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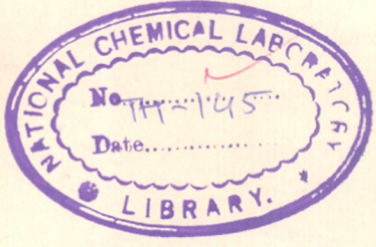
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PHOTOINDUCED HYDROXYLATION  
OF ALICYCLIC OLEFINS

REPORT NO. 145



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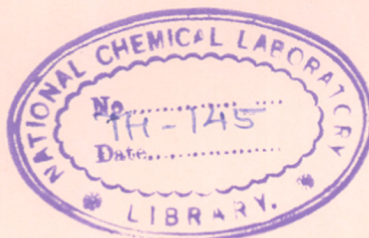
Department of Organic Chemistry  
National Chemical Laboratory  
POONA - 411 007  
December 1967

# PHOTOINDUCED HYDROXYLATION OF ALICYCLIC OLEFINS

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*A Thesis Submitted to the  
University of Poona  
for the degree of  
Master of Science*

(Partly by Papers Partly by Research)  
In Chemistry



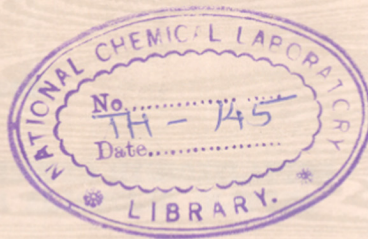
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RAMESH G, KELKAR

Division of Organic Chemistry  
(natural products)  
NATIONAL CHEMICAL LABORATORY  
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TO MY PARENTS



## C O N T E N T S

	Page
CHAPTER I	INTRODUCTION
	Hydroxylation of olefins 1
	References 24
CHAPTER II	PHOTO-INDUCED HYDROXYLATION OF CYCLOHEXENE AND 1-METHYLCYCLOHEXENE
	Introduction 29
	Present work 45
	Discussion 51
	Experimental 59
	Spectra 73
	References 86
CHAPTER III	PHOTO-INDUCED HYDROXYLATION OF OTHER ALICYCLIC OLEFIN
	Present work 90
	Discussion 99
	Experimental 102
	Spectra 112
	References 126
ACKNOWLEDGEMENTS	.. ... 127

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CHAPTER I  
INTRODUCTION

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A brief discussion of various methods available for the hydroxylation of olefins, as a synthetic tool for obtaining the corresponding alcohols, is presented. Only those methods are mentioned, which have some practical utility. Merits and demerits of each method are also outlined.

Olefins form a very convenient and easily accessible starting material to obtain various functionalized products like alcohols, ketones, halides etc. Conversion of olefins into alcohols is an important reaction in synthetic organic chemistry.

Various methods are employed to achieve this conversion. A brief summary of these methods, highlighting their utility in obtaining a particular type of product as well as their limitations, is presented to facilitate comparison among them. The emphasis throughout is only on the synthetic aspects.

#### 1. Acid catalyzed hydration of olefins

This is a well known method to obtain alcohols from olefins, wherein olefin and water are treated in the presence of an acid catalyst. The most common catalyst is obviously sulphuric acid, but other acids, such as nitric, may also be sometimes useful.



**Mechanism:** The mechanism of this reaction is electrophilic in nature and begins with electrophilic attack by a proton on the double bond. The reaction follows Markovnikov's rule and more substituted alcohol is obtained.

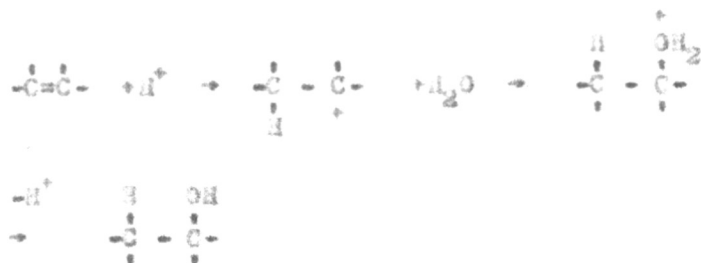


The initial attack of proton takes place in such a manner that more stable carbonium ion is formed, naturally the proton attaches itself to the least substituted carbon of the double bond. The negative attacking species, in this case  $-\text{OSO}_2\text{OH}$  would give the initial product as -



(I)

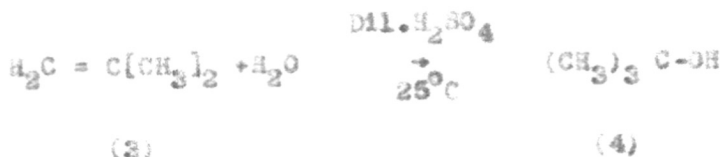
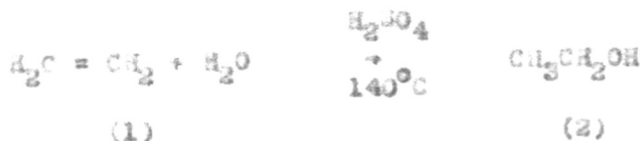
which may be isolated but generally under the reaction conditions, gets hydrolyzed to yield alcohols. However, the conjugate base of the acid is not the only possible species, which attack the incipient carbonium ion. The attack may also be by water.



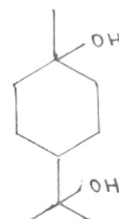
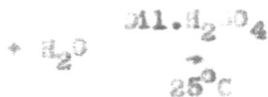
When the reaction proceeds by this pathway intermediates like I are not involved.

The alcohols obtained by this process are always

substituted and the only primary alcohol obtainable in this way is ethyl alcohol. This process is used extensively to get alcohols from petroleum by-products. Thus ethylene (1) gives ethyl alcohol (2), and 1,1-dimethylethylene (3) gives t-butyl alcohol (4). In another important reaction  $\alpha$ -pinene (5) gives terpin hydrate (6), the side chain hydroxy group incorporation is due to the opening of four membered ring.



(5)



(6)

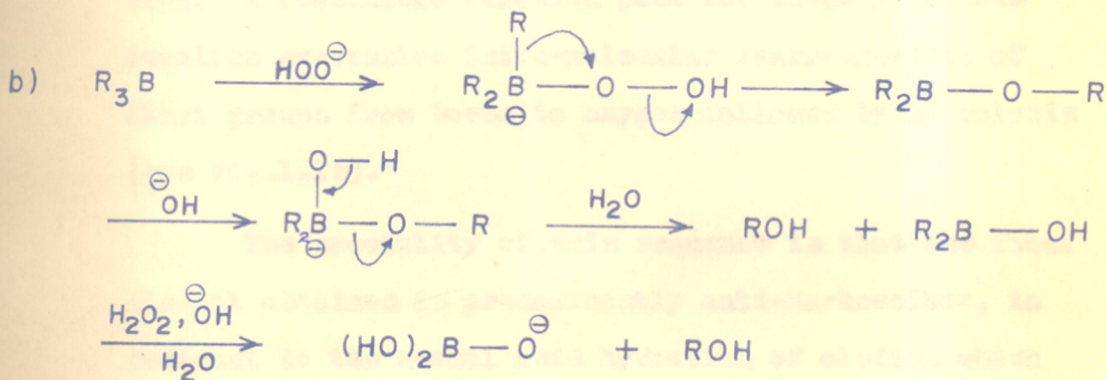
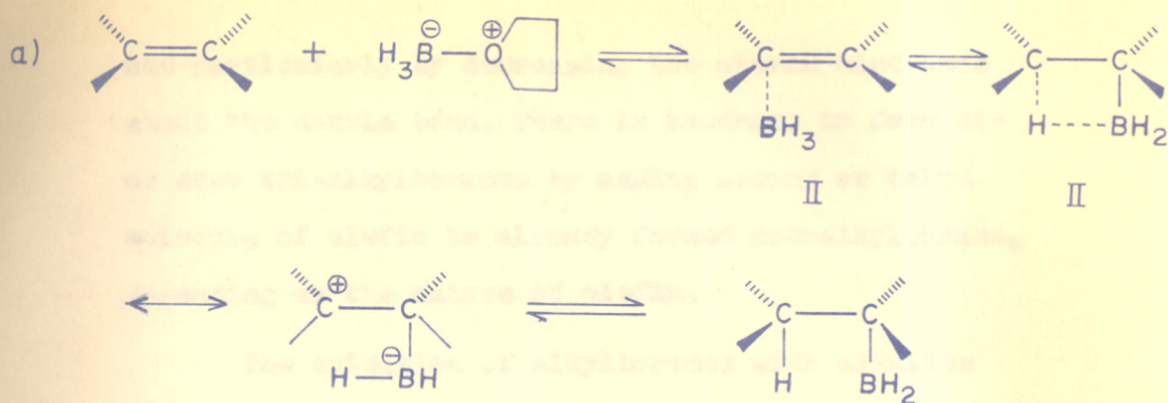
With substrates of the type  $-\text{C}=\text{C}-\text{Z}$ , where Z is an electron withdrawing group like  $-\text{CHO}$ ,  $-\text{COR}$  (including quinones),  $-\text{COOR}$ ,  $-\text{CONH}_2$ ,  $-\text{CN}$ ,  $-\text{NO}_2$ ,  $-\text{SOR}$ ,  $-\text{SO}_2\text{H}$  etc., the product is always  $\text{HO}-\text{C}-\text{CH}-\text{Z}$ , the mechanism is nucleophilic

and anti-Markovnikov products are obtained.

Stereochemistry of hydration: The stereochemistry of olefin hydration has been very scarcely studied. Collins and Hammond<sup>1</sup> studied the hydration of 1,2-dimethylcyclohexene and found to be nonstereospecific. This result would provide strong evidence for an open carbonium ion, but the conclusion remains tentative. Wolfe and Campbell<sup>2</sup> attempted to determine the stereochemistry of D<sub>2</sub>O addition to cyclohexene-3,3,6,6-d<sub>4</sub>, but found deuterium scrambling in the product making steric studies impossible.

## 2. Hydroxylation via hydroboration<sup>3,4</sup>:

Mechanism and Stereochemistry: The reaction between olefin and borane-tetrahydrofuran complex occurs possibly via a  $\pi$ -complex<sup>5,5a</sup> (II) leading to a four centered transition state by which the borane adds in cis conformation to the carbon-carbon double bond [see Fig.1.1a]. Although there is a slight tendency for the hydrogen to add to the carbon atom better able to tolerate positive charge the transition state appears to be relatively nonpolar, so that the direction of addition to unsymmetrical olefins is determined principally by steric factors. Thus the rate of hydroboration of a carbon carbon double bond is increased by increasing the electron density of the double bond, by increasing the strain present in the double bond,



Thus

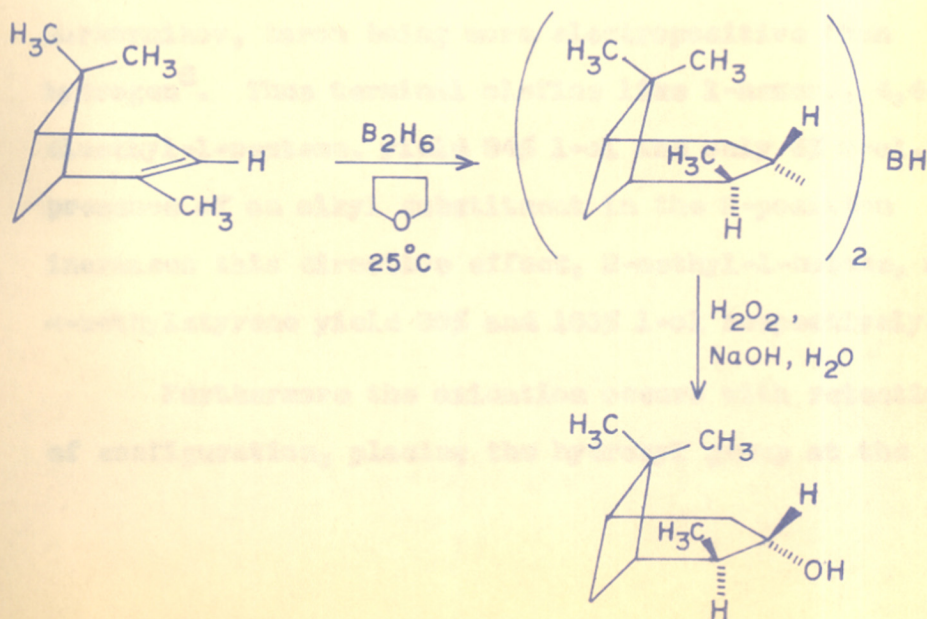


FIG. 1.1 MECHANISM AND STEREOCHEMISTRY OF HYDROXYLATION VIA HYDROBORATION

and particularly by decreasing the steric hindrance about the double bond. There is tendency to form di- or even tri-alkylboranes by adding second or third molecule of olefin to already formed monoalkylborane, depending on the nature of olefin.

The oxidation of alkylboranes with alkaline hydrogen peroxide proceeds with retention of configuration. A reasonable reaction path for these processes involves successive intra-molecular rearrangements of alkyl groups from boron to oxygen followed by hydrolysis [see Fig.1.1b].

