILE]+· VS σ+
12 eV
LOG [DIENE]+· / [DIENOPHILE]+·
1·4
1·0
0·6
0·2
-0·2
-0·6
-1·0
-1·4
-1·8
-2·2
CN
Br
Cl
H
Me
Me
-1·0
-0·5
0·5
1·0
σ+


LOG [DIENE]+· / [DIENOPHILE]+· VS σ+
70 eV
CN
Br
Cl
H
Me
Me
-1·0
-0·5
0·5
1·0
σ+

The effect of substituents at C_4 of the cyclohexene ring on the competing RDA processes was studied from the mass spectra of compounds XVII, XVIII and XXI (Table 5). In the nitro compound (XVIIA) the diene ion corresponds to the base peak and there is no peak due to the dienophile ion while in the amino (XXIA) and dimethyl amino (XVIIIA) compounds the base peaks are due to the dienophile ions. This difference in the product ion stability and relative charge distribution in the diene and dienophile ion could be due to the increasing electron releasing nature of the C_4-substituent as one goes from the nitro to the amino compounds.

A variation of k_1/k_2 or $[A_1]^+/[A_2]^+$ values with electron energy can be expected because of the variation of average internal energy of the molecular ion with ionising energy. From the spectra of the amino cyclohexenes recorded at different electron energies the ratios of the diene and dienophile ion abundances were calculated and plotted against electron energy (Figure 8). For electron releasing substituents (e.g., p-OCH_3, p-CH_3) the ratio is less than one and it decreases with decreasing electron energy.

TABLE - 5

Relative abundances of diene and dienophile ions in the mass spectra compounds XVIIA, XVIIIA and XXIA

Compound	[Diene]$^{+\cdot}$	[Dienophile]$^{+\cdot}$
XVIIA	100	-
XXIA	31.0	100.0
XVIIIA	2.3	100.0

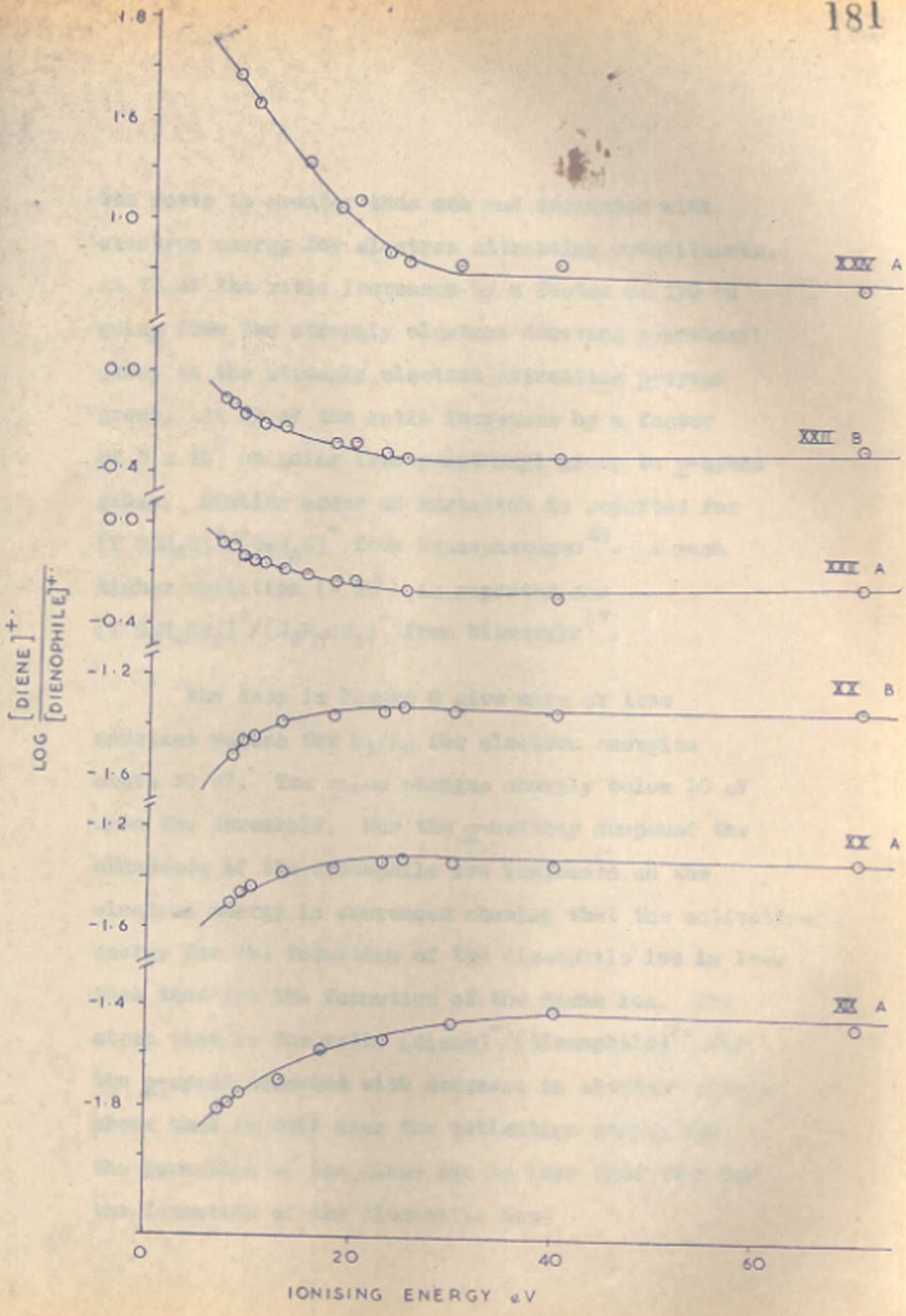

1·8
1·6
1·0
0·0
-0·4
0·0
-0·4
-1·2
-1·6
-1·2
-1·6
-1·4
-1·8
XXV A
XXII B
XXII A
XX B
XX A
XX A
0
20
40
60
IONISING ENERGY eV
LOG [DIENE]+· / [DIENOPHILE]+·

FIG – 8

The ratio is greater than one and increases with electron energy for electron attracting substituents. At 70 eV the ratio increases by a factor of 170 on going from the strongly electron donating p-methoxyl group to the strongly electron attracting p-cyano group. At 12 eV the ratio increases by a factor of 3×10^3 on going from p-methoxyl group to p-cyano group. Similar order of variation is reported for $[Y\ C_7H_4O]^+/[C_7H_5O]^+$ from benzophenones[18]. A much higher variation ($> 10^6$) is reported for $[Y\ C_6H_4CH_2]^+/[C_6H_5CH_2]^+$ from bibenzyls[17].

The data in Figure 8 give more or less constant values for k_1/k_2 for electron energies above 30 eV. The value changes sharply below 30 eV upto the threshold. For the p-methoxy compound the abundance of the dienophile ion increases as the electron energy is decreased showing that the activation energy for the formation of the dienophile ion is less than that for the formation of the diene ion. The steep rise in the ratio $[diene]^+/[dienophile]^+$ for the p-cyano compound with decrease in electron energy shows that in this case the activation energy for the formation of the diene ion is less than that for the formation of the dienophile ion.

It is clear that the nature of the substituent as well as electron energy have considerable influence on the ratio of the abundances of the diene and dienophile ions. Variation of the fragment ion intensity ratios with energy and substituent should arise from variation of rate constants for the two competing reactions. The observed differences in the ion abundances of the diene and dienophile fragments may be explained on the basis of the different product ion stability and also on the basis of the difference in the ionisation potentials of the neutral products. It is reasonable to assume that for two competing RDA fragmentation modes operating from a common molecular ion the ratio of the diene and dienophile ion abundances is a satisfactory measure of the ratio of the rate constant of the reaction provided other competing fragmentation and further decompositions of the RDA products are suppressed.

There is hardly any significant difference in the ratio of the diene and the dienophile ion intensities in the spectra of the epimeric pairs (XXA and B, XXIA and B and XXIIA and B) (Table 6).

TABLE - 6

Values of $[Diene]^{+\cdot}/[Dienophile]^{+\cdot}$ for the epimeric pairs at 12 eV

Compound (R)		$[diene]^{+\cdot}/[dienophile]^{+\cdot}$ A	B
XXI	(H)	0.29	0.31
XX	(p-CH_3)	0.38	0.38
XXII	(p-Cl)	0.88	0.82

The dependence of the ratios on electron energy for epimeric pairs XXA and B and XXIIA and B is shown in Figure 8. It appears that there is no steric effects on the competing RDA reactions. This is to be expected since the observed substituent effects on the charge distribution between the diene and the dienophile ions and the absence of metastable transitions for the RDA processes suggest that in this system RDA operates through a stepwise process.

The absence of measureable molecular ion peaks in the spectra of these compounds shows that the fraction of molecular ions with insufficient energy to decompose is insignificant. This fraction is significant only if the difference between the ionisation potential of the molecule and the appearance potential of the fragments is large[32]. This is also significant for lower electron beam energy. The absence of measureable molecular ion peaks in the spectra of these compounds shows that the activation energies for the competing RDA reactions are small.

The present work has clearly illustrated that the effect of the substituent is on the internal energy distribution in the decomposing molecular ion. This is reflected in the competing RDA reaction when no other competing processes operate, and when further fragmentations of the RDA product ions are absent. Energy distribution in the transition state is determined by the ionisation potentials of the neutral products of the reaction.

B. Experimental

The acetophenone ketals were introduced through the direct inlet at a source temperature below 80°C. The cyclohexene samples were also introduced through the direct inlet system and the spectra were recorded at a source temperature varying from 120° to 170°C. The beam monitor was steady during scanning and all the spectra were checked for reproducibility.

The acetophenone ketals were prepared according to the reported general procedure[33]. The compounds were checked for purity by TLC. The IR spectra were

recorded on Perkin Elmer Infracord spectrophotometer. The melting points were determined in a sulfuric acid bath and are uncorrected.