The speciality of this sequence is that the final alcohol obtained is predominantly anti-Markovnikov, in contrast to the normal acid hydration of olefins which yields Markovnikov products. However, the initial addition of the elements of borane is according to Markovnikov, boron being more electropositive than hydrogen<sup>6</sup>. Thus terminal olefins like 1-hexene, 4,4-dimethyl-1-pentene, yield 94% 1-ol and only 6% 2-ol. The presence of an alkyl substituent in the 2-position increases this directive effect, 2-methyl-1-butene, and  $\alpha$ -methylstyrene yield 99% and 100% 1-ol respectively.

Furthermore the oxidation occurs with retention of configuration, placing the hydroxyl group at the precise

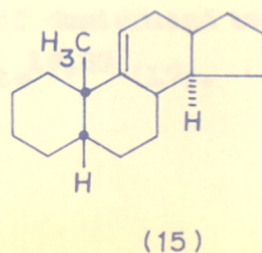
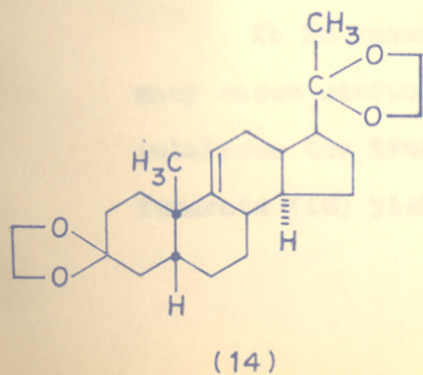
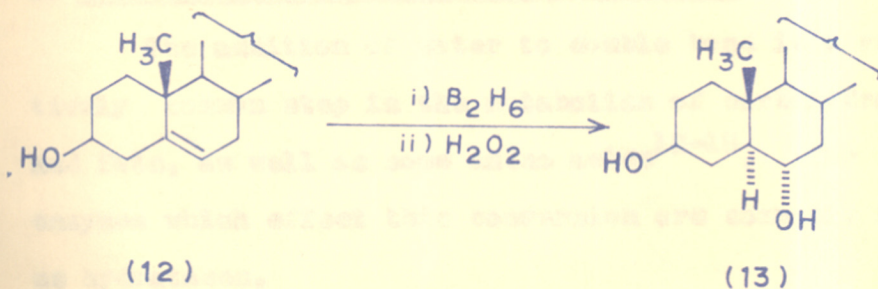
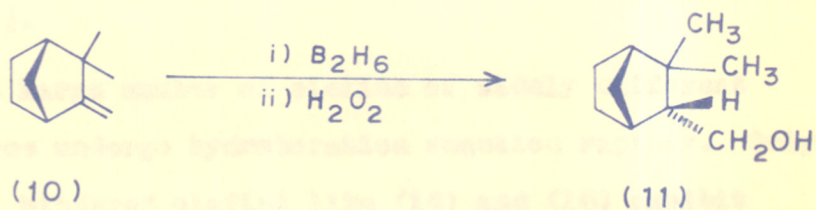
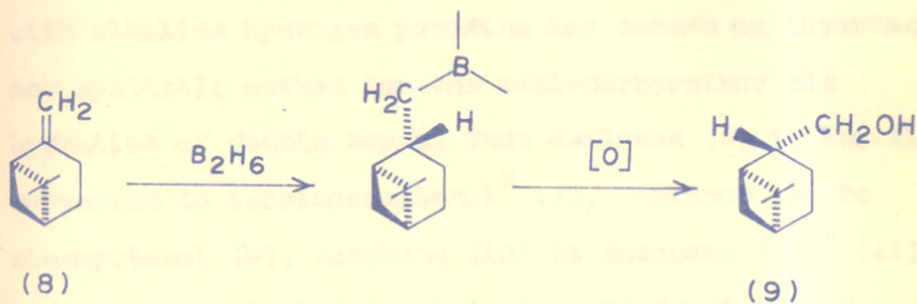
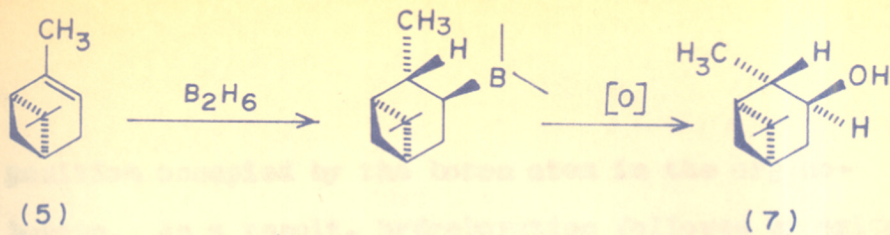


FIG. 1-2 HYDROXYLATION VIA HYDROBORATION

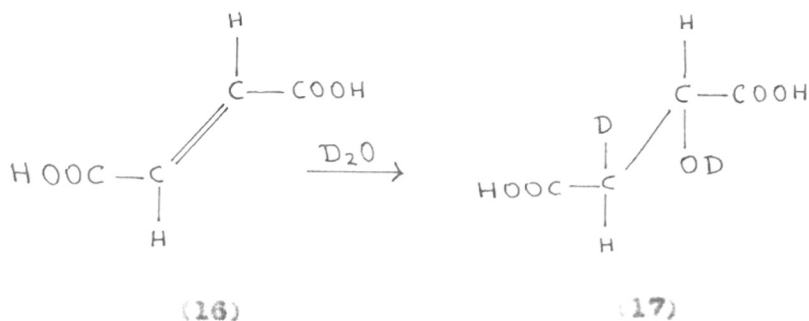
position occupied by the boron atom in the organo-borane. As a result, hydroboration followed by oxidation with alkaline hydrogen peroxide has become an important new synthetic method for the anti-Markovnikov cis hydration of double bonds. Thus  $\alpha$ -pinene (5) is readily converted to isopinocampheol<sup>7</sup> (7),  $\beta$ -pinene (8) to cis-myrtanol (9), camphene (10) to endocampheol<sup>9</sup> (11) and cholesterol (12) to cholestane-3 $\alpha$ -6 $\alpha$ -diol<sup>8</sup> (13) [Fig.1.2].

A large number of olefins of widely different structures undergo hydroboration reaction rapidly. Only the most hindered olefins like (14) and (15) exhibit resistance to hydroboration<sup>8,10</sup>.

### 3. Biological hydroxylation of double bond<sup>11</sup>

The addition of water to double bond is a relatively common step in the metabolism of carbohydrates and fats, as well as some amino acids<sup>12-18</sup>. The enzymes which effect this conversion are commonly known as hydratases.

It is known that the addition of water is in many cases stereospecific, for example fumarase [EC 4.2.1.2] catalyzes the trans-addition of deuterated water to fumarate (16) yielding  $\alpha$ -malate<sup>19,20</sup> (17).



Hydration of double bond is an important step in fatty acid oxidation<sup>21</sup> yielding secondary alcohols on the  $\beta$ -carbon of  $\alpha$ - $\beta$  unsaturated acid. The enzyme responsible for this conversion is enol hydratase.

However biological hydroxylation of double bond is rarely reported in synthetic work.

#### 4. Hydroxylation via oxymetallation<sup>22-24</sup>

Various methods for this conversion consist use of thallium (III), palladium (II) and mercury (II) salts, however oxymercuration<sup>25,26</sup> followed by sodium borohydride reduction is by far the most important.

Mercuric salts react in aqueous solution with olefins forming addition compounds; the groups  $\text{HgX}$  and  $\text{OH}$  entering the molecule at the point of unsaturation. The reactions of olefins with mercury salts proceed more



vigorously in alcoholic solution, with alcohol taking part in the reaction.



The mercury atom always attaches itself to the least substituted carbon atom. Thus oxymercuration-demercuration procedure leads to Markovnikov hydration of hydrocarbon alkenes<sup>27,28</sup> without rearrangement.

The stereochemistry of these additions depends upon the specific alkene undergoing the reaction; broadly they can be divided in two groups. The acyclic and monocyclic alkenes give trans addition product, whereas in bicyclic alkenes where double bond is sterically hindered to endo attack, cis addition product is obtained. Thus 2-methylene norbornene (18) gives 2-methyl-exo-norbornanol (19) in 93.5% yield. This preference for the formation of exo-alcohols increases as the steric hindrance to endo approach increases. This effect is similar to that observed in the lithium aluminum hydride reduction, of hindered ketones<sup>29</sup>. The oxymercuration-demercuration procedure shows a high degree of stereoselectivity in effecting substantially exo-hydration of norbornene (20), which yields more than 99.8% exonorbornanol (21) and

related compounds<sup>28</sup>.

### 5. Oxidation of olefins to yield $\alpha$ -glycols

There are four well known methods employed for this type of reaction.

- A] Potassium permanganate oxidation in alkaline medium, yielding cis-diols.
- B] Osmium tetroxide oxidation followed by hydrolysis, yielding cis-diols.
- C] Per-acid oxidation, usually yielding trans-diols.
- D] Iodine and silver carboxylates oxidation, yielding either cis or trans-diols, according to reaction conditions.

A] Potassium permanganate oxidation is a widely used method for cis hydroxylation of olefins, but needs careful control to avoid over-oxidation. Best results are obtained in alkaline solution, using water or aqueous organic solvents [acetone, ethyl alcohol or t-butanol]. In acid or neutral solutions  $\alpha$ -ketols or even cleavage products are formed. The method is specially suitable for the hydroxylation of unsaturated acids, which dissolve in the alkaline medium.

The reaction proceeds through the cyclic manganese esters. Thus cyclohexene (22) yields cis-1,2-cyclohexane-diol (23).

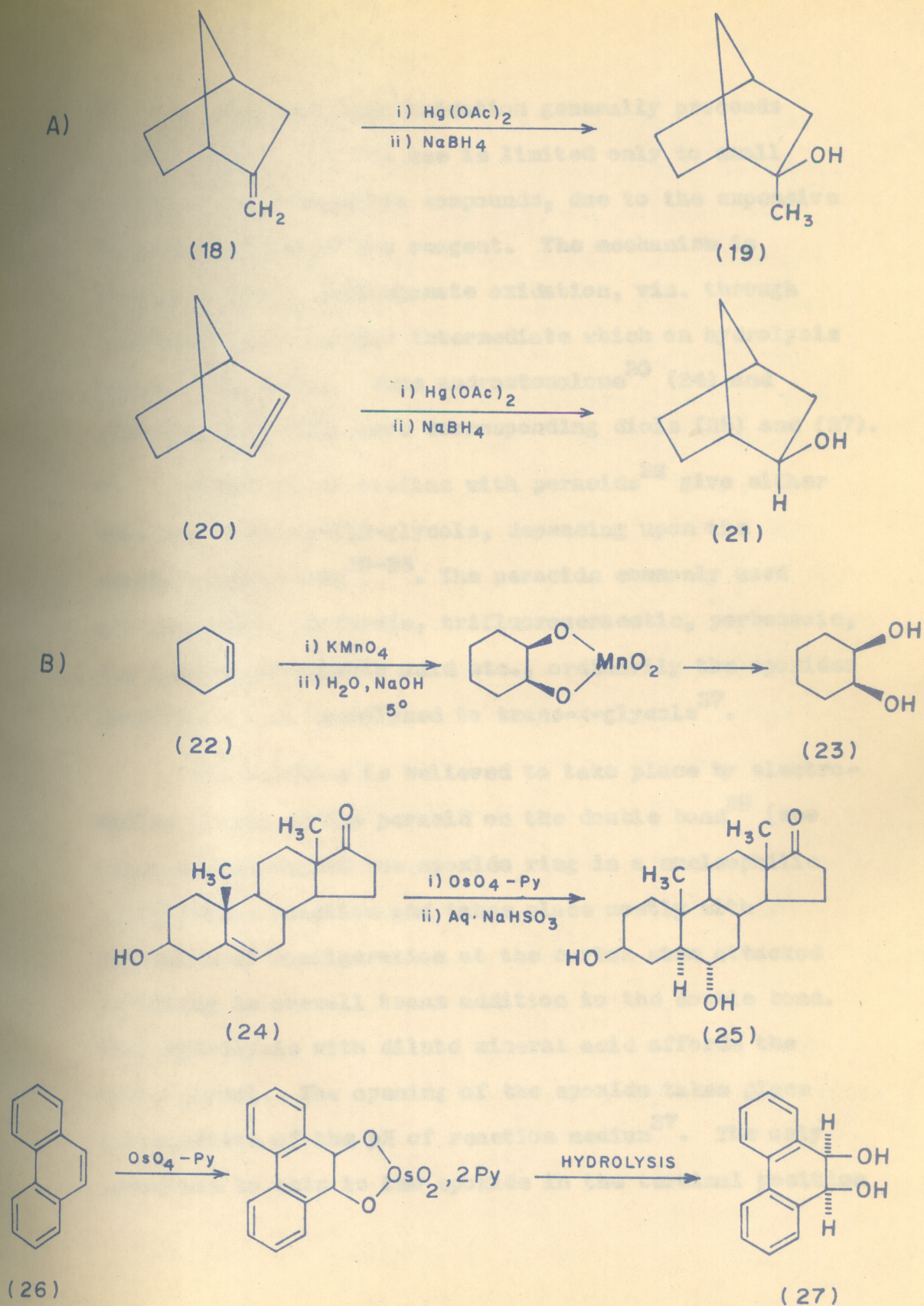


FIG. 1.3 A) HYDROXYLATION VIA OXYMERCURATION  
B) OXIDATION OF OLEFINS TO YIELD *cis*- $\alpha$ -GLYCOLS

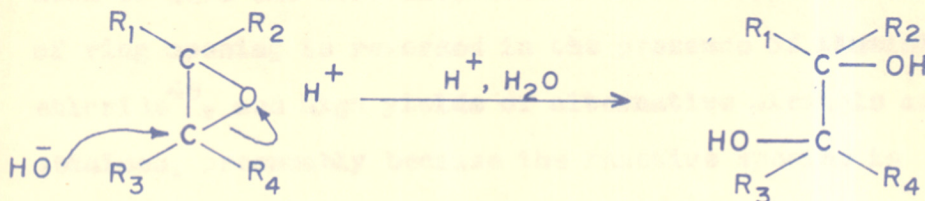
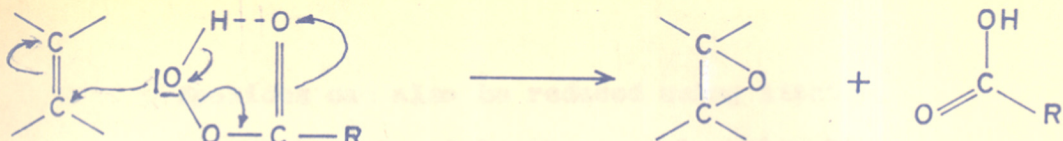
B] Osmium tetroxide oxidation generally proceeds in high yields, but its use is limited only to small scale work with valuable compounds, due to the expensive and toxic nature of the reagent. The mechanism is analogous to the permanganate oxidation, viz. through the formation of cyclic intermediate which on hydrolysis yields  $\alpha$ -cis diols. Thus androstenedione<sup>30</sup> (24) and phenanthrene<sup>31</sup> (26) gave corresponding diols (25) and (27).

C] Oxidation of olefins with peracids<sup>32</sup> give either epoxides or trans-1,2-glycols, depending upon the reaction conditions<sup>33-36</sup>. The peracids commonly used are peracetic, performic, trifluoroperacetic, perbenzoic, and *m*-chloroperbenzoic acid etc., ordinarily the epoxides isolated can be hydrolyzed to trans- $\alpha$ -glycols<sup>37</sup>.

The reaction is believed to take place by electrophilic attack of the peracid on the double bond<sup>38</sup> [see Fig.1.4], opening of the epoxide ring is a nucleophilic substitution reaction and takes place mostly with inversion of configuration at the carbon atom attacked resulting in overall trans addition to the double bond. Thus hydrolysis with dilute mineral acid affords the trans glycol. The opening of the epoxide takes place irrespective of the pH of reaction medium<sup>37</sup>. The only exception to this is the epoxide in the terminal position

of the aliphatic chain<sup>39,40</sup>. In accordance with this overall mechanism, the rate of epoxidation is increased by electron withdrawing groups in the peracids or electron donating groups on the double bond; thus trifluoroperacetic acid is more reactive than peracetic acid and terminal mono-olefins react only slowly with most peracids, but the rate of reaction increases with the degree of alkyl substitution. Epoxidation proceeds by cis addition to the double bond<sup>37,41</sup>. It has been shown by Witnauer and Swern<sup>42</sup> that oleic acid and oleil alcohol (both cis olefins), yield cis-9,10-epoxystearic acid and cis-9,10-epoxyoctadecanol, respectively, and the corresponding trans olefins, e.g. elaidic acid and elaidyl alcohol, yield trans-9,10-epoxystearic acid and trans-9,10-epoxyoctadecanol respectively, when treated with peracetic or perbenzoic acids.

In accordance with latter step of mechanism, the opening of 1-methylcyclopentene epoxide (28) yields trans-1-methylcyclopentan-1,2-diol (29). In conformationally rigid cyclohexane derivatives trans-diaxial alcohols rather than trans-diequatorial ones predominate. Thus, 2,3-epoxy, trans-decalin (30) gives a 90% yield of trans-diaxial diol (31).



Example

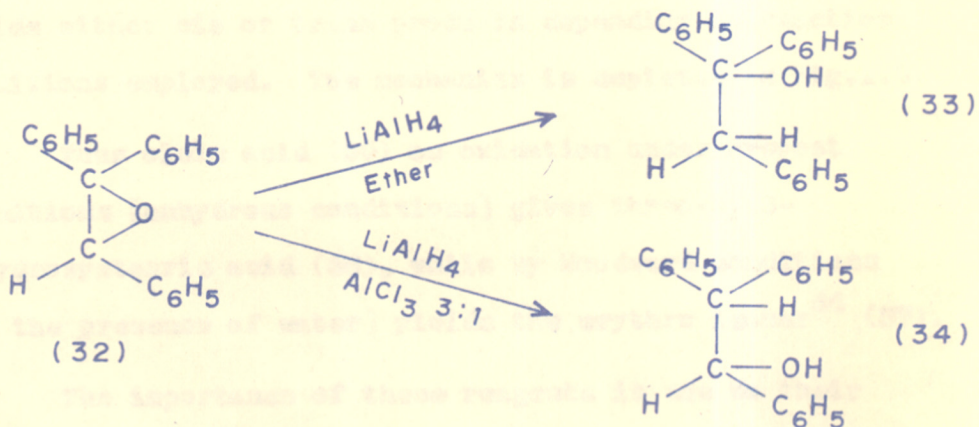
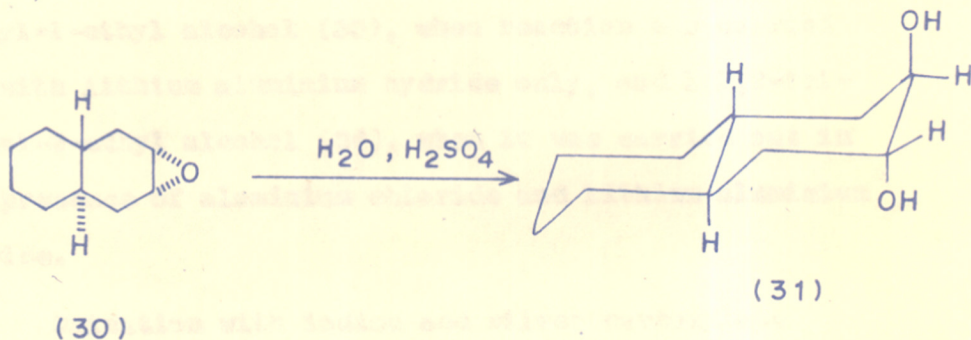


FIG. 1.4 HYDROXYLATION OF OLEFINS VIA EPOXIDATION

Epoxides can also be reduced using lithium aluminium hydride, to yield the monoalcohols. The reaction takes place at the least substituted carbon atom to give the more substituted carbinol. This mode of ring opening is reversed in the presence of aluminium chloride<sup>43</sup>, and high yields of alternative alcohols are obtained, presumably because the reactive species is now the electrophilic aluminium hydride formed in situ. Thus triphenylethylene epoxide (32), yielded 1,1,2-triphenyl-1-ethyl alcohol (33), when reaction was carried out with lithium aluminium hydride only, and 1,1,2-triphenyl-2-ethyl alcohol (34), when it was carried out in the presence of aluminium chloride and lithium aluminium hydride.

2] Oxidation with iodine and silver carboxylates yields either cis or trans products depending on reaction conditions employed. The mechanism is depicted in Fig.1.5.

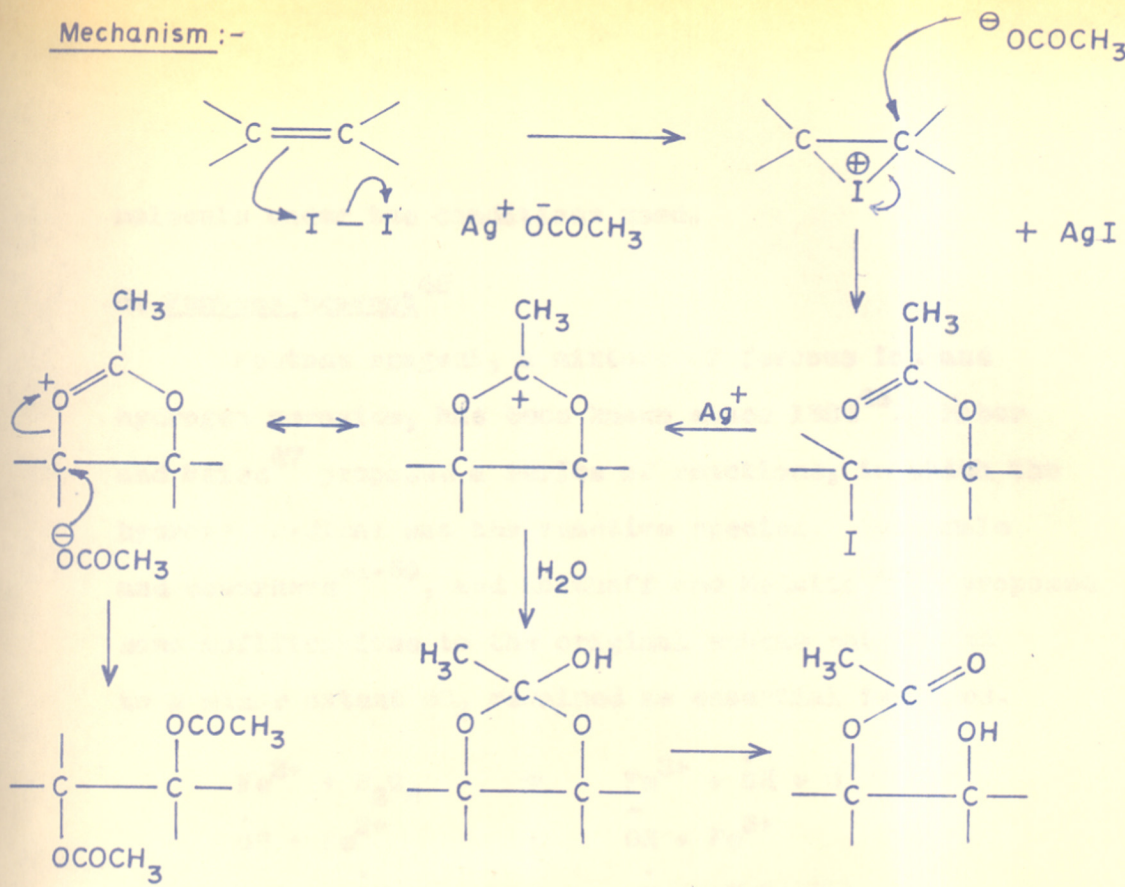
Thus oleic acid (35) on oxidation under Prevost conditions [anhydrous conditions] gives threo-9,10-dihydroxystearic acid (36), while by Woodward conditions [in the presence of water] yields the erythro isomer<sup>44</sup> (37).

The importance of these reagents is due to their specificity and to the mildness of the reaction conditions; free iodine hardly affects other sensitive groups in the

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Mechanism :-



Example :-

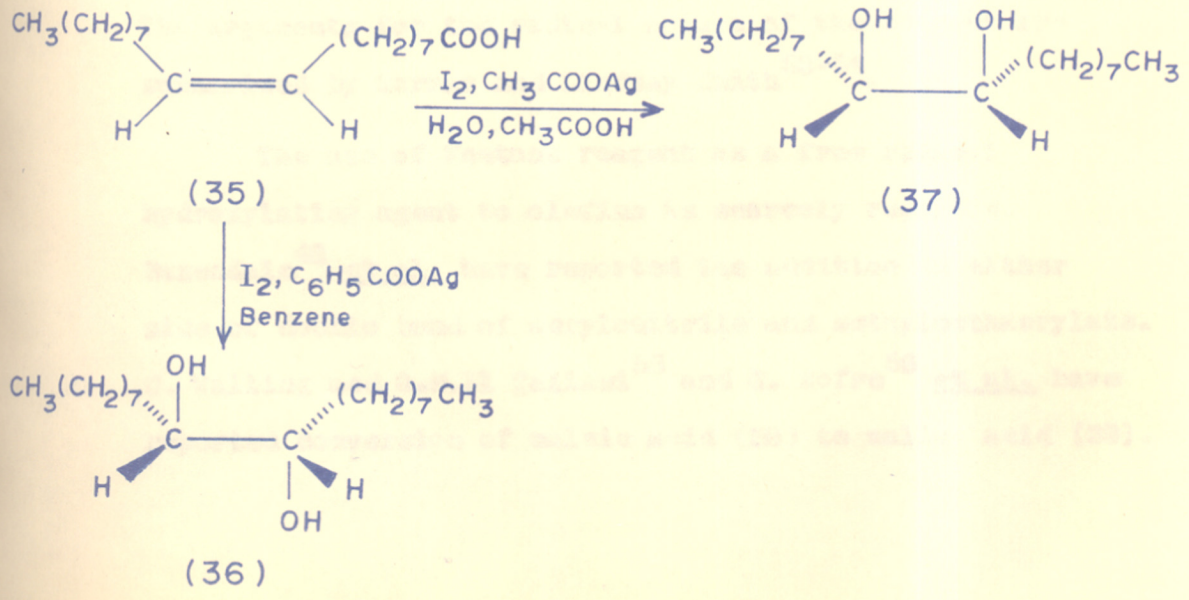


FIG. 1.5 OXIDATION WITH IODINE AND SILVER CARBOXYLATE



molecule under the conditions used.