2-Methyl-2-phenyl-1,3-dioxolane (VI)

24 g of acetophenone (dried over anhydrous sodium sulphate, 0.2 mole), 11.2 ml of ethylene glycol (0.2 mole), 0.1 g of p-toluene sulfonic acid and 40 ml of dry benzene were refluxed in a modified Dean Stark apparatus until no more water was formed (48 hours). The acid was neutralized by the addition of anhydrous sodium carbonate (excess) and the solvent from the unfiltered reaction mixture was removed under vacuum and the product distilled under reduced pressure. The fraction distilling between 70-78°/30 mm was collected.
Yield 29 g. MP, 60°. Lit.[33] 60-61°.
IR (Nujol) ν 1040, 1070 (C-O of a ketal)
Analysis calculated for $C_{10}H_{12}O_2$: C, 73.2; H, 7.3
Found: C, 72.78; H, 7.26%

2-Methyl-2-(p-methoxyphenyl)-1,3-dioxolane (I)

2 g of p-methoxy acetophenone, 2 ml of ethylene glycol and 0.1 g of p-toluene sulfonic acid were refluxed in 20 ml of benzene with azeotropic removal of water

using Dean Stark apparatus. After 36 hours the reaction mixture was cooled and the acid was neutralised with anhydrous sodium carbonate. The benzene was removed under vacuum and the product distilled under reduced pressure. The fraction distilling between 72-76°/3 mm was collected.

Yield 1.8 g. Lit.[34] BP, 136°/13 mm

IR (liquid film) ν 1040, 1090 (C-O of a ketal), 1100 (ether)

Analysis calculated for $C_{11}H_{14}O_3$: C, 68.05; H, 7.22%

Found: C, 68.29; H, 7.64%

2-Methyl-2-(p-hydroxy phenyl)-1,3-dioxolane (II)

1.3 g of p-hydroxy acetophenone (prepared by Fries' rearrangement of phenyl acetate), 5 ml of ethylene glycol and 0.2 g of p-toluene sulfonic acid were refluxed in 20 ml of dry benzene. After 55 hours of azeotropic distillation using a Dean Stark phase separator the reaction mixture was cooled and the acid was neutralized with anhydrous sodium carbonate and the solvent removed under vacuum. It was distilled under reduced pressure. The fraction boiling at 108-109°/7 mm was collected.

Yield 1.2 g.

IR (Nujol) ν 1040, 1080 (C-O of a ketal), 3500 (-OH)

Analysis calculated for $C_{10}H_{12}O_3$: C, 66.5; H, 6.65.

Found: C, 66.42; H, 6.56%

2-Methyl-2-(p-bromophenyl)-1,3-dioxolane (III)

4 g of p-bromoacetophenone, 1.2 ml of ethylene glycol, 0.2 g of p.toluene sulfonic acid and 20 ml benzene were refluxed in a Dean Stark apparatus for 24 hours. The reaction mixture was cooled and the acid was neutralised by adding anhydrous sodium carbonate. The solvent was removed under vacuum and the product distilled under reduced pressure. The fraction distilling at 112°/7 mm was collected. Yield 3.4 g.

It was recrystallized from dilute alcohol.

MP, 42.5°. Lit.[35] 44-45°

IR (Nujol) ν 1040, 1080 (C-O of a ketal)

Analysis calculated for $C_{10}H_{11}BrO_2$: C, 49.39, H, 4.53.

Found: C, 49.68; H, 4.74%

2-Methyl-2-(p-chlorophenyl)-1,3-dioxolane (IV)

3 g of p-chloroacetophenone 0.2 g of p-toluene sulfonic acid, 1.2 ml of ethylene glycol and 10 ml of dry benzene were refluxed in a Dean Stark apparatus for 24 hours. The reaction mixture was cooled and the acid was neutralised with anhydrous sodium carbonate and the solvent removed under vacuum. The product was

distilled under reduced pressure. The fraction distilling at 74-76°/4 mm was collected.

Yield 2.9 g.

IR (liquid film) ν 1040, 1085 (C-O of a ketal)

Analysis calculated for $C_{10}H_{11}ClO_2$: C, 60.43; H, 5.54.

Found: C, 60.66; H, 5.62%

2-Methyl-2-(p-fluorophenyl)-1,3-dioxolane (V)

3 g of p-fluoroacetophenone (prepared by Friedel-Crafts' reaction of fluorobenzene), 1.3 ml of ethylene glycol, 0.1 g of p-toluene sulfonic acid and 20 ml of dry benzene were refluxed in a Dean Stark apparatus for 48 hours. The reaction mixture was cooled. The acid was neutralised with anhydrous sodium carbonate and the solvent removed under vacuum. The product was distilled under reduced pressure. The fraction boiling at 64°/6 mm was collected.

Yield 3.1 g.

IR (liquid film) ν 1040, 1080 (C-O of a ketal), 1228 (C-F).

2-Methyl-2-(p-cyanophenyl)-1,3-dioxolane (VII)

1.5 g of p-cyano acetophenone (prepared from p-bromo acetophenone and cuprous cyanide[36]) 0.1 g of p-toluene sulfonic acid, 3 ml of ethylene glycol and 20 ml of benzene were refluxed in a Dean Stark apparatus

for 24 hours. The reaction mixture was cooled and the solvent was distilled off under vacuum. The product was distilled under reduced pressure. The fraction boiling at 120-122°/3 mm was collected. It was recrystallized from methanol.

Yield 1.8 g. MP, 71°.

IR (Nujol) ν 1040, 1080 (C-O of a ketal), 2225 (C $\equiv$N)

Analysis calculated for $C_{11}H_{11}NO_2$: C, 70.41; H, 5.82.

Found: C, 70.15; H, 6.14%

2-Methyl-2-(p-nitrophenyl)-1,3-dioxolane (VIII)

3.5 g of p-nitroacetophenone, 1.5 ml of ethylene glycol, 0.1 g of p-toluene sulfonic acid and 10 ml of dry benzene were refluxed in a Dean Stark apparatus for 48 hours. The reaction mixture was cooled and the acid was neutralized. The solvent was removed under vacuum and the product was distilled under reduced pressure. The fraction boiling at 177-178°/25 mm was collected.

Yield 3.9 g. It was recrystallized from ethanol.

MP, 76°. Lit.[37] 74-75°.

IR (Nujol) ν 1035, 1080 (C-O of a ketal), 1510, 1340 (C-NO_2).

Analysis calculated for $C_{10}H_{11}NO_4$: C, 57.42; H, 5.26.

Found: C, 57.75; H, 5.59%.

The nitro cyclohexenes X and XIV were gifts from Dr. Nitya Anand, CDRI, Lucknow. Compounds IX and XVI were prepared according to the general procedure[38].

3,6-Diphenyl-5-(p-anisyl)-4-nitro-Δ^1-cyclohexene (IX)

4.8 g of p-methoxy-β-nitrostyrene, 4.0 g of 1,4-diphenyl butadiene, 25 mg of hydroquinone and 20 ml of o-dichlorobenzene were refluxed for 10 hours. The solvent was removed under vacuum and the product was crystallised from methanol (3 g). TLC of the product in benzene-petroleum ether (1:1) showed the presence of two closely moving components. The slow moving component was present only in traces. The fast moving component was isolated by careful column chromatography on 150 g silica gel. Elution with petroleum ether gave the unreacted diene (0.3 g). Elution with 20% benzene-petroleum ether gave the pure fast moving component (IX). It was crystallised from benzene-petroleum ether, colourless crystals, 1.8 g MP, 127°.

NMR (CCl_4) τ 4.0 (s, 2H, H-1 and H-2), 5.13 (t, 1H, H-4), 5.82 (d, 1H, H-3), 6.05 (q, 1H, H-5), 6.15 (bs, 1H, H-6) 6.35 (s, 3H, $-OCH_3$).

Analysis calculated for $C_{25}H_{23}NO_3$: N, 3.64. Found: N, 3.58%

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

1 g of p-cyano-β-nitrostyrene, 1 g of 1,4-diphenyl butadiene and 25 mg of hydroquinone were refluxed in 5 ml of o-dichlorobenzene for 10 hours. The solvent was distilled off under vacuum and the product was crystallised from ether (1.6 g). It was chromatographed on 70 g of silica gel. Elution with petroleum ether gave no unchanged diene. The product was eluted with 1:1 mixture of benzene and petroleum ether and crystallised from benzene-petroleum ether, colourless crystals, 1.3 g. MP, 175°. Lit.[39] 177°. NMR (CCl_4) τ 4.0 (s, 2H, H-1 and H-2), 5.1 (t, 1H, H-4), 5.82 (d, 1H, H-3), 6.05 (q, 1H, H-5), 6.3 (bs, 1H, H-6). Analysis calculated for $C_{25}H_{20}N_2O_2$: N, 7.38. Found: N, 7.25%

The syntheses of the other nitro cyclohexenes are described in Chapter V. The preparation of the amino compounds are described in Chapter III. The dimethyl amino analogues XVIIIA and B were prepared by the reductive alkylation[40] of the corresponding amino compounds.

3,5,6-Triphenyl-4-dimethyl amino-Δ^1-cyclohexene (XVIIIA and B)

0.65 g of the corresponding amino compound XXI was added to 0.5 g of formic acid cooled in ice. 0.45 ml of formalin was added and the solution refluxed for 12 hours. Water was distilled off. The reaction mixture was cooled and 1.5 ml of 10N sodium hydroxide solution was added and stirred. It was extracted with benzene. The benzene layer was washed with 2 ml water, dried over anhydrous sodium sulfate and the benzene was distilled off. The product on crystallisation from benzene-petroleum ether gave 0.4 g of XVIIIA. MP, 198°.

NMR (CCl_4) τ 3.05 (m, 15H, aromatic protons), 4.2 (bs, 2H, H-1 and H-2), 6.25 (m, 4H), 7.85 (s, 6H, $N(CH_3)_2$).

Analysis calculated for $C_{26}H_{27}N$: N, 3.96. Found: N, 3.92%

The isomer B was crystallised from petroleum ether, colourless crystals, 0.45 g. MP, 88°.

NMR (CCl_4) τ 3.1 (m,15H, aromatic protons), 4.35 (bs, 2H, H-1 and H-2), 6.4 (m, 3H), 7.15 (t, 1H, H-5), 8.25 (s, 6H, $N(CH_3)_2$).