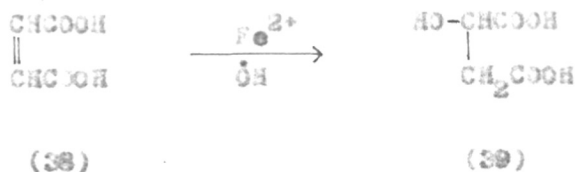
### 6. Fentons Reagent<sup>45</sup>

Fentons reagent, a mixture of ferrous ion and hydrogen peroxide, has been known since 1894<sup>46</sup>. Haber and Weiss<sup>47</sup> proposed a series of reactions, in which the hydroxyl radical was the reactive species. Maxendale and coworkers<sup>48-50</sup>, and Kolthoff and Medalia<sup>51-52</sup> proposed some modifications to the original scheme but  $\dot{\text{O}}\text{H}$  and to a minor extent  $\dot{\text{O}}_2$  remained as essential features.



The arguments for the radical nature of the reagent are summarized by Norman and Lindsay Smith<sup>53-54</sup>.

The use of Fentons reagent as a free radical hydroxylating agent to olefins is scarcely reported. Maxendale<sup>48</sup> et al. have reported the addition on either side of double bond of acrylonitrile and methylmethacrylate. C. Walling and G.M.El Taliawi<sup>55</sup> and C. Nofre<sup>56</sup> et al. have reported conversion of maleic acid (38) to malic acid (39).



However, it is widely used for the hydroxylation of aromatic<sup>57-61</sup> and heterocyclic<sup>62,63</sup> compounds.

7. Photoinduced hydroxylation in aqueous solutions in the presence of sensitizers<sup>64</sup>

Marshall and Hochstetler<sup>65</sup> have reported 1-methylcyclohexene (40) and 1-methene (43) yielding corresponding tertiary alcohols (41) and (44) along with isomeric olefins (42) and (45), under irradiation in the presence of sensitizers. Acyclic olefins, exocyclic olefins cyclopentenes, cyclooctenes and larger ring olefins fail to undergo analogous addition and isomerization reactions. It was suggested<sup>64</sup> that these addition and isomerization reactions proceed by way of a common cationic intermediate derived from the triplet state of the cycloalkene. These reactions were observed in the case of octalins also. Thus deuterated octalin (46) in aqueous t-butyl alcohol-xylene mixture<sup>66</sup> gave axially deuterated alcohols (47), 22% and (48), 17% along with axially deuterated exocyclic olefin (49), 61%.

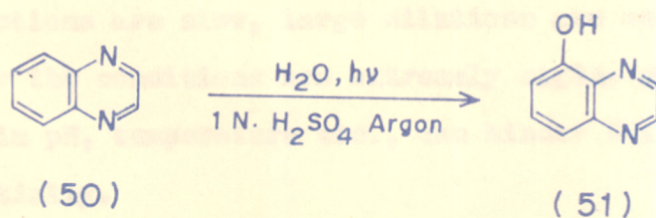
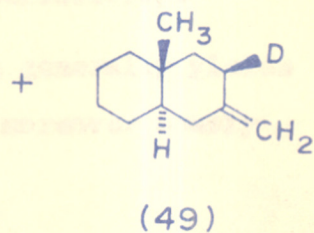
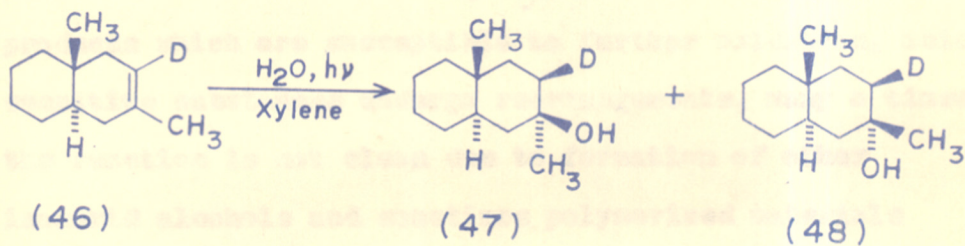
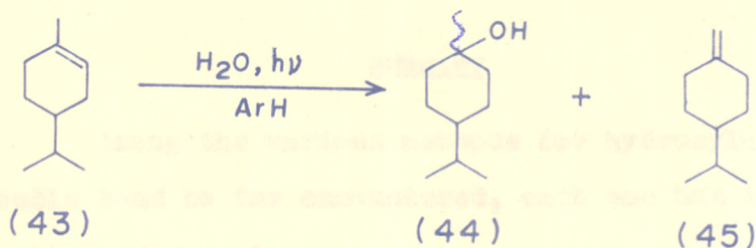
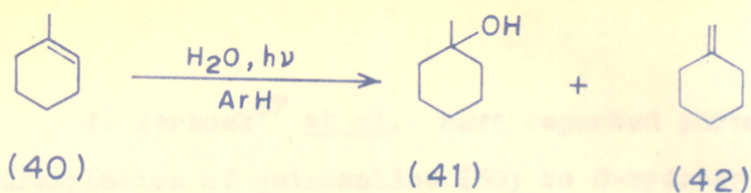


FIG. 1.6 PHOTOINDUCED HYDROXYLATION IN AQUEOUS SOLUTIONS IN THE PRESENCE OF SENSITIZERS

J. Verbeck<sup>57</sup> et al. have reported photosensitized hydroxylation of quinoxaline (50) to 5-hydroxy quinoxaline (51).

#### SUMMARY

Among the various methods for hydroxylation of double bond so far encountered, each one has its own merits and demerits.

Hydroxylation with aqueous mineral acids yields products which are susceptible to further oxidation, acid-sensitive substances undergo rearrangements, many a times the reaction is not clean due to formation of other isomeric alcohols and sometimes polymerized materials also. The reaction also lacks stereoselectivity.

Hydroxylation via hydroboration generally yields products, which are anti-Markovnikov, moreover costly reagents are required.

Biological hydroxylations are extremely specific, and a particular enzyme attacks only a particular substrate. The reactions are slow, large dilutions are encountered, moreover the conditions are extremely rigid, even a slight change in pH, temperature etc., can hinder the reaction substantially.

Potassium permanganate oxidation needs very careful control to avoid overoxidation resulting in some other products like ketones. Osmium tetroxide is toxic and costly, making a large scale use very expensive. These two reagents along with per acids yield  $\alpha$ -glycols and hence are of little use when monoalcohols are required.

Hydroxyl radical addition to olefins yielding alcohols is the basis of Fentons reagent. However this reaction remains neglected in the case of olefins. The reported photoinduced hydroxylations in aqueous solutions in the presence of sensitizers are confined only to particular ring sized olefins and only tertiary alcohols in low conversions are obtained. Photoinduced hydroxylation of olefins is also rarely reported in literature, which we propose to study in details. The next Chapter contains the results of cyclohexene and 1-methylcyclohexene hydroxylation using hydroxyl radicals generated in situ from hydrogen peroxide under UV irradiation, with a brief review of earlier work pertaining to the topic under investigation.

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CHAPTER II

PHOTOINDUCED HYDROXYLATION OF CYCLOHEXENE  
AND 1-METHYLCYCLOHEXENE

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### Free radical addition to olefins

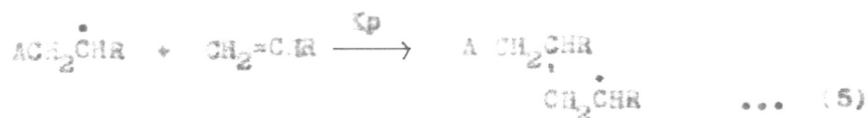
The free radical addition to olefins is known for quite a long time. In 1937, Kharasch<sup>1</sup> and coworkers and May and Waters<sup>2</sup> simultaneously reported the "anti-Markovnikov" addition of hydrogen bromide to unsymmetrical olefins in the presence of ultra-violet light or peroxides.

Addition of a reagent AB across the unsaturated linkage of an alkene  $RCH=CH_2$  in a free-radical reaction consists of two chain propagating steps, one an addition reaction [equation 1], and other a displacement reaction [equation 2].



In free-radical additions, the displacement (or abstraction) reaction is often referred to as the chain transfer-step. The free radical chemistry of the adduct radical with both the alkene and the adding reagent will dictate largely what the distribution of products will be in the addition of a given reagent to a given unsaturated linkage. The reactivity ratio,  $k_{tr}/k_p$ , referred to as the chain transfer constant, is a measure of the reactivity of the addition reagent with respect to the unsaturated

compound toward reaction with the adduct radical.



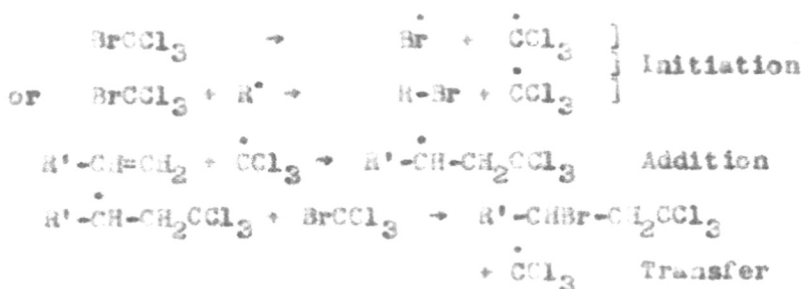
An adding reagent-unsaturated system with a high chain-transfer constant ( $K_{tr}/K_p > 10$ ) results in high yields of the simple 1:1 addition product, whereas a system with a low chain-transfer constant ( $K_{tr}/K_p < 1$ ) will give mainly telomeric products. The ideal situation in addition reaction for formation of simple 1:1 addition product would be one in which the chain transfer constant ( $K_{tr}/K_p$ ) is considerably greater than unity.

#### Chemistry of Adding Reagents

A. Polyhalomethanes: In 1947, Kharasch<sup>3</sup>, Jensen and Urry reported the addition of number of halomethanes, namely  $CCl_4$ ,  $CH_2Br_2$ ,  $CHBr_3$ ,  $CHCl_3$  to olefins such as 1-octene, styrene and ethylene. This work has led to extensive study on the addition of halomethanes to olefins in general and has proved to be of great theoretical interest and wide synthetic applications.

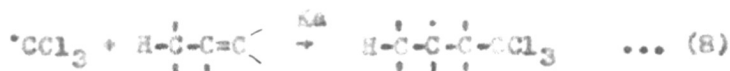
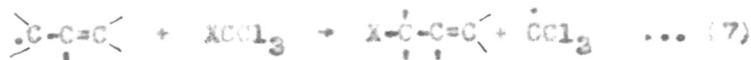
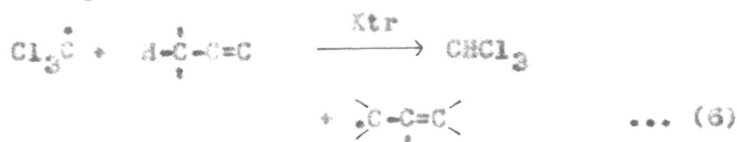
The mechanism operative in the addition of bromo-trichloromethane, which is typical of this group of reactions

is given below:



The yields of the simple addition product are very high in the reactions of bromotrichloromethane with alkenes indicating that the abstraction of bromine atom from this polyhalomethane is more facile than abstraction of chlorine from carbon tetrachloride.

One of the serious side reactions, aside from telomer formation, that occurs in the reaction of  $\text{CCl}_4$  and  $\text{BrCCl}_3$  with alkenes is halogenation of the allylic position of the molecule by the chain sequence shown below in equations 6-8.



Abstraction of an allylic hydrogen by the trichloromethyl

radical competes with the addition of this radical to the unsaturated linkage. The relative reactivity ratio  $K_a/K_{tr}$ , a measure of the relative amount of addition and allylic hydrogen abstraction by the trichloromethyl radical has been determined for several alkenes using  $BrCCl_3$ <sup>4,5</sup>.

TABLE 2.1 - Relative reactivities of double bonds with respect to Allylic Hydrogens toward reaction with trichloromethyl radicals.

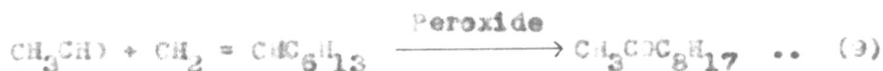
Alkene	Temperature °C	$K_a/K_{tr}$
1-Octene	77.8	44
1-Decene	77.8	48
2-Pentene	77.8	5.7
3-Heptene	77.8	3.5
3-Heptene	40.0	5.0
4-Methyl-2-pentene	77.8	1.26
4-Methyl-2-pentene	40.0	1.68
cis-2-butene	99.0	34.00
trans-2-butene	99.0	26.00
Cyclohexene	77.8	1.20
Cyclopentene	77.8	5.4
Cycloheptene	77.8	5.5

The data in Table 2.1 show that allylic hydrogen abstraction occurs more readily with non-terminal alkenes where the addition is slow because of steric effects. Furthermore, the reactivities of allylic hydrogens increases in the order primary << secondary < tertiary as evidenced by the reactivity ratios noted for cis- and trans- 2-butenes, 2-pentene and 4-methyl-2-pentene, all of which should be about equally reactive towards addition by the trichloromethyl radical but have primary, secondary and tertiary allylic hydrogens respectively available for abstraction. Conformational effects must also play a role in determining either the addition or abstraction reactions of cycloalkenes. The temperature effect indicates that allylic hydrogens of non-terminal alkenes could be suppressed by performing the reactions at low temperatures.

### B. Aldehydes, Ketones and Alcohols

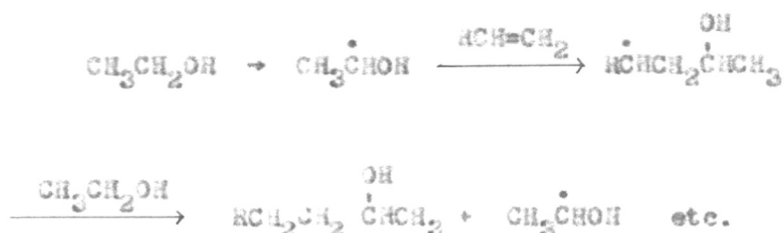
Free-radical additions of aldehydes to unsaturated compounds yield ketones. For example, the peroxide induced reaction of acetaldehyde with 1-octene yields 2-decanone in a chain sequence involving addition of an acetyl radical to the alkene yielding an adduct radical which abstracts the aldehyde hydrogen from the aldehyde<sup>6</sup>.





Ketones do not add homolytically to olefins generally. It appears that cyclohexanone is the most reactive ketone in this sense. It reacts with 1-octene to give 2-octylcyclohexanone<sup>7</sup>.

The radical-induced addition of primary and secondary alcohols to olefins results in the formation of secondary and tertiary alcohols<sup>7</sup> respectively.

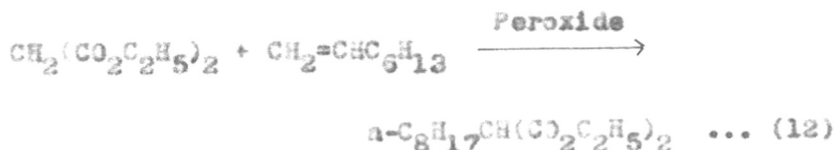


The transfer constants for such reactions are small and extreme conditions of dilutions are necessary in order to produce radical chains leading to low molecular weight products.

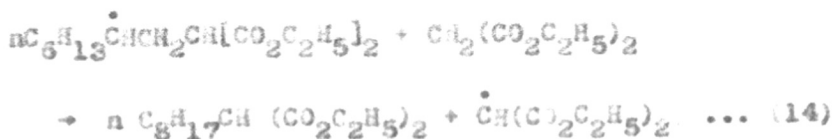
### C. Esters and Acids

Esters and acids can be alkylated in the  $\alpha$ -position by free-radical addition to an appropriate

alkene<sup>8,9</sup>. The peroxide induced addition of malonic ester to 1-octene yielding n-octyl malonic ester is illustrative of this reaction.



via



Ester-alkene combinations have fairly high chain-transfer constants in part because of a favourable resonance contribution in the displacement reaction due to the stabilizing effect of a carbonyl function. The alkylation of free acids in the  $\alpha$ -position also proceeds by a similar free-radical chain reaction.

#### Orientation of Free-radical Addition

Generally in the radical-chain additions to olefins of the type  $\text{RC}=\text{CH}_2$ , the point of initial attack has been found mostly at the terminal  $\text{CH}_2$  group. This specificity has generally been explained on the basis of

the greater stability of the intermediate radical  $\text{R}\dot{\text{C}}\text{HCH}_2\text{Y}$  formed by addition of the radical  $\text{Y}\cdot$  to the olefin, compared with that of  $\text{RCHY}\dot{\text{C}}\text{H}_2$ <sup>10</sup>. The polar and steric factors have been considered to be less important.

Important contributions to our knowledge of the problem of the orientation in free radical reactions have been made by Hasseldine<sup>11</sup> and his co-workers, who demonstrated the relative unimportance of the polarization of the double bond in  $\text{RCH}=\text{CH}_2$  (where  $\text{R} = \text{CF}_3, \text{CN}, \text{CH}_3, \text{F}, \text{Cl}$  and  $\text{COOCH}_3$ ); in determining the point of attack by trifluoromethyl radical or bromine atom<sup>11</sup>. It has been assumed that the main factor is the relative stability of the two possible radicals. The tertiary radicals are more stable than secondary which in turn are more stable than primary, viz.  $\text{R}_3\dot{\text{C}} > \text{R}_2\dot{\text{C}}\text{H} > \text{R}\dot{\text{C}}\text{H}_2$ .

#### Stereochemistry of Radical-addition Reactions

The preferred mode of addition by radicals has been shown to be trans. Skell<sup>12</sup> studied the addition of deuterium bromide to cis- and trans-2-butenes (1 and 3 respectively) at  $-80^\circ\text{C}$  and from the fact that he obtained the threo (2) product from the former and the erythro (4) product from the latter concluded that DBr had added trans to the double bond.

The homolytic additions of HBr to 1-chloro-, 1-bromo

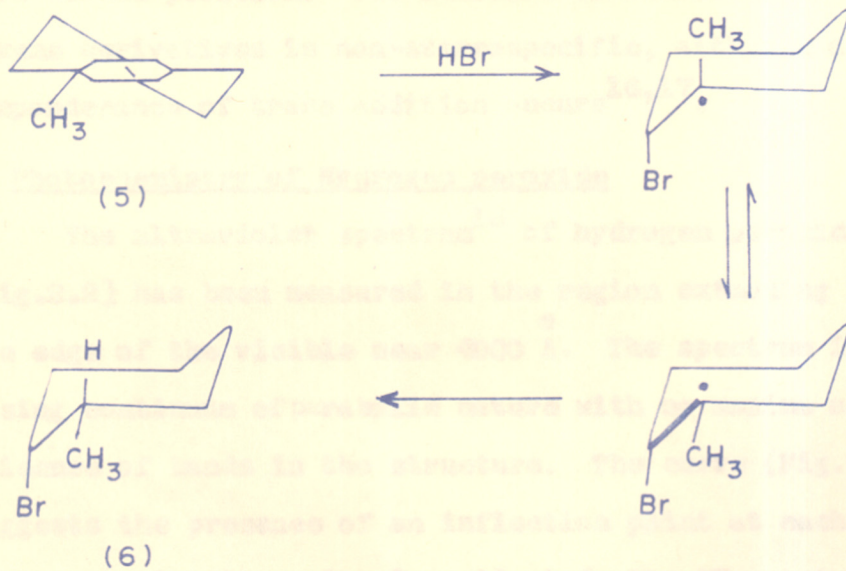
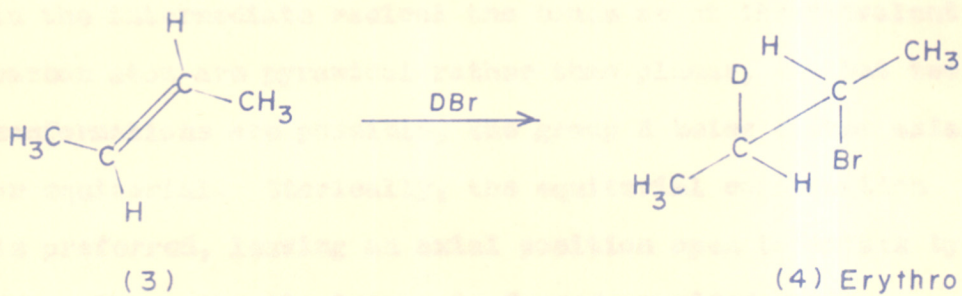
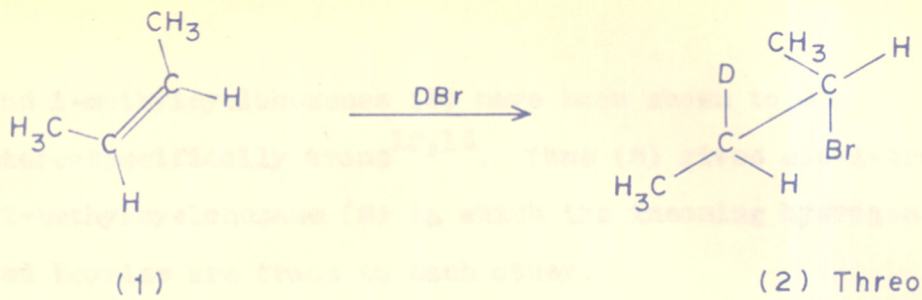


FIG. 2.1 STEREOCHEMISTRY OF RADICAL ADDITION REACTIONS

and 1-methylcyclohexenes (5) have been shown to be stereospecifically trans<sup>13,14</sup>. Thus (5) gives cis-1-bromo-2-methylcyclohexane (6) in which the incoming hydrogen and bromine are trans to each other.

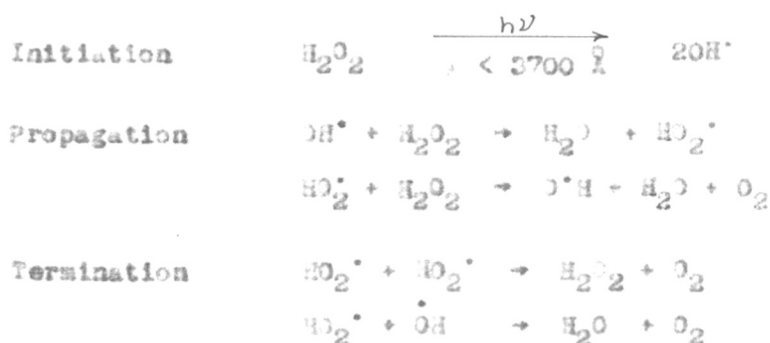
It has been suggested by Brand and Stevens<sup>15</sup> that in the intermediate radical the bonds about the trivalent carbon atom are pyramidal rather than planar, so that two conformations are possible, the group R being either axial or equatorial. Sterically, the equatorial conformation is preferred, leaving an axial position open to attack by HBr. Thus, the cis isomer is formed provided chain transfer occurs before ring inversion, for such inversion would place the bromine atom in the thermodynamically more stable position. The addition of thiols to cyclohexene derivatives is non-stereospecific, although a preponderance of trans addition occurs<sup>16,17</sup>.

## 2) Photochemistry of Hydrogen peroxide

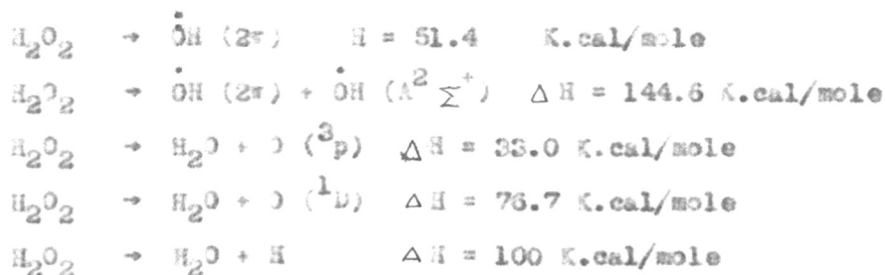
The ultraviolet spectrum<sup>18</sup> of hydrogen peroxide [Fig.2.2] has been measured in the region extending from the edge of the visible near 4000 Å. The spectrum is a rising continuum of parabolic nature with no maxima and evidence of bands in the structure. The curve [Fig.2.2] suggests the presence of an inflection point at each end of the wavelength region investigated. The UV spectrum of

hydrogen peroxide in aqueous and vapour phase shows a considerable similarity.

Based on photolysis studies Minton and Rowbottom<sup>19</sup> have proposed the following reaction sequence for hydrogen peroxide.



Independent studies of the vapour phase<sup>20</sup> and aqueous<sup>21</sup> solution photodecomposition of hydrogen peroxide at 2537 Å have shown that at relatively high intensities and low peroxide concentrations, the chain reaction may be suppressed. Volman<sup>22</sup> has proposed the following primary process for the photodecomposition of hydrogen peroxide.