Analysis calculated for $C_{26}H_{27}N$: N, 3.96. Found: N, 4.3%

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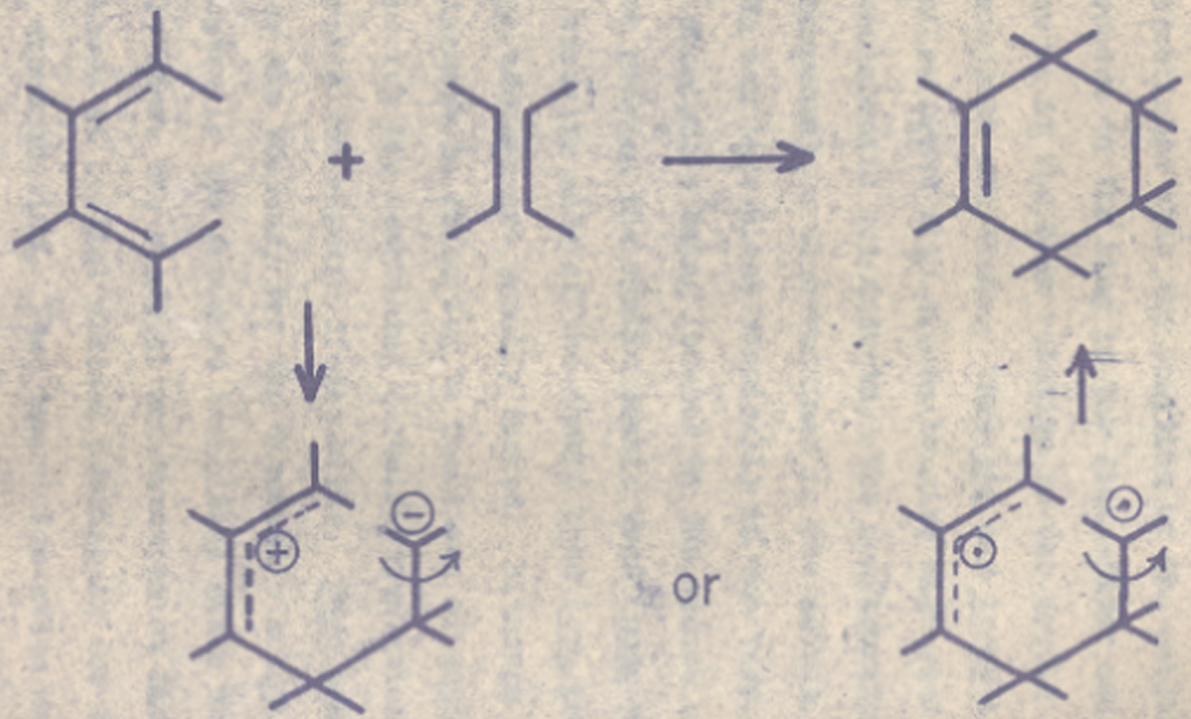
CHAPTER - V

SYNTHESIS, STEREOCHEMISTRY AND ANALYSIS OF SOME DIELS-ALDER ADDUCTS

A. Introduction

The Diels-Alder reaction is a general reaction (4+2 cycloaddition) involving the combination of a conjugated diene with a dienophile to form a six-membered cyclohexene ring.

It can be a concerted or a stepwise process. The synchronous or non-synchronous nature (Scheme 1) of the Diels-Alder reaction has been discussed extensively[1-3]. The extreme views of a synchronous reaction require the two new bonds to be formed to an equal extent in the transition state[4] and of a non-synchronous reaction involve a diradial intermediate[5]. Doering et al.[6] tentatively concluded that the mechanism of Diels-Alder reaction is concerted, perhaps two stage, but not two step.



SCHEME-I

The stereochemical and structural orientation of Diels-Alder reaction is of great interest[1,7,8]. It has been established that the position of the substituents with respect to the ring in the Diels-Alder adducts is the same as it had been relative to the double bond in the dienophile and diene. Thus cis and trans isomeric dienophiles react with dienes to give high yields of pure diastereoisomeric 1:1 adducts. The configuration of the diene component is also retained in the adduct. Finally, reaction can take place sterically in two ways, substituents in the dienophile being located in the adduct either on the same side as the cyclic double bond (endo position) or on the opposite side of the double bond (exo position). The endo adducts are usually formed. Although the term endo is a misnomer in referring to reactions of acyclic dienes, it is useful for describing certain orientational preferences with cyclic and acyclic dienes alike. Endo addition thus involves the tendency for the dienophile substituents to be so oriented in the favoured transition state that they lie directly above the residual unsaturation of the diene, whether for reasons of spatial orbital overlap or for reasons of steric accommodation. That transition state which is best stabilized by spatial orbital overlap and simultaneously

least destabilized by unfavourable steric repulsions has the lowest free energy of all possible transition states, and consequently predominates in the kinetically determined product. The concept of the fairly rigid transition state, with secondary attractive forces preventing conformational inversions of either component,[1] underlies the preservation, in the adduct, of the orientation of the addends in the transition state. Not only the double bonds which take part directly in the addition step must be counted, but also the π bonds of the socalled activating ligands in the diene or dienophile. The addition of maleic anhydride and cyclopentadiene leads almost exclusively to the <u>endo</u> adduct. The thermodynamically more stable <u>exo</u> compound is formed in yields of less than 1.5%.[9]

The earliest deviations noted from the strict adherence to the rule of <u>endo</u> addition were the fulvene-maleic anhydride adducts in which considerable amounts of <u>exo</u> products accompanied the <u>endo</u> isomers. It was found that the easy reversibility of the reaction on warming allows isomerisation to the thermodynamically more stable <u>exo</u> isomer[8].

The stereochemistry of the compounds obtained from open-chain dienes and cyclic dienophiles is often

determined by the rule of maximum accumulation of double bonds. In the addition of open-chain dienophiles to cyclic dienes, the endo addition rule is not always obeyed. From cyclopentadiene and ethyl acrylate the endo and exo adducts were obtained in a ratio 3:1[10]. Open-chain dienes and dienophiles fulfil the rule of maximum concentration of double bonds only at low temperatures. At higher temperatures the stereoselectivity is often lost.

The most revealing indication of the delicate balance among the forces which encourage and oppose endo orientation comes from the use of dienophiles with substituents on opposite sides of the double bond in which case groups are pitted against each other in their ability to control the stereochemistry. Which of the possible transition states is the one of the lowest energy will depend upon a combination of several factors. The most important among them are (a) the relative capacity of each dienophile substituent to interact with the electron freed by primary bond formation, (b) the relative strength of the secondary attractive forces between the diene and each of the dienophile substituents, and (c) the relative magnitude of non-bonded steric repulsions between the dienophile substituents and the diene in each orientation. The magnitude and relative weight given to

each of these factors are difficult to assess, and the delicate balance among the forces which govern the orientation of the adducts makes any prediction tenuous. Nevertheless in a restricted series of closely related compounds, electronic effects are clearly evident. The careful analysis of the reaction of cyclopentadiene with a series of trans / cinnamic acids[11] gives an evaluation of the effect of polar substituents on the steric course of addition. It was found that as the electron withdrawing power of the p-substituent in the aromatic ring increases, the ability of the aryl group to interact with the electrons of the diene increases, and this is reflected in the increasing percentage of endo aryl isomer formed. Similar results have been observed in the reaction of cyclopentadiene with 2-aryl acrylic acids[12].

Structural isomers are formed when 1- and 2-substituted dienes condense with unsymmetrical dienophiles. A vast amount of information has accumulated on the structural orientation (regiospecificity) of Diels-Alder reactions[7,13].

The steric and structural direction of Diels-Alder reaction is obviously governed by the geometrical configuration

of the transition state. In addition to the secondary attractive forces held responsible for endo addition, steric repulsions between substituents on the diene and dienophile may be of equal or greater importance in determining both stereochemical and structural orientation of the addends. Generally, both overlap forces and steric repulsions act in concert to join the addends first at the less substituted carbon atoms and to direct endo addition. Mellor et al.[14] concluded from a study of the Diels-Alder reaction of different dienophiles with cyclopentadiene and methyl cyclopentadiene that regiospecificity is controlled by primary orbital overlap and endo- selectivity is controlled by a combination of secondary orbital overlap, repulsive non-bonding interactions and dipolar interactions.

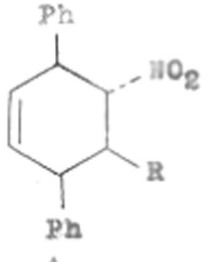
When Diels-Alder reaction gives rise to both exo and endo adducts the ratio of the isomers is determined by chemical and physical methods. Iodolactonisation was used to find out the exo:endo ratio in the Diels-Alder reaction between cyclopentadiene and cinnamic acid derivatives[11]. Analytical techniques such as IR[11,15], NMR[15] and GLC[12] have been successfully used to estimate the isomeric Diels-Alder adducts.

The ion current integration method of mass spectral analysis developed by Major et al.[16,17] is widely used for the quantitative estimation of organic compounds. In this method the mass spectrometer is tuned to the selected m/e value before the evaporation begins and the ion current is recorded during the whole course of the evaporation of a small sample. The area under the curve so obtained is directly proportional to the integrated ion current and hence to the weight of the sample evaporated. A calibration graph is prepared from the area under the ion current curve obtained with known amounts of sample. The area under the ion current curve obtained with the unknown sample is measured and the amount of the unknown sample is directly read from the calibration graph. Major and Perry[18] have extended this technique to analyse a mixture of isomers. In some cases the integrated ion current peaks due to two isomers resolved completely. Structural isomers and cis- trans isomers were found to exhibit the fine structure. However, the resolution of the ion current curve of a mixture of trans- and cis- stilbene was very poor[18].

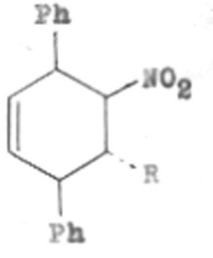
B. Present Work

The present work deals with the synthesis, assignment of stereochemistry and the determination of the composition of the mixture of isomers obtained by the Diels-Alder reaction between trans- trans- 1,4-diphenyl butadiene and nitro ethylene and its trans-2-substituted analogues. The electron impact behaviour of these adducts is discussed in Chapter II. Since the synthesis has not been described in the earlier Chapter, it is discussed here. The mixtures of isomers obtained were separated by column chromatography. Proper knowledge of the stereochemistry of the isomers was necessary for the mass spectral study. This was done by the analysis of their NMR spectra. The composition of the mixture was determined by the integration of the signal of 4-H which had different chemical shifts in the spectra of the individual isomers. An attempt was made to use the ion current integration method of mass spectral analysis to determine the composition of the mixture. The results support the previous observations of Nitya Anand et al.[19] on the effect of substituents on the stereochemical course of Diels-Alder reactions.

The following compounds were prepared by the Diels-Alder reaction of <u>trans</u>- <u>trans</u>- 1,4-diphenyl butadiene with nitro ethylene and its substituted analogues.



A



B

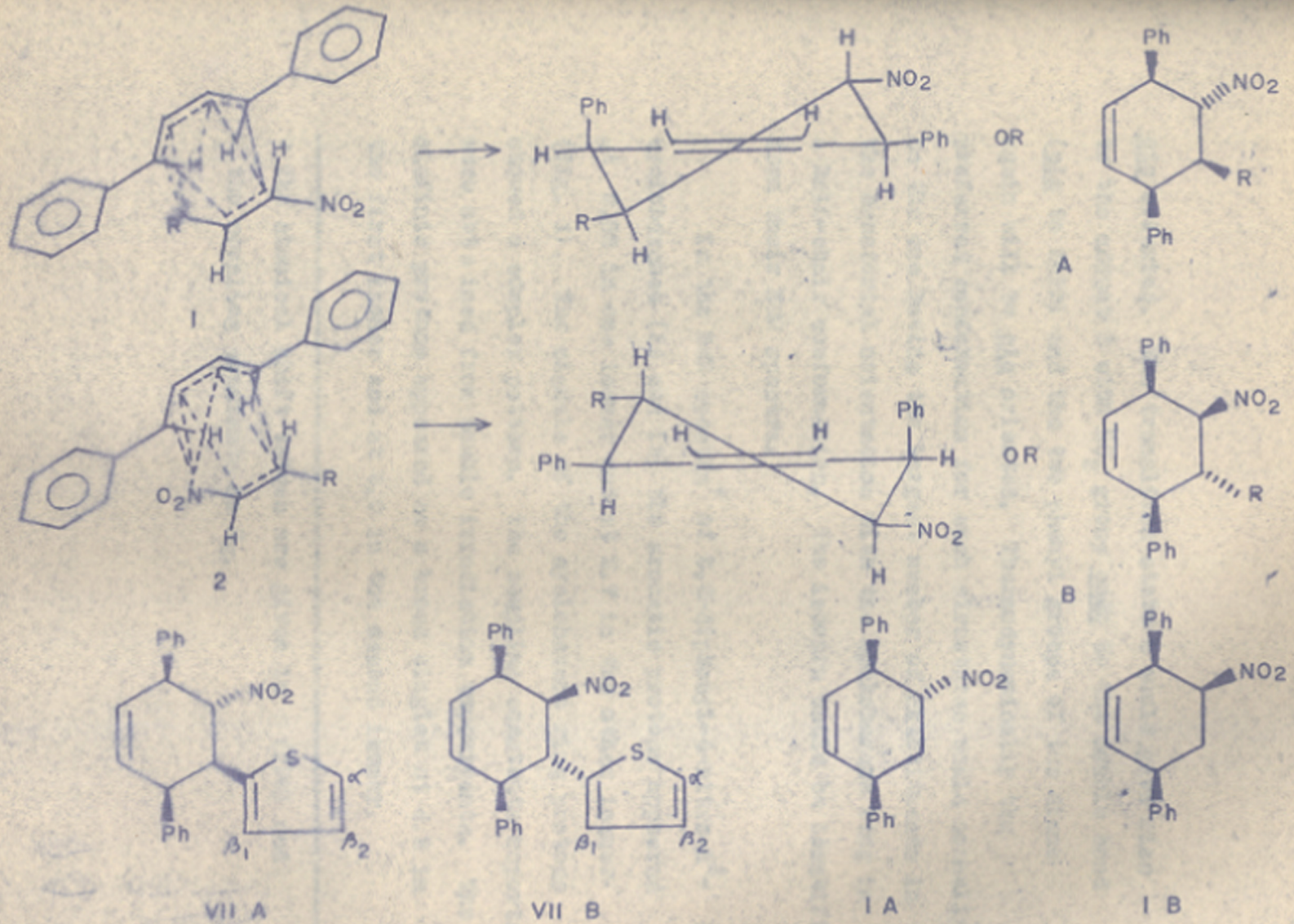
R		R	
IA	H	IB	H
IIA	C_6H_5	IIB	C_6H_5
IIIA	p-Br C_6H_4	IIIB	p-Br C_6H_4
IVA	p-ClC_6H_4	IVB	p-ClC_6H_4
VA	p-$CH_3C_6H_4$	VB	p-$CH_3C_6H_4$
VIA	2-Furyl	VIB	2-Furyl
VIIA	2-Thienyl	VIIB	2-Thienyl

1. Synthesis

Trans- trans- 1,4-diphenyl butadiene was prepared from phenyl acetic acid and cinnamaldehyde. Nitro ethylene was obtained by the reaction between nitromethane and paraformaldehyde. The substituted β-nitro ethylenes were synthesised from the corresponding aldehydes and nitromethane. The reaction between 1,4-diphenyl butadiene and nitro ethylene in a sealed tube gave a product which showed two spots on TLC. The Diels-Alder reaction between 1,4-diphenyl butadiene and the substituted β-nitro ethylenes were carried out in o-dichlorobenzene at reflux temperature. TLC of the reaction mixture showed the presence of two products. The mixtures of isomers obtained by the Diels-Alder reactions were separated into the components by column chromatography on silica gel.

2. Assignment of stereochemistry

The two possible transition states which determine the stereochemistry of the Diels-Alder adducts of trans-trans- 1,4-diphenyl butadiene and nitro ethylene or trans-2-substituted nitro ethylenes are 1 and 2 (Scheme 2). The transition state 1 would lead to the formation of adduct A with NO_2 group exo to the double bond (trans to 3-Ph) and the two phenyl groups of the diene will be



SCHEME-2

cis oriented. The transition state 2 would give rise to the adduct 3 with NO_2 group endo to the double bond (cis to 3-Ph) and the two phenyl groups of the diene again will be cis oriented. Thermodynamically the preferred conformation for such structures would normally be the one having the largest number of substituents in the equatorial orientation with the cyclohexene ring in a half-chair conformation. The isomers could be identified from their NMR spectra.

In the NMR spectra* of 3,6-diphenyl-4-nitro-Δ^1-cyclohexenes (IA and IB) the aromatic protons appeared at 2.88 in one isomer and at 2.7 in the other isomer (Fig. 1). The signals of the cyclohexene ring protons showed a complex pattern. The coupling constants reported were obtained from double irradiation experiments. The olefinic protons appeared as a broad singlet at 4.2 in the first isomer and at 4.0 in the second isomer.

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* The chemical shift values are given in τ (PPM) and the coupling constants in H_z.

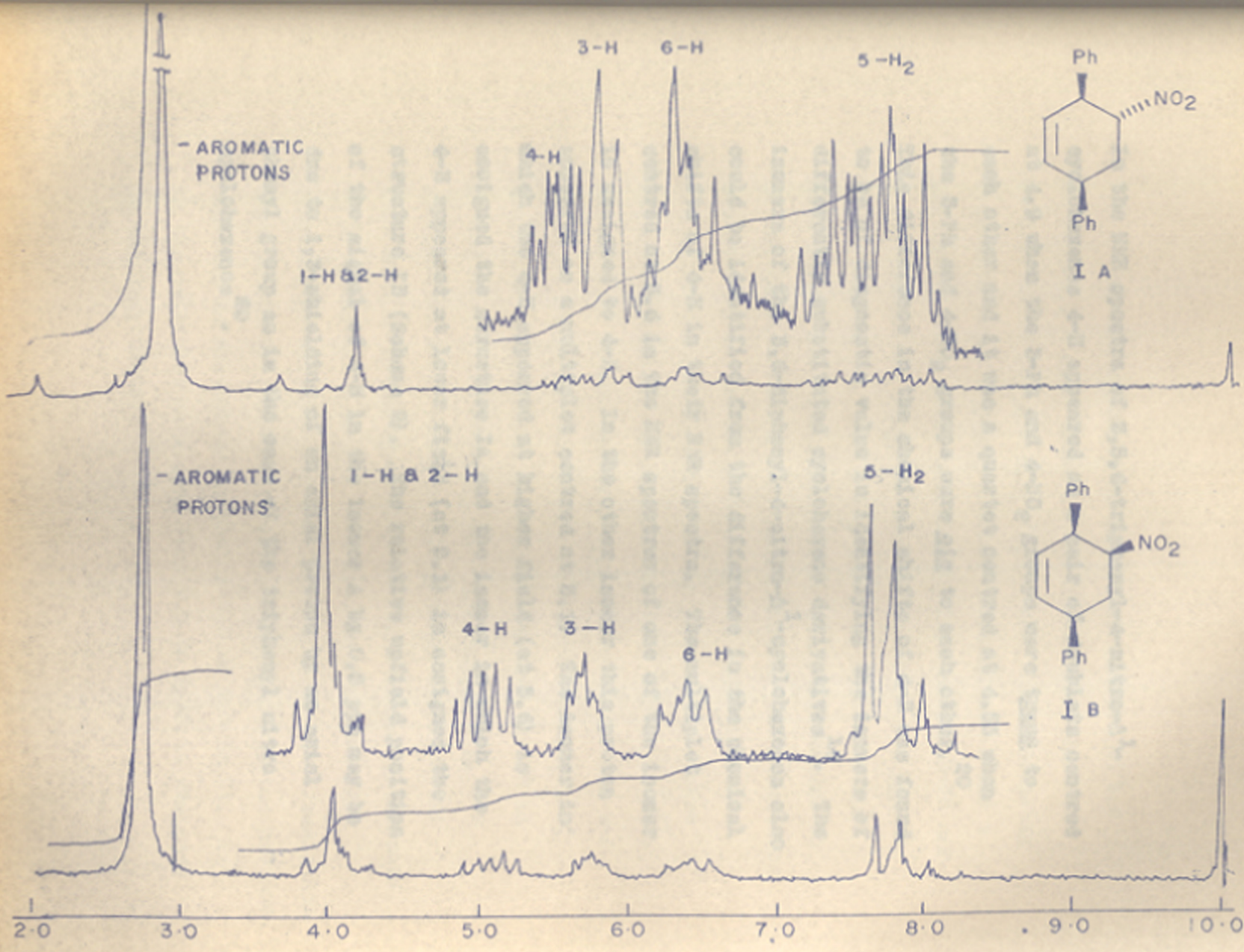
3-H
6-H
5-H2
4-H
AROMATIC PROTONS
1-H & 2-H
Ph
NO2
Ph
I A
AROMATIC PROTONS
1-H & 2-H
5-H2
4-H
3-H
6-H
Ph
NO2
Ph
I B
2·0
3·0
4·0
5·0
6·0
7·0
8·0
9·0
10·0 PPM (τ)

FIG. 1.