While reviewing the photochemistry of hydrogen peroxide,

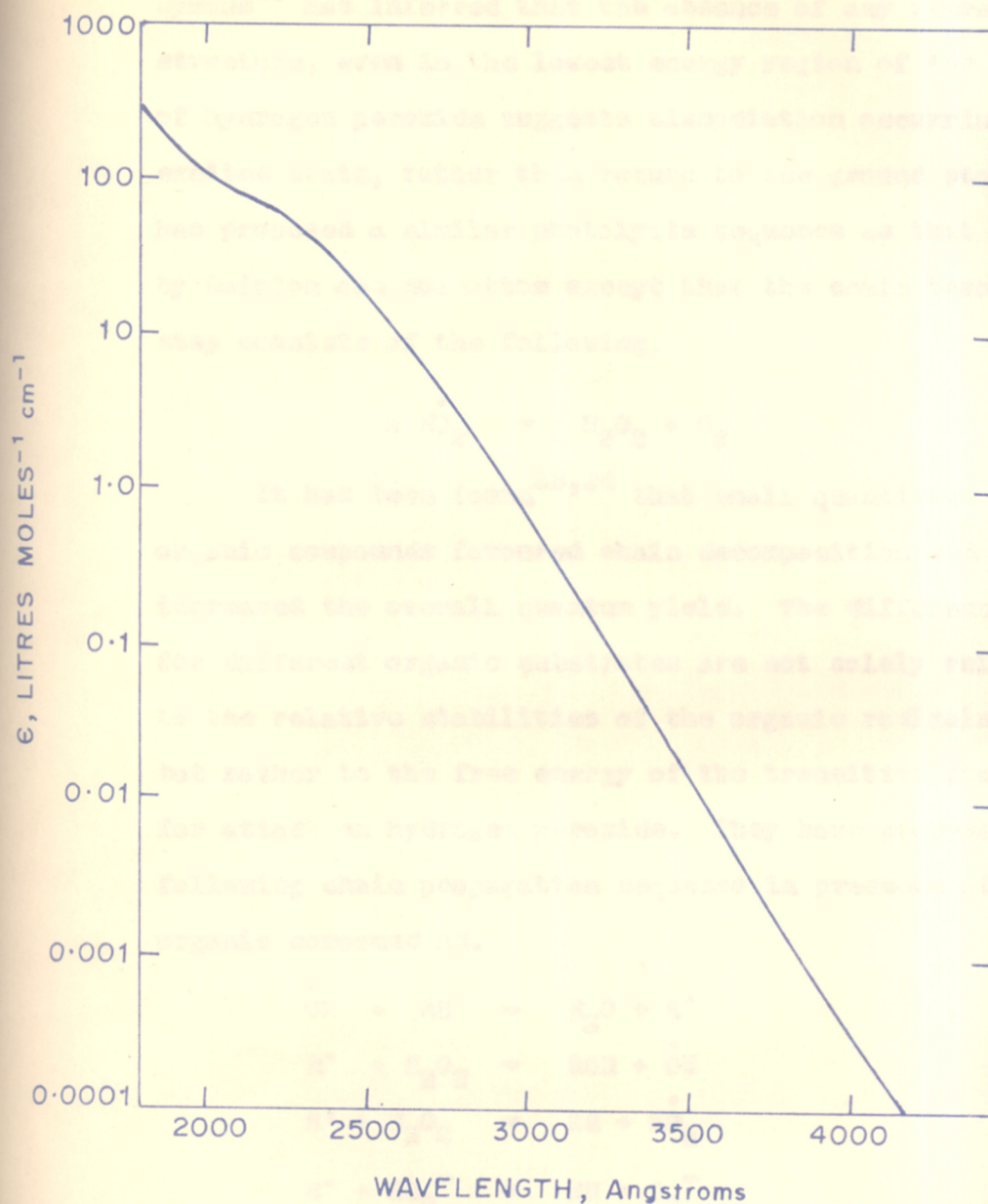


FIG. 2.2 UV ABSORPTION SPECTRUM OF HYDROGEN PEROXIDE  
(COMPOSITE CURVE BASED ON MEASUREMENTS ON  
NEAT LIQUID, AQUEOUS SOLUTION AND VAPOR  
 $\epsilon = \log (I_0/I) C^{-1} L^{-1}$  LITRES MOL<sup>-1</sup> CM<sup>-1</sup>)

Symons<sup>23</sup> has inferred that the absence of any vibrational structure, even in the lowest energy region of the spectrum of hydrogen peroxide suggests dissociation occurring in the excited state, rather than return to the ground state. He has proposed a similar photolysis sequence as that suggested by Dainton and Howbottom except that the chain termination step consists of the following.



It has been found<sup>23,24</sup> that small quantities of some organic compounds favoured chain decomposition and thus increased the overall quantum yield. The difference found for different organic substrates are not solely related to the relative stabilities of the organic radicals produced, but rather to the free energy of the transition state for attack on hydrogen peroxide. They have proposed the following chain propagation sequence in presence of an organic compound RH.



#### Properties and reactions of hydroxyl radical

The OH radical is a strong oxidizing agent<sup>25</sup> [E<sup>o</sup> = +2V] and it behaves as a weak acid<sup>26,27</sup>, pKa = 11.9, its protonation to give H<sub>2</sub>O<sup>+</sup> has been suggested and a pKa < 0 proposed<sup>28</sup>. The



reactions of  $\text{OH}^\cdot$  and  $\text{O}^\cdot$  radicals with aliphatic molecules and ions are similar but the rate constants of  $\text{O}^\cdot$  are generally lower. They show distinct differences in their reactions with aromatic and olefinic compounds<sup>29-31</sup>. The rate of addition of  $\text{OH}^\cdot$  is much higher than that of  $\text{O}^\cdot$ , whereas the rates for hydrogen atom abstraction are comparable. The reactions of hydroxyl radical can be classified in four different types<sup>32</sup>.

- 1) Addition to aromatic or unsaturated aliphatic compounds to form a hydroxy adduct free radical.
- 2) Hydrogen abstraction to form water, and a free radical.
- 3) Electron transfer from ions to form ionic products in a higher valance state and
- 4) A reaction with other  $\text{OH}^\cdot$  or different free radicals in a process of dissociation or disproportionation.

Milas Reaction: In 1937 Milas<sup>33</sup> and co-workers first reported addition of hydroxyl radicals derived from hydrogen peroxide under UV irradiation to unsaturated compounds. They used 10% hydrogen peroxide and converted allyl alcohol into glycerol, crotonic acid into hydroxybutyric acid and maleic acid into mesotartaric acid without using any solvent. The reaction periods were as high as 160-170 hours.

Later, Volman and Chen<sup>34</sup> reported irradiation of allyl alcohol in the presence of hydrogen peroxide to yield 1,2- and 1,3-propane diols along with glycerol and 2,3-dihydroxymethyl-1,4-butanediol. Unfortunately this important reaction remained neglected for quite a long time and only in late fifties interest of some workers revived but their work remained confined only to aromatic compounds<sup>35-39</sup>. Norman and Badda<sup>37</sup> reported hydroxylation of fluorobenzene in all the three isomeric positions, the ratio ortho:meta:para being 37:18:45 respectively; but anisole gave only ortho and para isomers in the ratio 84:16 respectively. Omura and Matsuura<sup>38</sup> found that ultraviolet irradiation mixtures of phenols and hydrogen peroxide in aqueous solutions gave predominantly ortho- dihydroxy compounds, small quantities of para-derivatives were also formed but there was no substitution meta to existing group. p-Carboxy and p-methoxy-phenols gave hydroquinones in addition to the usual catechol derivatives.

The incorporation of hydroxy radicals into olefins to give new radicals has been established by many workers using E.S.R.<sup>40,41</sup> and mass spectral<sup>44</sup> techniques. Griffiths<sup>40</sup> et al. obtained E.S.R. spectra attributable to radicals formed by the primary addition of hydroxyl radicals to olefins

Mass and Volman<sup>42</sup> proved abstraction of  $\alpha$ -hydrogen from alcohols in alcohol-hydrogen peroxide mixture by hydroxy radicals produced in primary reaction to yield hydroxy allylic radicals. Hydrogen abstraction by hydroxy radicals is also reported by Ichikawa and Kawata<sup>43</sup>. Morris<sup>44</sup> et al. reported m/e signals attributable to olefin + OH adduct derived from reaction between hydroxyl radical and ethylene, propylene and acetaldehyde in a discharge flow system.

Davis<sup>45</sup> et al. reported the formation of the hydroxy aromatic compounds, in the kinetic study of the hydroxyl radicals with aromatic substrates.

The literature survey revealed that a very little work has been reported on the free radical additions of hydroxyl radicals to olefins as compared to the similar studies with other radicals and a systematic study is lacking. Since hydroxylation is an important reaction both from theoretical and preparative point of view, it was considered worthwhile to carry out a systematic study of this reaction using alicyclic olefins as substrates. The hydroxyl radicals were generated in situ by the photodecomposition of concentrated hydrogen peroxide.

Present work: Cyclohexene and 1-methylcyclohexene were selected as model compounds to study the photoinduced hydroxylation in the presence of hydrogen peroxide under UV irradiation and the results of these experiments are described in the following paragraphs.

Results:

A. Cyclohexene - Hydrogen peroxide

A solution of cyclohexene and hydrogen peroxide in acetonitrile was irradiated under nitrogen atmosphere till the disappearance of  $H_2O_2$ . The reaction product obtained in 80% conversion (based on  $H_2O_2$ ) was found to be a mixture of four components by GLC [Fig.2.3]. The major components corresponding to peak numbers one [53%] and three and four together [29%] were isolated in the pure form by preparative GLC. While the component corresponding to peak number two could not be isolated in sufficiently pure form and hence its characterization was difficult. However mixed GLC indicated that this component was not cyclohexanone. The component corresponding to peak number one was characterized as cyclohexanol from its spectral data and through comparison with authentic sample. The components corresponding to peak numbers 3 and 4 were collected together and on the basis of its spectral data was assigned the structure as

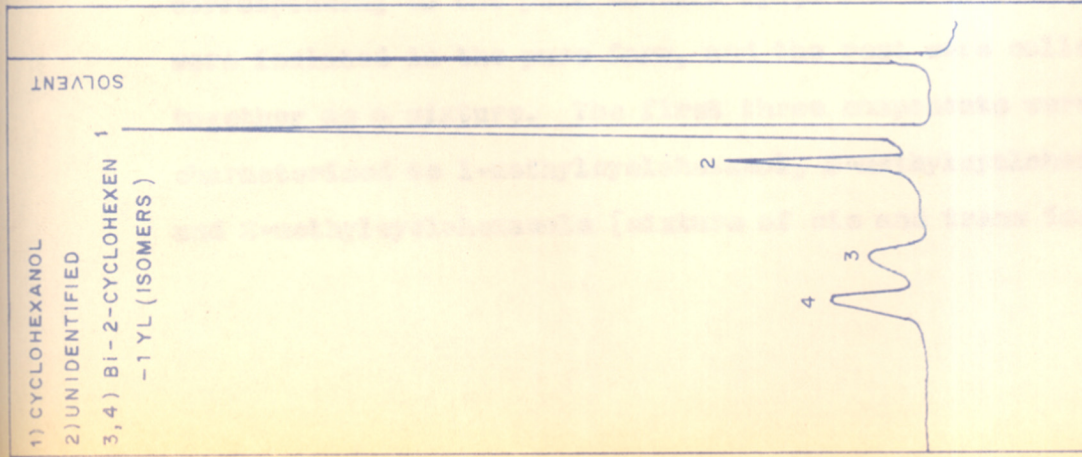


FIG. 2.3 GLC OF CYCLOHEXENE - H<sub>2</sub>O<sub>2</sub> REACTION PRODUCT

FIG. 2.3

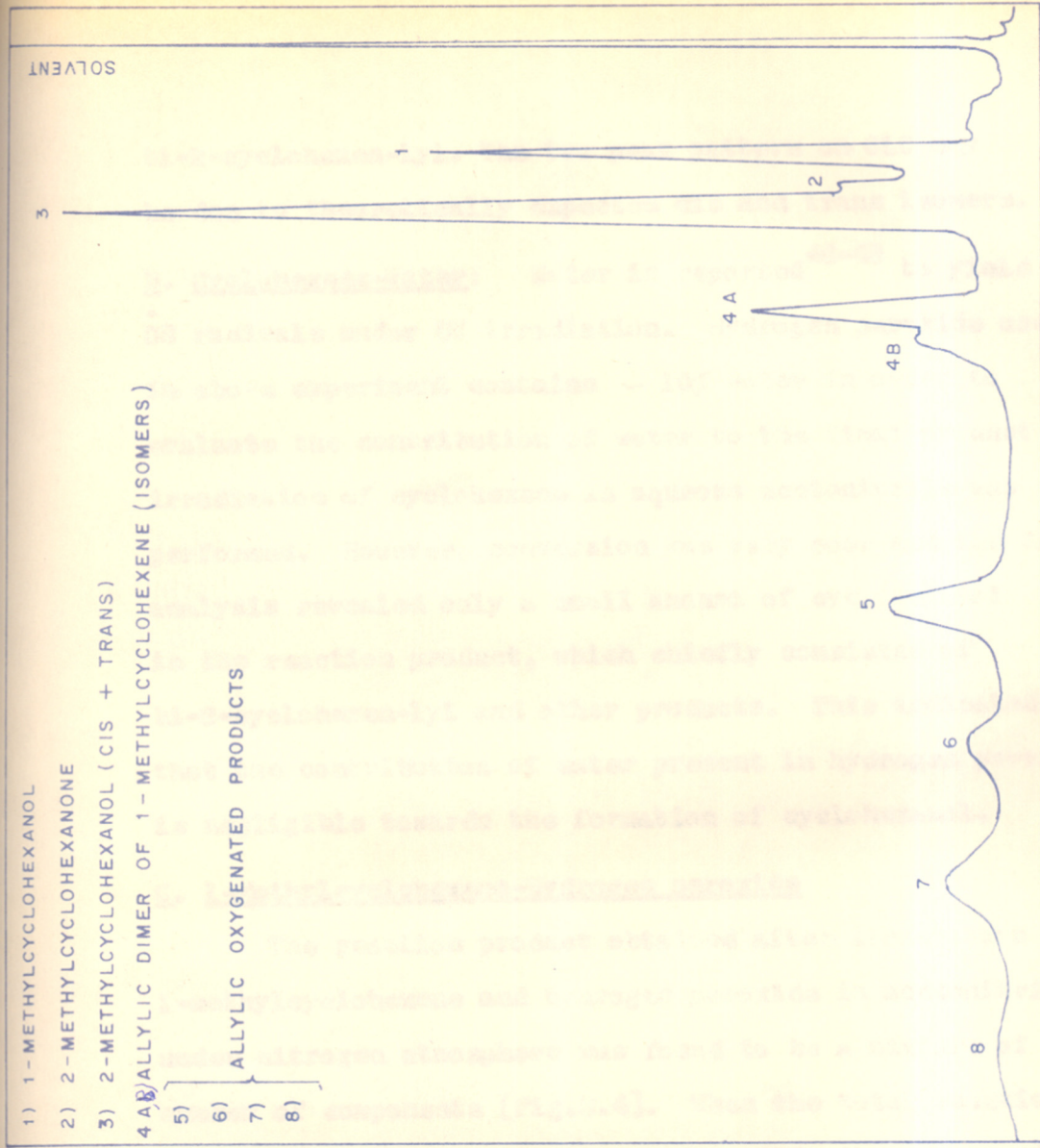


FIG. 2.4 GLC OF 1-METHYLCYCLOHEXENE - H<sub>2</sub>O<sub>2</sub> REACTION PRODUCT

FIG. 2.4

bi-2-cyclohexen-yl. The two peak pattern on GLC may be due to theoretically expected cis and trans isomers.