In the NMR spectra of 3,5,6-triphenyl-4-nitro-Δ^1-cyclohexenes 4-H appeared as a pair of doublets centred at 4.9 when the 3-Ph and 4-NO_2 groups were trans to each other and it was a quartet centred at 4.55 when the 3-Ph and 4-NO_2 groups were cis to each other.[20] This difference in the chemical shifts of 4-H was found to be of diagnostic value in identifying the isomers of differently substituted cyclohexene derivatives[19]. The isomers of the 3,6-diphenyl-4-nitro-Δ^1-cyclohexenes also could be identified from the difference in the chemical shifts of 4-H in their NMR spectra. The multiplet centred at 5.6 in the NMR spectrum of one of the isomer is assigned to 4-H. In the other isomer this proton appeared as a multiplet centred at 5.1. The isomer in which the 4-H appeared at higher field (at 5.6) is assigned the structure IA and the isomer in which the 4-H appeared at lower field (at 5.1) is assigned the structure IB (Scheme 2). The relative upfield position of the signal of 4-H in the isomer A by 0.5 ppm may be due to 1,3-shielding of an axial proton by an axial phenyl group as in the case of the triphenyl nitro cyclohexenes[20].

The 3-H appeared as a doublet centred at 5.9 in IA ($J_{3,4}$ = 8.5) while it was a multiplet centred at 5.17 in IB ($J_{3,4}$ = 6.5; $J_{2,3}$ = 4). These coupling constants imply a <u>trans</u> diaxial coupling in IA and a <u>cis</u> equatorial axial coupling in IB. Hence, 3-Ph and 4-NO_2 groups are <u>trans</u> to each other in IA and <u>cis</u> to each other in IB. The 4-NO_2 group is equatorial in both IA and IB. The 3-Ph will be quasi-equatorial in IA and quasi-axial in IB. This confirms the structures assigned to IA and IB. The dihedral angle between 2-H and 3-H would be about 90° in IA and thus there would be virtually no coupling between 2-H and 3-H[21]. However, in IB the dihedral angle between 2-H and 3-H would be about 35° and this would show a coupling of the order of 3.5. The multiplets centred at 6.4 in IA and at 6.45 in IB ($J_{5a,6a}$ = 10; $J_{5e,6a}$ = 6) are assigned to 6-H. These coupling constants indicate that 6-Ph is quasi-equatorial in IB. 6-Ph can be assumed to be quasi-axial in IA. Attempts to find out the coupling between 5-H and 6-H in IA from double irradiation experiments were not successful. The C_5-methylene protons appeared as multiplets extending from 7.0 to 8.0 in IA. In IB the multiplet extending from 7.5 to 8.25 is assigned to the C_5-protons.

The NMR spectra of 3,6-diphenyl-5-aryl-4-nitro-Δ^1-cyclohexenes were similar to those of 3,5,6-triphenyl-4-nitro-Δ^1-cyclohexenes reported in literature. However, the NMR spectra of 3,6-diphenyl-5-(2-thienyl)-4-nitro-Δ^1-cyclohexenes (VIIA and VIIB, Fig.2) are briefly discussed. As in the case of the triphenyl compounds the 4-H appeared as a pair of doublets at higher field (5.07) in the isomer A while it appeared as a quartet centred at 4.8 in the isomer B. The observed coupling constants $J_{4,5} = 12$ and $J_{3,4} = 10$ in VIIA imply two trans diaxial couplings and $J_{4,5} = 12$ and $J_{3,4} = 6$ in VIIB indicate one trans diaxial and one cis equatorial-axial coupling. Thus 3-Ph and 4-NO_2 groups are trans to each other in VIIA and cis to each other in VIIB. In both the isomers 4-NO_2 and 5-(2-thienyl) groups are trans to each other. There is considerable overlap of the signals due to 3-, 5- and 6- H in VIIA. These signals extend from 5.64 to 6.3. The poorly resolved signal centred at 5.85 in VIIB is assigned to 3-H. The signals of 5-H and 6-H overlap each other and extend from 6.3 to 6.55.

Because of the shielding effect of sulphur, the α-H of the thiophene ring appeared along with the aromatic protons in both the isomers as indicated by integration.

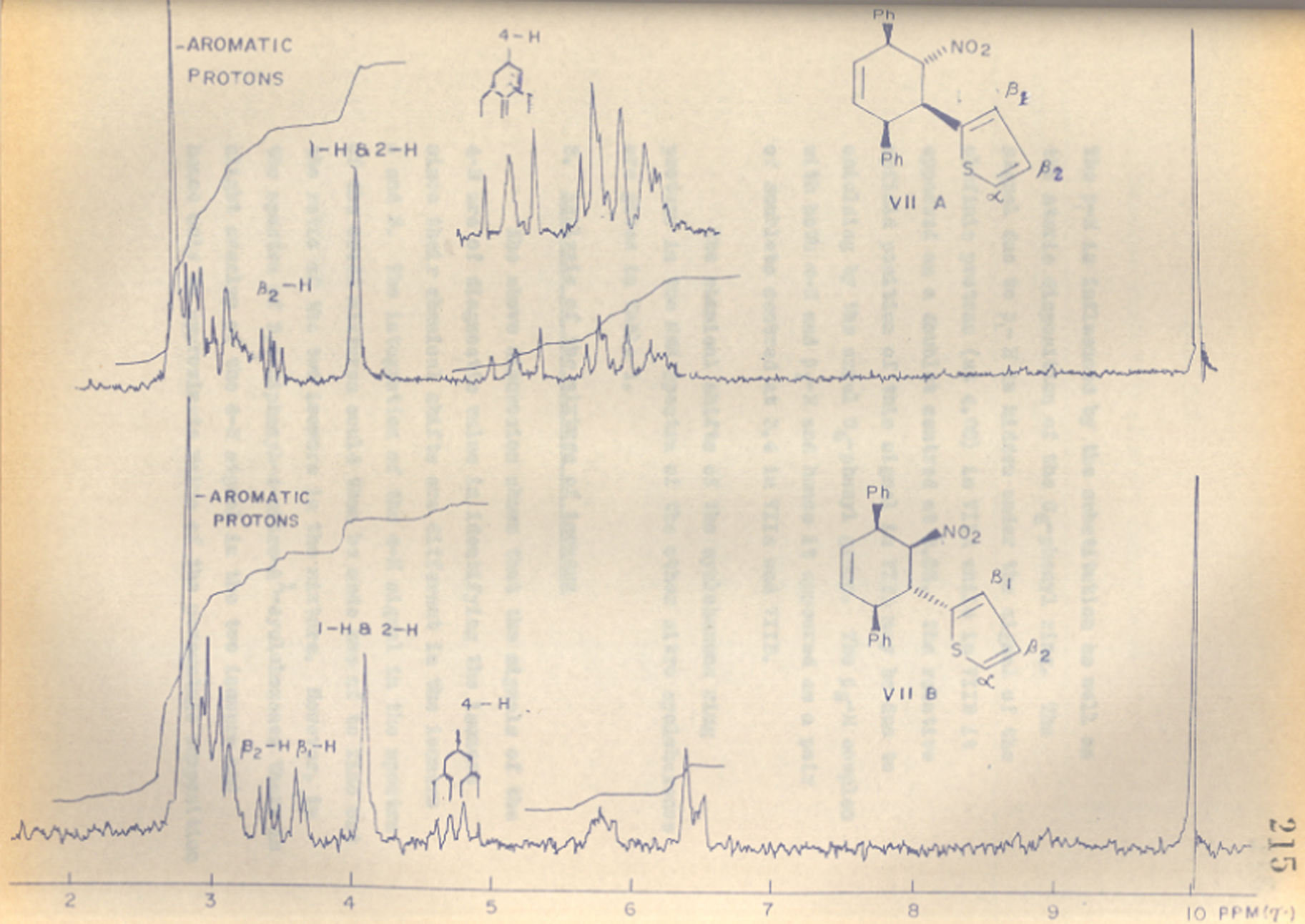
-AROMATIC PROTONS
4-H
1-H & 2-H
β_2-H
Ph
NO_2
β_1
Ph
S
β_2
α
VII A
-AROMATIC PROTONS
1-H & 2-H
4-H
β_2-H β_1-H
Ph
NO_2
β_1
Ph
S
β_2
α
VII B
2
3
4
5
6
7
8
9
10 PPM(τ)

FIG. 2.

The β_1-H is influenced by the substitution as well as the steric disposition of the C_6-phenyl ring. The signal due to β_1- H is hidden under the signal of the olefinic protons (at 4.08) in VIIA while in VIIB it appeared as a doublet centred at 3.55. The relative upfield position of this signal in VIIA may be due to shielding by the axial C_6-phenyl group. The β_2-H couples with both α-H and β_1-H and hence it appeared as a pair of doublets centred at 3.4 in VIIA and VIIB.

The chemical shifts of the cyclohexene ring protons in the NMR spectra of the other nitro cyclohexenes are given in Table 1.