B. Cyclohexene-water: water is reported<sup>46-48</sup> to yield OH radicals under UV irradiation. Hydrogen peroxide used in above experiment contains ~ 10% water in order to evaluate the contribution of water to the final product irradiation of cyclohexene in aqueous acetonitrile was performed. However, conversion was very poor and the GLC analysis revealed only a small amount of cyclohexanol in the reaction product, which chiefly consisted of bi-2-cyclohexen-yl and other products. This indicated that the contribution of water present in hydrogen peroxide is negligible towards the formation of cyclohexanol.

C. 1-Methylcyclohexene-Hydrogen peroxide

The reaction product obtained after irradiation of 1-methylcyclohexene and hydrogen peroxide in acetonitrile under nitrogen atmosphere was found to be a mixture of number of components [Fig.2.4]. When the total reaction product was subjected to preparative GLC, the components corresponding to the peak numbers 1,2,3 and 4 (A and B) were isolated in the pure form, and the rest were collected together as a mixture. The first three components were characterized as 1-methylcyclohexanol, 2-methylcyclohexanone and 2-methylcyclohexanols [mixture of cis and trans isomers

$^1\text{H NMR}$  indicates both isomers in almost equal amounts] by their spectral properties and through comparison with authentic samples. The mass spectral analysis of the fourth component revealed it to be allylic dimers of 1-methylcyclohexene. The  $^1\text{H NMR}$  spectrum also supported this conclusion [see Experimental]. Since the material in hand was insufficient, it was not further investigated. The spectral properties of the mixture of remaining components indicated it to be a mixture of allylic oxidation products, such as alcohols and ketones. Since main interest was in the products obtained by the addition of hydroxyl radicals to double bond, the allylic oxidation products were not further investigated.

In order to get more information regarding the regioselectivity and stereoselectivity of the present photoinduced hydroxylation reaction, number of experiments were carried out using different molar ratios of olefin to hydrogen peroxide. The product composition in each case was carefully determined by GLC analysis and the results are presented in Table 2.2.

In order to check whether there can be some change in product composition depending upon concentration of olefin in acetonitrile, one experiment [number 6 in Table 2.2]

was performed. This revealed a substantial increase in addition product and a corresponding decrease in allylic oxygenated products, and dimeric products as compared to the experiment with the same olefin/hydrogen peroxide ratio but olefin being only about 20% of this experiment. The conditions of experiment No.6 were found to be most suitable for getting addition products.



In order to check whether there can be some regioselectivity and/or stereoselectivity in the reaction product by choosing a particular range of wavelength for irradiation an experiment [experiment No.2 in Table 2.2] was performed using corex filter [transmission  $\lambda > 260 \text{ m}\mu$ ]. However the use of filter did not make much difference in the product composition.

#### D. 1-Methylcyclohexene-water

As in the case of cyclohexene, in order to evaluate the contribution of water present in the hydrogen peroxide used in above experiments an experiment was performed by irradiating 1-methylcyclohexene in aqueous acetonitrile. The conversion was extremely poor and the reaction product revealed only a small amount of alcohols when subjected to GLC analysis. This indicates that the contribution of water towards formation of alcohol is negligible.



TABLE 2.2 - Photoinduced hydroxylation of 1-methylcyclohexene: Product distribution pattern (1) Acetonitrile (300 ml) was used as a solvent, hydrogen peroxide used was ~ 90% w/v in all the experiments.

Expt. No.	Olefin (moles)	Molar ratio $H_2O_2$ / olefin	Conversion based on $H_2O_2$ (%)	Product Distribution		Addition allylic oxygenated product ratio.	Product composition in addition component			
				Addition	Allylic oxygenated.					
1	0.028	1	27.14	68	8	24	2.83	28	66	6
2	0.028	1	24.42	56	11	33	1.70	25	71	4
[A, B]										
3	0.028	2	37.87	63	12	25	2.52	26	68	6
4	0.028	5	51.05	51	12	37	1.38	23	70	7
5	0.028	10	54.00	31	12	57	0.54	23	71	6
6	0.150	10	80.25	64	6	30	2.01	30	59	6
[C]										

Notes: A) Reaction period was 6.5 - 8 hours except in expt. No. 2, where it was 20 hours.  
 B) Corex filter was used in expt. No. 2 only, all other experiments were without filter.  
 C) Addition component of expt. No. 6 contains 5% unidentified product along with three usual components.

## DISCUSSION

It is well known that hydrogen peroxide on UV irradiation furnishes two hydroxyl radicals. Therefore the stoichiometry of the addition reaction of hydroxyl radical will involve one mole of hydrogen peroxide reacting with two moles of olefins giving rise to two moles of monohydroxylated addition product and it was found to be the case in the present study. The percentage conversion based on hydrogen peroxide reported in the present work are based on this relationship. At the same time, it must be pointed out that the corresponding diols were found to be completely absent under the reaction conditions employed.

This was confirmed by preparing an authentic sample of the trans-1,2-cyclohexene-diol<sup>57</sup>. Careful GLC analysis of the total reaction products from cyclohexene-hydrogen peroxide clearly demonstrated that this compound was absent in the reaction mixture. The residue also clearly demonstrated the absence of this compound.

In the Milas reaction certain olefins are known to furnish diols by photolysis in the presence of hydrogen peroxide by addition of  $\cdot\text{OH}$  radicals to double bond. These reactions are usually run in the absence of hydrogen donor solvents, because of this any radical species created

would prefer to react with the hydroxyl radicals to furnish diols. In the presence of hydrogen donor solvent these radicals would prefer to abstract hydrogen atoms rather than react with hydroxyl radicals to give the hydration products.

The reaction products obtained on photoinduced hydroxylation of cyclohexene consisted of cyclohexanol (53%) and bi-2-cyclohexen-yl (29%). It is obvious that the addition of hydroxyl radical to cyclohexene resulted in the formation of cyclohexanol, while the allylic radical formed by the abstraction of allylic hydrogen atom by hydroxyl radical, dimerized to give bi-2-cyclohexen-yl from the results it is clear that there are two competing reactions, addition and hydrogen abstraction which are typical of free radical reactions of olefins.

In order to get the information regarding the regioselectivity and or stereoselectivity in the addition reaction, 1-methylcyclohexene was selected as a substrate and the reaction was studied in greater details. Since the present study was intended to investigate mainly the addition reaction, the possible allylic oxygenated products were not looked into.

The results summarized in Table 2.2 using different molar ratios of olefin to hydrogen peroxide indicate that

the percentage of conversion are higher at higher molar ratios, while the corresponding percentage of addition products goes down [see Experiments 1,3,4,5] due to the increase in the dimeric and other allylic oxygenated products. This is ver well reflected in the ratios of addition to allylic oxygenated products, where the highest ratio of 2.83 is obtained when the olefin/hydrogen peroxide ratio is one.

This may be attributed to the fact that at lower concentrations of hydroxyl radical [hydrogen peroxide], the selectivity is more and the products obtained are kinetically controlled, i.e. those products are formed which are formed at faster rate. From the results it appears that this is the allylic product. This is also reasonable as the allylic radical is obviously more stable, and hence its formation would involve lesser energy.

When the concentration of the reactant is increased (as compared to solvent) the concentration of hydroxyl radicals is larger. Furthermore, the amount of these which were dissipated by collision with solvent or abstraction of hydrogen from solvent is now reduced, further increasing the concentration of hydroxyl radicals. Because of this high radical concentration the reaction

selectivity diminishes and the concentration of the more stable product [addition product] increases.

Mechanistically the reaction of hydroxyl radicals with olefins seems to be quite complex and more work, particularly the study of the kinetics of the reaction will be necessary for its better understanding.

Another feature of the addition reaction is that it is highly regioselective, resulting in the formation of 2-methylcyclohexanol as the major reaction product. However, it is not stereoselective since 2-methylcyclohexanol formed is found to be a mixture of almost equal amounts of cis- and trans- isomers.

The formation of 2-methylcyclohexanol as the major addition reaction product may be attributed to the higher stability of the resulting tertiary radical. The formation of 2-methyl cyclohexenone is probably by two routes: (A) The hydroxyl radical on abstraction of hydrogen atom from 2-methylcyclohexanol may give rise to ketyl radical which in turn may lead to 2-methylcyclohexenone; or (b) the tertiary radical formed by the addition of hydroxyl radical may afford the enol of 2-methylcyclohexenone on further loss of hydrogen atom. However, the contribution through route A seems negligible as photolysis of trans-2-methyl-cyclohexanol in the presence

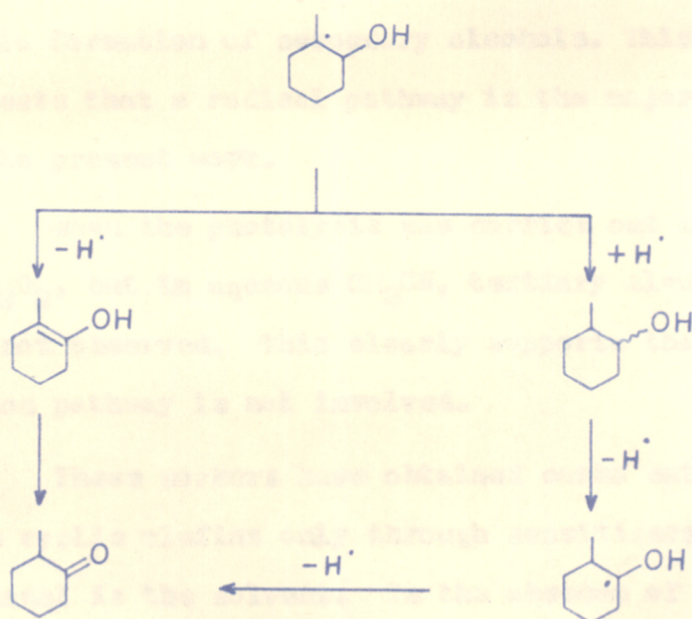
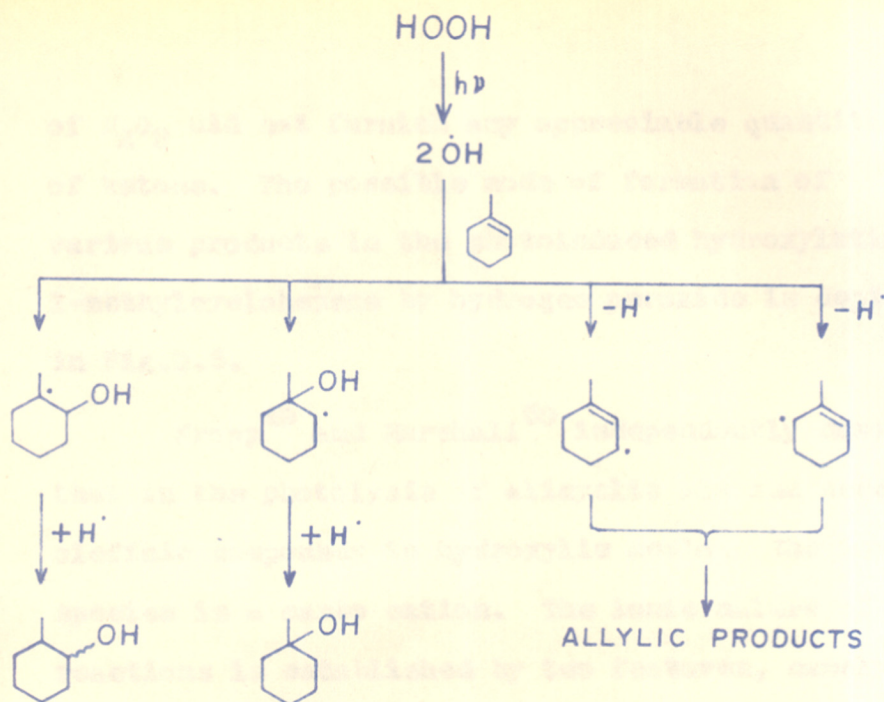


FIG. 2.5 PLAUSIBLE MODE OF FORMATION OF VARIOUS PRODUCTS IN THE PHOTOINDUCED HYDROXYLATION OF 1-METHYL-CYCLOHEXENE BY  $H_2O_2$

of  $H_2O_2$  did not furnish any appreciable quantities of ketone. The possible mode of formation of various products in the photoinduced hydroxylation of 1-methylcyclohexene by hydrogen peroxide is depicted in Fig.2.5.