3. Analysis of the mixture of isomers

The above discussion shows that the signals of the 4-H are of diagnostic value in identifying the isomers since their chemical shifts are different in the isomers A and B. The integration of the 4-H signal in the spectra of the crude mixtures could thus be made use of to find out the ratio of the two isomers in the mixture. However, in the spectra of 3,6-diphenyl-4-nitro-Δ^1-cyclohexenes there is slight overlap of the 4-H signal in the two isomers and hence only an approximate value of the percentage composition

TABLE - 1

Chemical shift data of nitro cyclohexenes

Compound	Substituent	H-1 and H-2	H-3	H-4	H-5	H-6
IA		4.2	5.9	5.6	7.0-8.0	6.4
B	H	4.0	5.77	5.1	7.5-8.25	6.45
IIA		4.18	5.9	5.1	6.1	6.3
	C_6H_5					
B		4.1	5.8	4.6	6.8	6.4
IIIA		4.1	5.8	5.1	6.05	6.3
	p-BrC_6H_4					
B		4.0	5.75	4.6	6.82	6.55
IVA		4.0	5.84	5.11	6.1	6.3
	p-ClC_6H_4					
B		4.02	5.75	4.6	6.8	6.44
VA		4.1	5.83	5.05	6.05	6.3
	p-$CH_3C_6H_4$					
B		4.1	5.84	4.67	6.92	6.55
VIA		4.04	5.82	5.44	5.9	6.02
	2-Furyl					
B		3.95	5.76	4.6	6.6	6.25
VIIA		4.08	5.64	5.07	5.8	6.1
	2-Thienyl					
B		4.17	5.85	4.8	6.5	6.4

of the mixture could be obtained. In the 3,6-diphenyl-5-aryl-4-nitro-Δ^1-cyclohexenes the 4-H signals were well-separated in the isomers (Fig. 3 and 4) and an unambiguous determination of the isomeric composition of the mixtures was thus possible. The results are summarised in Table 2.

An attempt was made to use the ion current integration method of mass spectral analysis to determine the isomeric composition of the reaction mixtures. As the mass spectra of these compounds did not show molecular ion peaks, the base peak at m/e 206 was selected for integration. 10 µg of an artificial mixture of the pure isomers IIA and IIB was introduced into the instrument at different temperatures varying from 130 to 170°. The m/e 206 peak was recorded with the m/e 205 peak of the reference compound (perfluorokerosene). No fine structure could be discerned in the ion current curves obtained with different amounts of sample. Hence, the ion current integration method was not used for the analysis of the mixtures.

In the Diels-Alder reaction between 1,4-diphenyl butadiene and nitro ethylene the ratio of IA and IB was

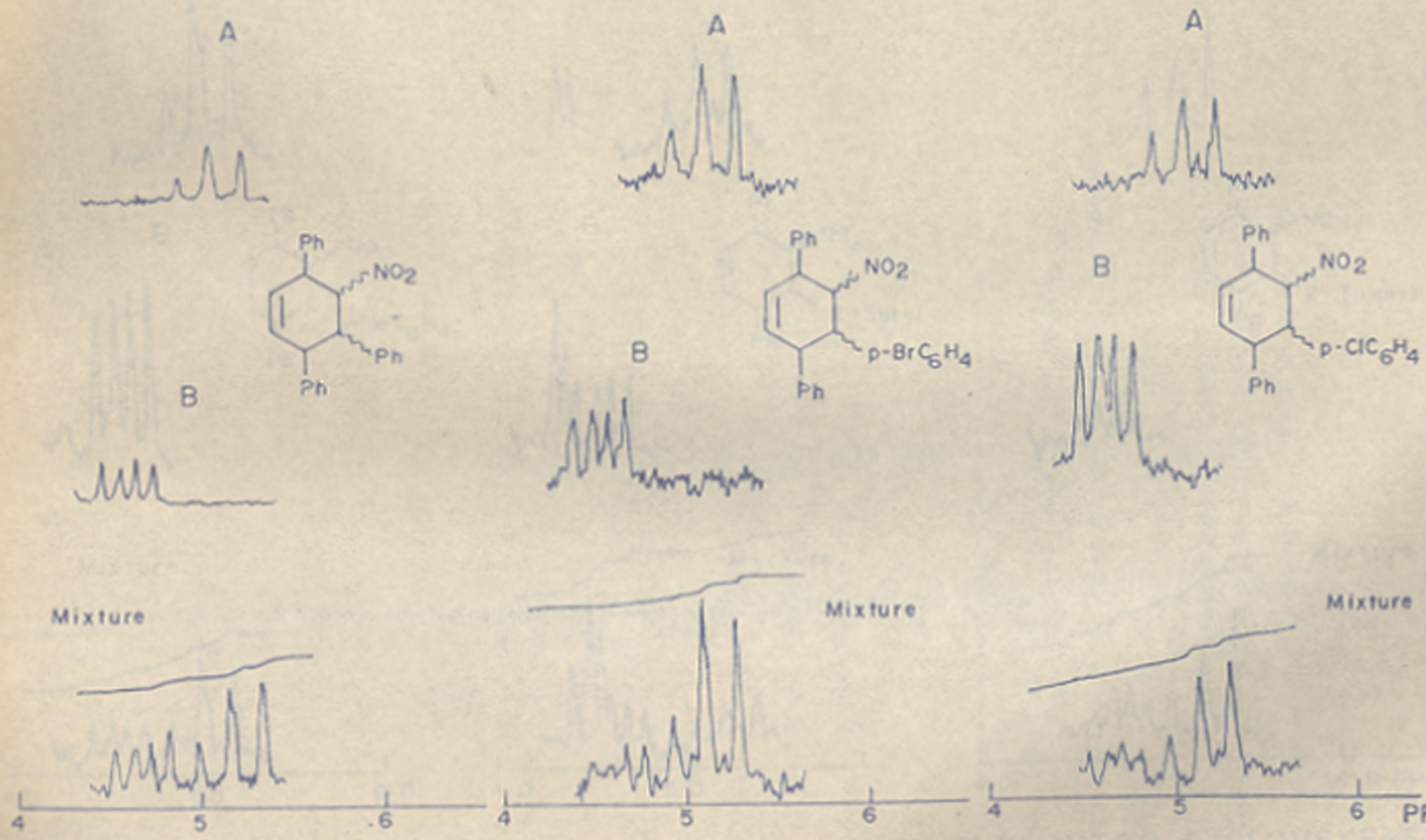

FIG. 3. H-4 SIGNAL IN THE NMR SPECTRA OF THE TRIPHENYL NITRO CYCLOHEXENES

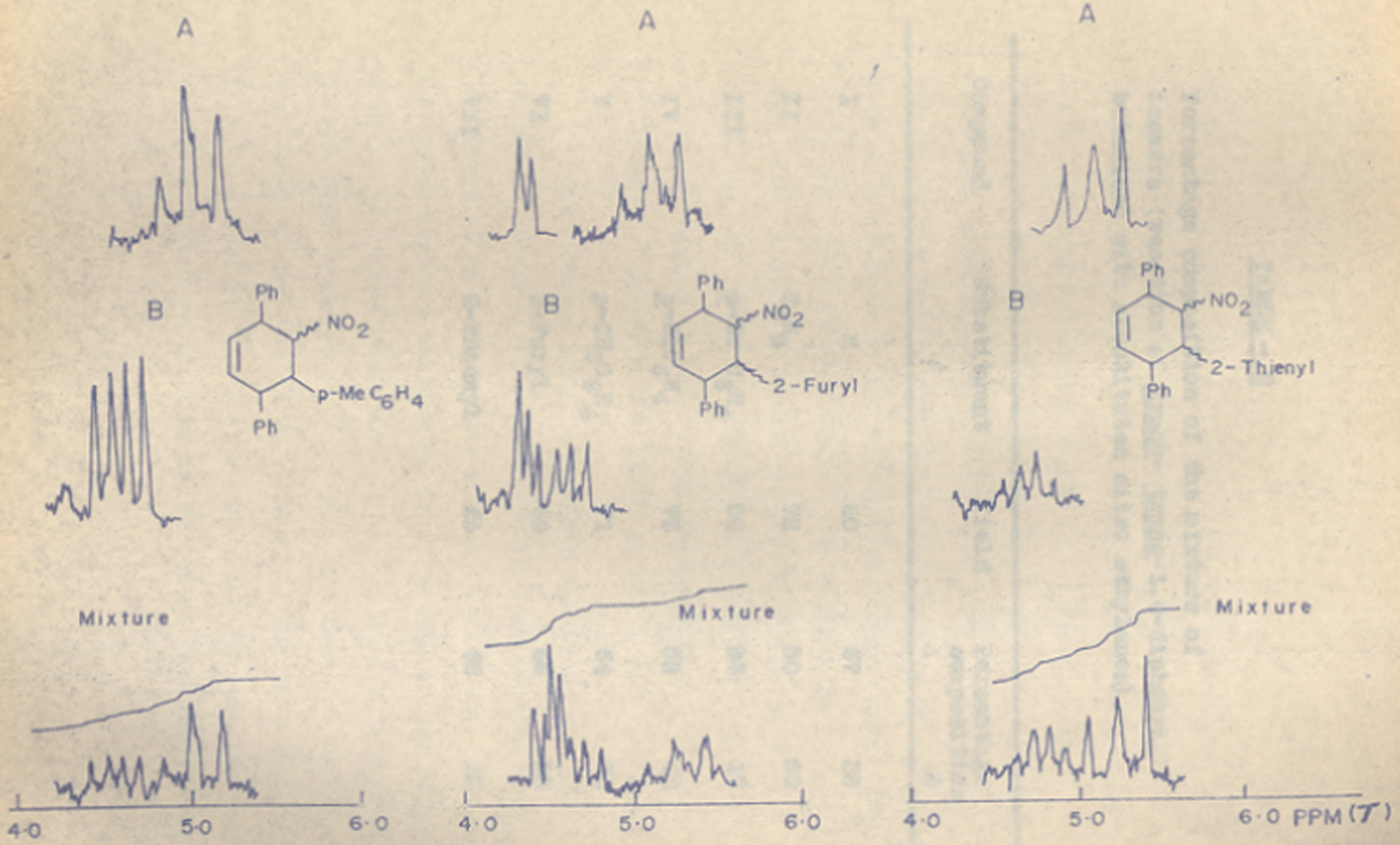

FIG 4 H-4 SIGNAL IN THE NMR SPECTRA OF THE TRIPHENYL NITRO CYCLOHEXENES

TABLE - 2

Percentage composition of the mixture of isomers (reaction of trans- trans-1,4-diphenyl butadiene with substituted nitro ethylenes).

Compound	Substituent	Yield	Percentage composition A	B
I	H	60	67	33
II	C_6H_5	72	50	50
III	p-Br C_6H_4	50	83	17
IV	p-ClC_6H_4	73	58	42
V	p-$CH_3C_6H_4$	71	64	36
VI	2-Furyl	69	45	55
VII	2-Thienyl	65	62	38

found to be 2:1. If a phenyl group is introduced into the β-position of the nitro ethylene the Diels-Alder reaction with 1,4-diphenyl butadiene gives an adduct mixture containing equal amounts of isomer A and B. The phenyl and the nitro groups take part equally in secondary bonding interactions with the π-electron system of the diene. However, introduction of various aryl substituents in the β-position of the nitro ethylene alter the ratio considerably. The results in Table 2 show that in all the cases except the 5-(2-furyl) analogues the isomer in which the nitro and 3-phenyl groups are trans to each other predominates. In the 5-(2-furyl) compounds the ratio is VIA : VIB = 45:55.

The factors which determine the stereochemical course of Diels-Alder reaction have been indicated in the introduction. Previous workers have shown that strongly electron attracting substituents on the phenyl ring of the β-nitrostyrene led to the exclusive formation of the endo -aryl isomer[19]. This has been explained on the basis of the increased ability of the aryl group to take part in secondary bonding interactions between the highest occupied molecular orbital of the diene and the lowest

vacant molecular orbital of the dienophile. No explanation has been given for the influence of electron donating substituents in altering the isomeric ratio. In the present study compounds containing strongly electron attracting substituents have not been examined. With the limited data available on electron donating substituents it is not possible to explain satisfactorily the effect of electron donating substituents in changing the steric course of Diels-Alder reaction. However, it seems reasonable to assume that in the present system the effect of different dienophile substituents in changing the isomeric composition of the adduct may be due to the different electron affinities of the substituents.

It is clear from the above discussion that the cycloaddition reaction of trans- trans-1,4-diphenyl butadiene with nitro ethylene and trans-2-substituted nitro ethylenes gives both the possible isomers. The stereochemistry of these compounds has been established from their NMR spectra. The isomeric ratios of the Diels-Alder adducts were determined by the integration of the 4-H signal in the NMR spectra of the crude mixtures. In almost all the cases the isomer in which the nitro and the 3-Ph groups are trans to each other predominates.

This shows that the substituents have significant influence on the nature of secondary bonding interactions between the diene and the dienophile.

C. Experimental

The melting points were determined in a sulfuric acid bath and are uncorrected. Purity of all the compounds was checked by TLC. They are characterised by spectral and analytical methods. IR spectra were recorded on a Perkin Elmer Infracord Spectrophotometer. NMR spectra were recorded on a Varian T-60 spectrometer using CCl_4 as solvent and TMS as internal standard.

Nitro ethylene

It was prepared by the dehydration of 2-nitroethanol[22].

2-Nitroethanol

2-Nitroethanol was prepared according to a reported procedure[23]. 100 ml of nitromethane and 5 g of paraformaldehyde were heated to boiling. 100 mg of potassium carbonate was added and the reaction mixture was refluxed for 3.5 hrs with occasional shaking. The reaction mixture was cooled, acidified with concentrated hydrochloric acid, filtered and the excess nitromethane was distilled off under suction on a water bath. The residue (reddish

brown oil, 14.4 g) was distilled under reduced pressure. The fraction boiling at 82-84°/3 mm was collected. Yield, 9.3 g Lit.[24] BP, 102°/11 mm.

Nitro ethylene

2-Nitroethanol was dehydrated with phthalic anhydride[22]. 8.2 g of 2-nitroethanol and 14.8 g of phthalic anhydride were mixed in a small distillation apparatus with a short fractionating column. It was evacuated to 80 mm and heated by means of an oil bath. The bath temperature was maintained at 140-150° until the mixture was homogeneous. The bath temperature was then raised to 175° and held at 175-180° until distillation ceased. The distillate was dried over anhydrous $CaCl_2$ and redistilled. The fraction boiling at 40°/90 mm was collected. Yield, 7.3 g Lit.[22] BP, 38-39°/80 mm.

Trans-β-Nitrostyrene

61 g of nitromethane and 106 g of benzaldehyde were placed in a one litre three-necked flask fitted with a mechanical stirrer and a thermometer and kept in freezing mixture bath. 200 ml of methyl alcohol was added and when the temperature was below 5° a solution of 42 g of sodium hydroxide in 100 ml of water cooled in ice was

added slowly so that the temperature of the mixture was between 10 to 15°. After the addition was over it was allowed to stand for 15 minutes. 600 ml cold water containing crushed ice was added to it and this solution was added to 200 ml cold concentrated hydrochloric acid diluted with 300 ml ice water. The precipitate was allowed to settle. The major portion of water was decanted and the precipitate was filtered and washed with water. The solid was melted in a beaker. On cooling the separated water was decanted and the solid material was crystallised from methanol, yellow crystals, 106 g.
MP, 57°. Lit.[25] 57-58°.

Trans-trans-1,4-Diphenyl butadiene

43 g of phenyl acetic acid, 35 g of powdered litharge, 42.1 g of freshly distilled cinnamaldehyde and 44.5 ml of acetic anhydride were placed in a round bottomed flask equipped with a reflux condenser and protected by a guard tube. The mixture was boiled for 5 hrs. During the first half-an-hour the flask was heated gently and shaken several times. It was poured into a beaker while still hot and kept overnight. The contents were stirred to a soft pulp and filtered. The solid was washed with two 15 ml portions of ethyl alcohol. The cake

was transferred to a beaker, stirred with 20 ml ethyl alcohol, filtered, washed with 20 ml ethyl alcohol and dried in air. Light yellow flakes were obtained (19 g). The material was decolourised with charcoal in benzene solution. The benzene filtrate was treated with 130 ml of hot ethyl alcohol, heated to boiling and cooled to 10° with shaking. It was filtered and washed with 20 ml ethyl alcohol and dried, colourless flakes, 16 g.
MP, 153°. Lit.[26] $152.5-153.5^{\circ}$.

3,6-Diphenyl-4-nitro-Δ^{1}-cyclohexene (I)

1 g of 1,4-diphenyl butadiene, 0.17 g of nitro ethylene, 25 mg of hydroquinone and 1 ml of benzene were sealed in a thick-walled glass tube at -20° and heated at 120° for 20 hrs. The tube was cooled in liquid air and it was opened. The product was chromatographed on 60 g. of silica gel. Elution with petroleum ether gave the unchanged diene (0.3 g). The crude mixture of the adducts (0.9 g) followed on elution with benzene. This was used for the NMR analysis. The crude mixture was separated into the isomeric components by chromatography on 40 g silica gel. Elution with benzene-petroleum ether gave the two isomers of 3,6-diphenyl-4-nitro-Δ^{1}-cyclohexene. Isomer A was a thick liquid (0.45 g).
BP, $120^{\circ}/5$ mm (bath temperature).
MW (mass spectrum), 279.

IR (CCl_4) ν 1560, 1378 (C-NO_2).

Analysis calculated for $C_{18}H_{17}NO_2$: N, 5.04. Found: N, 5.07%.

Isomer B was recrystallised from benzene-petroleum ether, colourless crystals, 0.2 g. MP, 122°.

MW (mass spectrum), 279.

IR ν 1560, 1370 (C-NO_2).

Analysis calculated for $C_{18}H_{17}NO_2$: N, 5.04. Found: N, 5.1%.

2,5,6-Triphenyl-4-nitro-Δ^1-cyclohexene (II)

A mixture of 10 g of trans-β-nitrostyrene, 10 g of trans-trans- 1,4-diphenyl butadiene, 40 ml of o-dichlorobenzene and 25 mg of hydroquinone was refluxed for 10 hrs. The dichlorobenzene was removed in vacuo and the residue was chromatographed on silica gel (600 g) column. Elution with petroleum ether gave the unreacted diene (1 g). Elution with benzene gave 10.8 g of a mixture of isomers A and B. This mixture was used for NMR analysis. It was separated into the components by chromatography on 400 g of silica gel. Elution with 20% benzene-petroleum ether followed by elution with 30% benzene-petroleum ether gave the isomeric nitro cyclohexenes.

Isomer A, 3.8 g, was recrystallised from ether, colourless crystals, 3.5 g.

MP, 158°. Lit.[20] 158-159°.

MW (mass spectrum), 355.

IR (CCl_4) ν 1550, 1360 (C-NO_2).

Analysis calculated for $C_{24}H_{21}NO_2$: C, 81.2; H, 5.92; N, 3.94.

Found: C, 81.5; H, 6.1; N, 4.1%.

Isomer B, 3.2 g was recrystallised from benzene-petroleum ether, colourless, crystals, 3.0 g.

MP, 173°. Lit.[20] 169°.

MW (mass spectrum), 355.

IR (CCl_4) ν 1560, 1370 (C-NO_2).

Analysis calculated for $C_{24}H_{21}NO_2$: C, 81.2; H, 5.9; N, 3.94.

Found: C, 81.0; H, 5.8; N, 4.07%.

2,6-Diphenyl-5-(p-bromophenyl)-4-nitro-Δ^1-cyclohexene (III)

p-Bromo-β-nitrostyrene[27] (3 g), 1,4-diphenyl butadiene (2 g), o-dichlorobenzene (10 ml) and hydroquinone (25 mg) were refluxed for 10 hrs. The o-dichlorobenzene was removed under vacuum and the residue was chromatographed on 200 g silica gel. Elution with petroleum ether gave 0.2 g of the unreacted diene. 2.3 g of the mixture of isomers followed on elution with benzene. It was rechromatographed on 100 g of silica gel. Elution with 20% benzene-petroleum ether gave the two isomers.

Isomer A, 1.6 g, was recrystallised from ether, colourless crystals, 1.4 g.

MP, 163.5°.

MW (mass spectrum), 433.

IR (CCl_4) ν 1560, 1370 (C-NO_2).

Analysis calculated for $C_{24}H_{20}BrNO_2$: N, 3.23.

Found: N, 3.5%.

Isomer B, 0.4 g, was recrystallised from ether, colourless, crystals, 0.35 g. MP, 215°.

MW (mass spectrum), 433.

IR (CCl_4) ν 1550, 1370 (C-NO_2).

Analysis calculated for $C_{24}H_{20}BrNO_2$: N, 3.23.

Found: N, 3.4%.

2,6-Diphenyl-5-(p-chlorophenyl)-4-nitro-Δ^1-cyclohexene (IV)

5 g of p-chloro-β-nitrostyrene,[27] 4 g of 1,4-diphenyl butadiene, 20 ml of o-dichlorobenzene and 25 mg of hydroquinone were refluxed for 10 hrs. The solvent was removed in vauco and the residue was chromatographed on 350 g of silica gel. Elution with petroleum ether gave the unreacted diene (0.2 g). The isomeric mixture (6.3 g) followed on elution with benzene. This product was chromatographed again on 250 g of silica gel. Elution with 20% benzene-petroleum ether gave the pure isomers.

Isomer A, 3.8 g, was recrystallised from benzene-petroleum ether, colourless crystals, 3.6 g. MP, 171.5°.

MW (mass spectrum), 389.

IR (CCl_4) ν 1560, 1370 (C-NO_2).

Analysis calculated for $C_{24}H_{20}ClNO_2$: N, 3.6.

Found: N, 3.7%.

Isomer B, 1.4 g. was recrystallised from benzene-petroleum ether, colourless crystals, 1.2 g. MP, 196°.

MW (mass spectrum), 389.

IR (CCl_4) ν 1560, 1370 (C-NO_2).

Analysis calculated for $C_{24}H_{20}ClNO_2$: N, 3.6. Found: N, 3.6%.

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

4 g of p-methyl-β-nitrostyrene[27], 4 g of 1,4-diphenyl butadiene, 20 ml of o-dichlorobenzene and 25 mg of hydroquinone were refluxed for 10 hrs. The product was chromatographed on silica gel (350 g). Elution with petroleum ether gave 0.3 g of the unreacted diene. Elution with benzene gave 4.7 g of the product mixture. It was rechromatographed on 200 g of silica gel. The isomer A was eluted with 25% benzene-petroleum ether and elution with 1:1 benzene-petroleum ether gave the isomer B. Isomer A was recrystallised from benzene-petroleum ether, colourless crystals, 2.1 g. MP, 142°.

MW (mass spectrum), 369.

IR (CCl_4) ν 1560, 1370 (C-NO_2).

Analysis calculated for $C_{25}H_{23}NO_2$: N, 3.79.

Found: N, 3.76%.

Isomer B was recrystallised from benzene-petroleum ether, colourless crystals, 1.1 g.

MP, 135°.

MW (mass spectrum), 369.

IR (CCl_4) ν 1560, 1368 (C-NO_2).

Analysis calculated for $C_{25}H_{23}NO_2$: N, 3.79. Found: N, 3.9%.

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

5 g of 1-(2-furyl)-2-nitroethene[28], 5 g of 1,4-diphenyl butadiene, 25 ml of o-dichlorobenzene and 25 mg of hydroquinone were refluxed for 10 hrs. The solvent was removed under vacuum and the residue was chromatographed on 400 g silica gel. The unreacted diene (0.4 g) was eluted down the column with petroleum ether. Elution with benzene gave the mixture of the isomers (5.3 g). It was separated into the components by rechromatography on 200 g silica gel. The pure isomers were eluted with 30% benzene-petroleum ether. Isomer A was crystallised from ether, colourless crystals, 1.1 g. MP, 134°.

MW (mass spectrum), 345.

IR (CCl_4) ν 1560, 1368 (C-NO_2).

Analysis calculated for $C_{22}H_{19}NO_3$: N, 4.06.

Found: N, 4.19%.

Isomer B was recrystallised from ether, colourless crystals, 1.25 g. MP, 164-165°.

MW (mass spectrum), 345.

IR (CCl_4) ν 1560, 1370 (C-NO_2).

Analysis calculated for $C_{22}H_{19}NO_3$:

N, 4.06. Found: N, 4.14%.

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

4 g of 1-(2-thienyl)-2-nitroethene[28], 4 g of 1,4-diphenyl butadiene and 25 mg of hydroquinone were refluxed in 25 ml of o-dichlorobenzene for 10 hrs. The solvent was removed under vacuum and the product was chromatographed on 350 g of silica gel. 0.2 g of unreacted diene came out on elution with petroleum ether. 4.2 g of the mixture of isomers were obtained on elution with benzene. It was chromatographed again on silica gel (160 g). The pure isomers eluted down with 1:1 benzene-petroleum ether. Isomer A was recrystallised from benzene-petroleum ether, colourless crystals, 2.0 g.

MP, 182°.

MW (mass spectrum), 361.

IR (CCl_4) ν 1550, 1350 (C-NO_2).

Analysis calculated for $C_{22}H_{19}NO_2S$: N, 3.87. Found: N, 3.77%.

Isomer B was recrystallised from benzene-petroleum ether, colourless crystals, 1.0 g.

MP, 214-215°.

MW (mass spectrum), 361.

IR (CCl_4) ν 1550, 1350 (C-NO_2).

Analysis calculated for $C_{22}H_{19}NO_2S$: N, 3.87. Found: N, 3.64%.

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SUMMARY

The thesis consists of five Chapters. The necessary background information for the proper appraisal of the present work is given in the first Chapter. The electron impact induced fragmentation modes operating in 4-nitro-Δ^1-cyclohexene and in some mono-, di- and triphenyl derivatives are discussed in the second Chapter. The effect of substituents, stereochemistry and saturation of the double bond on the major fragmentation modes of 4-nitro-Δ^1-cyclohexene has been studied. The introduction of phenyl groups in the molecule, as expected, has led to the formation of the m/e 91, 117 and 167 ions. In the triphenyl compounds peaks at m/e 193 and 206 are also observed. The effect of phenyl group in altering the fragmentation mode and in changing the relative abundances of the common ions has been rationalised on the basis of energetics. It is known that the introduction of a phenyl group in a molecule lowers the ionisation potential of the parent molecule and thereby changes the activation energies for the various competing fragmentation pathways. A characteristic fragmentation mode of the isomeric 3,6-diphenyl-4-nitro-Δ^1-

cyclohexenes is the loss of $^{\cdot}NO$ from the molecular ion. Considerable substituent effects were observed for the loss of $^{\cdot}NO$, $^{\cdot}NO_2$, HNO_2 and $^{\cdot}H_2NO_2$ and for the formation of RCH_2^+ (R corresponds to the C_5-substituent). Significant steric effects were observed for the formation of the $[M-HNO_2]^{+\cdot}$ and $[M-H_2NO_2]^+$ ions in the fragmentation of the isomeric 3,6-diphenyl-4-nitro-Δ^1-cyclohexenes. Saturation of the double bond of the cyclohexene ring was found to have some effect on the loss of $^{\cdot}NO$. In all the compounds except the triphenyl nitro cyclohexanes considerable reduction of this fragmentation mode was observed. A possible mechanism has been proposed for the loss of $^{\cdot}NO$ in 3,6-diphenyl-4-nitro-Δ^1-cyclohexenes.

In Chapter III the unimolecular ion decompositions of isomeric 3,6-diphenyl-5-aryl-4-amino-Δ^1-cyclohexenes under electron impact in the source and in the first field-free region, under chemical ionisation and field desorption conditions are discussed. The pyrolytic behaviour has also been studied. Retro Diels-Alder reaction is a favoured decomposition mode under EI, CI, FD and pyrolytic conditions. Both the diene and dienophile ions are observed in EI spectra of these amino compounds. The absence of metastable transitions and the significant influence of substituents

on the RDA fragment ion abundances suggest that the RDA process in the amino cyclohexenes is a stepwise process. The only reaction which competes with RDA reaction under EI condition is the formation of the m/e 234 ion. But this process gives rise only to minor peaks in the spectra whereas under CI conditions the loss of neutral molecule effectively competes with the RDA reaction. $[M+H]^+$ ions give rise to the most intense peak in the CI spectra and loss of ammonia from the $[M+H]^+$ ion is a favoured process. In the FD spectra the molecular ion is the base peak. The only fragment ions observed are due to RDA reaction products. The pyrolytic behaviour of these compounds is similar to that observed under EI conditions.

The effect of substituents on molecular and fragment ion abundances is discussed in Chapter IV. One of the important structural informations provided by the mass spectrum of a compound is the molecular weight. The effect of both electron donating and electron withdrawing substituents on the relative abundances of the molecular ions in the spectra of acetophenone ketals has been studied. As expected, it was observed that an electron donating substituent enhances the molecular ion abundance. Substituent effects on competing

RDA reaction and $^{\bullet}NO_2$ elimination reaction operating in 3,6-diphenyl-5-aryl-4-nitro-Δ^1-cyclohexenes have been studied. The ratio of the abundances of the diene and the $[M-NO_2]^+$ ions was correlated with σ^+ constants. For the competing RDA fragmentation modes operating in 3,6-diphenyl-5-aryl-4-amino-Δ^1-cyclohexenes the effect of substituent and energy on the ratio of the diene and dienophile ion abundances was looked into. It has been found that the nature of the substituent and electron energy have considerable influence on the ratio of the abundances of the diene and dienophile ions. The results indicate that for two competing RDA fragmentation modes operating from a common molecular ion the ratio of the diene and dienophile ion abundances is a satisfactory measure of the rate constant of the reaction provided other competing fragmentation modes and further decomposition of the RDA products are suppressed.

In the last Chapter the cycloaddition reactions of trans- trans -1,4-diphenyl butadiene with nitroethylene and trans -2-substituted nitro ethylenes are discussed. In all the cases isomeric mixtures of adducts were obtained. The isomers were separated by column

chromatography on silica gel. The stereochemistry of the isomers was established from the analysis of their NMR spectra. The composition of the mixture was determined by the integration of 4-H signal in the NMR spectra of the crude mixture. The results show that in almost all cases the isomer in which the nitro and 3-Ph groups are trans to each other predominates.

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(K.P. Madhusudanan)