Kropp<sup>49</sup> and Marshall<sup>50</sup> independently demonstrated that in the photolysis of alicyclic six and seven membered olefinic compounds in hydroxylic media, the intermediate species is a carbo cation. The ionic nature of these reactions is established by two features, namely the exclusive formation of tertiary alcohols and isomerized olefins, in contrast to results presented showing appreciable formation of secondary alcohols. This clearly suggests that a radical pathway is the major pathway in the present work.

When the photolysis was carried out in absence of  $H_2O_2$ , but in aqueous  $CH_3OH$ , tertiary alcohol formation was not observed. This clearly supports that a carbocation pathway is not involved.

These workers have obtained carbo cation intermediates from cyclic olefins only through sensitizers and when methanol is the solvent. In the absence of these conditions in present work, products from carbocation intermediates have not been observed.

The product composition of addition products does not vary much as the molar ratio of olefin/hydrogen peroxide is changed from one to ten. The present study reveals another important feature of hydroxyl radical, namely that there is a preference for addition reaction over allylic attack and this may be attributed to the electrophilic<sup>51</sup> character of the hydroxyl radical. Here it may be pointed out that this property of hydroxyl radical is in contradiction to the other oxygen radicals such as t-butoxy radical which shows an unusual preference for allylic attack<sup>52</sup>.



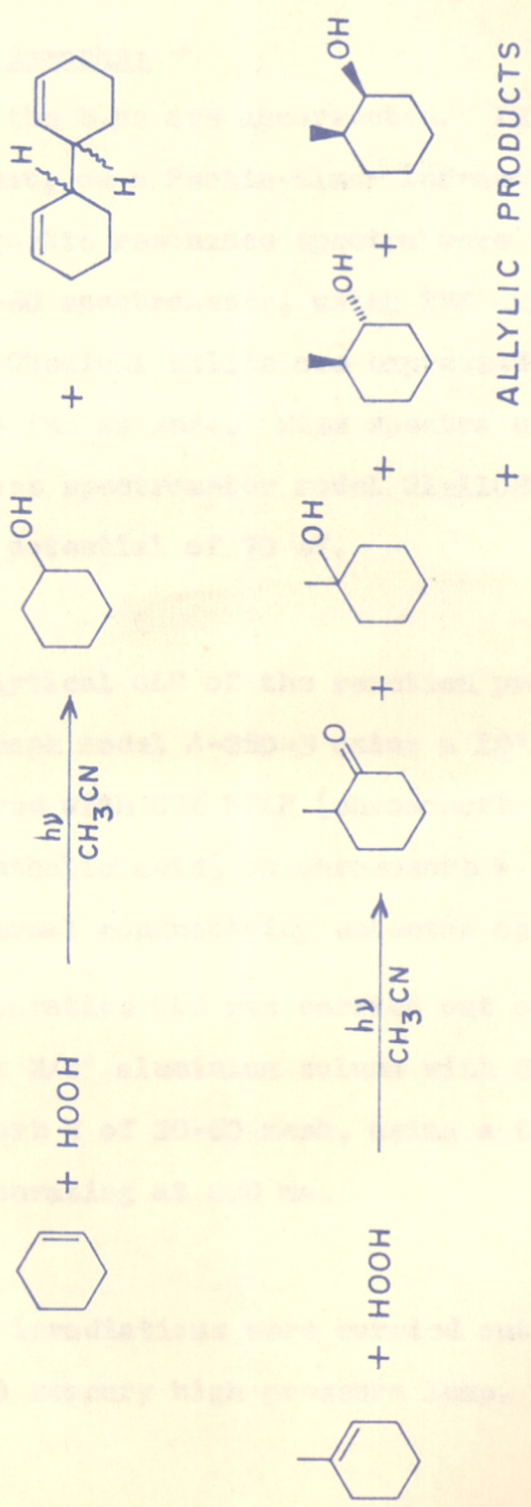


FIG-2.6 PRODUCTS FROM THE PHOTOINDUCED HYDROXYLATION OF CYCLOHEXENE AND 1-METHYLCYCLOHEXENE

## E X P E R I M E N T A L

A. General Remarks:

All the b.ps are uncorrected. IR spectra were recorded neat, on a Perkin-Elmer Infracord model 137-E. Nuclear magnetic resonance spectra were taken in  $\text{CCl}_4$  on a Varian T-60 spectrometer, using TMS as the internal standard. Chemical shifts are expressed in ppm ( ) relative to TMS as zero. Mass spectra were recorded on a CEC-Mass spectrometer model 21-110B, using an ionization potential of 70 eV.

B. GLC

Analytical GLC of the reaction products were run on a Aerograph model A-350-B using a 10' x 14" aluminium column packed with 20% FFAP [chromosorb 20M reacted with nitroterephthalic acid] on chromosorb W of 60-80 mesh, using a thermal conductivity detector operating at 200 ma.

Preparative GLC was carried out on the same model using 12' x 3/8" aluminium column with 30% FFAP packed on chromosorb W of 30-60 mesh, using a thermal conductivity detector operating at 200 ma.

C. UV lamp

All irradiations were carried out using Hanovia (450 Watts) mercury high pressure lamp.

#### D. Materials

1. Acetonitrile was obtained from M/s. "ISCO Chemical Industries, Bombay 2 and dried thoroughly by refluxing and then distilling over phosphorous pentoxide. The traces of phosphorous pentoxide were removed by finally distilling over anhydrous potassium carbonate<sup>53</sup>.
2. Hydrogen peroxide ~ 90% (w/v) was prepared by slow removal of water by distillation [45-50°C/30-35 mm] from a commercially available [30% w/v] sample supplied by Sarabhai M. Chemicals Ltd., India. The strength of hydrogen peroxide was determined by titrating with sodium thiosulphate solution.
3. Cyclohexene was prepared by dehydration<sup>54</sup> of cyclohexanol, obtained from BDH India Ltd., using orthophosphoric acid and then it was distilled over metallic sodium before use.
4. 1-Methylcyclohexene was prepared by dehydrating 1-methylcyclohexanol using iodine. The alcohol<sup>55</sup> was prepared by Grignard reaction of cyclohexanone and methyl iodide.

#### E. General procedure for irradiation

A solution of an appropriate quantity of olefin in acetonitrile [0.3 lt.] was placed in the reaction vessel,

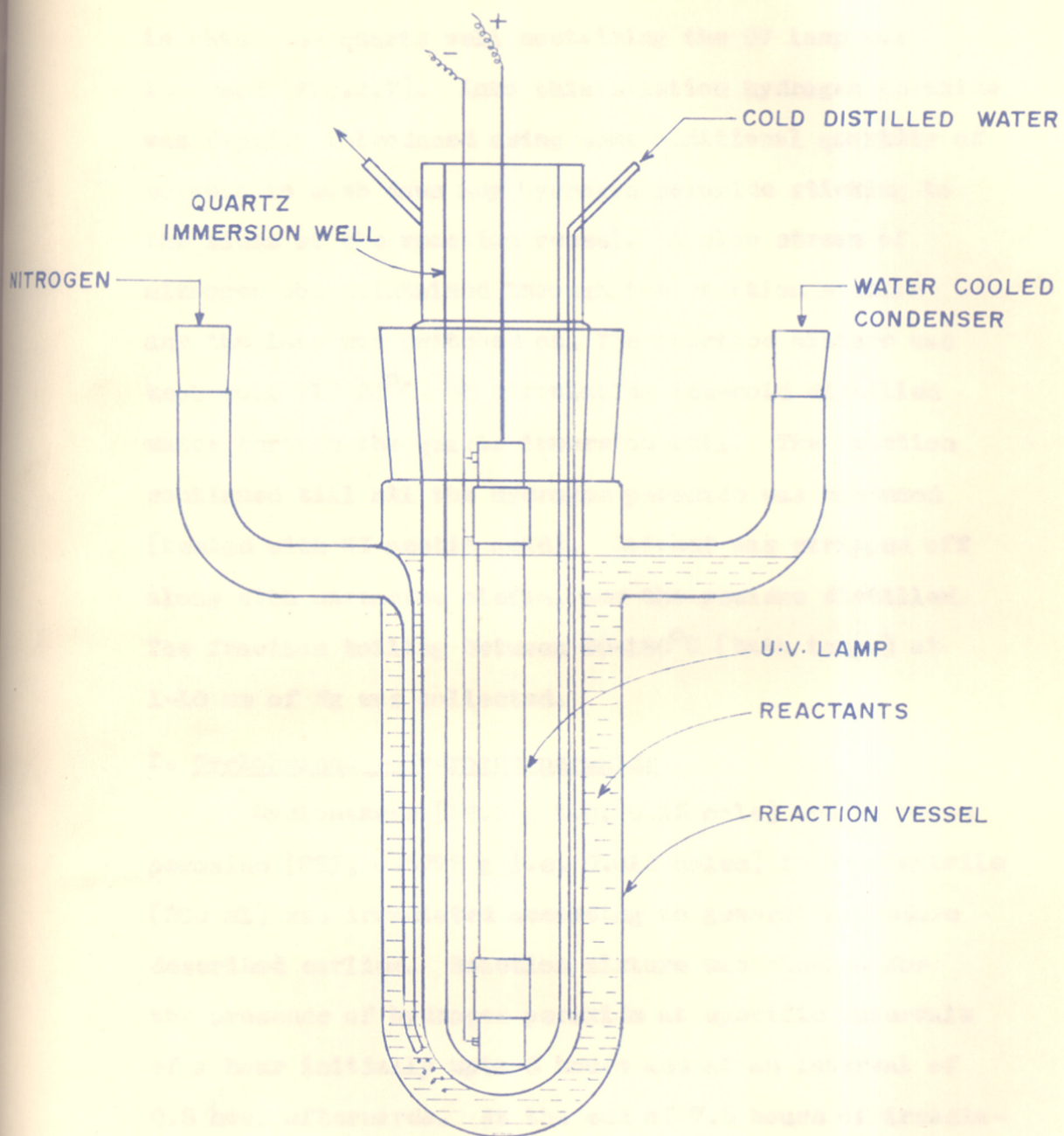


FIG.2.7 IRRADIATION APPARATUS

in which the quartz well containing the UV lamp was immersed [Fig.2.7]. Into this solution hydrogen peroxide was rapidly introduced using some additional quantity of solvent to wash down any hydrogen peroxide sticking to the sides of the reaction vessel. A slow stream of nitrogen was maintained through the reaction mixture and the lamp was switched on. The reaction mixture was kept cool [15-20°C] by circulating ice-cold distilled water through the quartz immersion well. The reaction continued till all the hydrogen peroxide was consumed [tested with KI-acetic acid]. Solvent was stripped off along with unreacted olefin, and the residue distilled. The fraction boiling between 90-180°C [bath temp.] at 1-10 mm of Hg was collected.

#### I. Cyclohexene - Hydrogen peroxide

Cyclohexene [13.3 g i.e. 0.15 mole] and hydrogen peroxide [88%, 0.5795 g i.e. 0.015 moles] in acetonitrile [300 ml] was irradiated according to general procedure described earlier. Reaction mixture was checked for the presence of hydrogen peroxide at specific intervals of 1 hour initially upto 6 hours and at an interval of 0.5 hour afterwards. At the end of 7.5 hours of irradiation, reaction mixture showed total absence of hydrogen peroxide. Material was transferred to distillation assembly

and acetonitrile and unreacted cyclohexene were distilled off. Residual material was finally distilled under reduced pressure using oil bath within a range of 1-10 mm of Hg pressure and bath temp. range 80-160°C (oil bath).

Weight of distilled material: 2.4 g

#### II. 1-Methylcyclohexene-hydrogen peroxide

1-Methylcyclohexene [14.4 g i.e. 0.15 mole] and hydrogen peroxide [88%, 0.5795 g i.e. 0.015 mole] in acetonitrile [0.3 litre] was irradiated according to general procedure described earlier. Reaction mixture was checked periodically, as described in above experiment for the presence of hydrogen peroxide and at the end of 8 hours it was found that hydrogen peroxide has been reacted completely. The reaction mixture was transferred to distillation assembly and acetonitrile along with unreacted 1-methylcyclohexene were distilled off. Residual material was distilled under reduced pressure using oil bath and fraction boiling between 80-180°C (oil bath) within a range of 1-10 mm of Hg pressure was collected.

Wt. of distilled material: 2.74 g.

#### III. trans-2-Methylcyclohexanol-hydrogen peroxide

In order to check the contribution through route A

(Fig.2.5) towards the formation of 2-methylcyclohexanone, trans-2-methylcyclohexanol [0.100 g] was irradiated in the presence of hydrogen peroxide [0.034 g] in acetonitrile [60 ml]. However, it was found that no appreciable quantity of ketone was present in reaction product indicating that contribution through route A is negligible.

#### F. Analysis of Products

Analytical GLC of the reaction products from cyclohexene- $H_2O_2$  was carried out on Aerograph model using FFAP column at  $100^{\circ}C$  column temp., flow rate of hydrogen as carrier gas was 60 ml/min. [Fig.2.3]. The analytical GLC of 1-methylcyclohexene- $H_2O_2$  experiments was also carried out on the same model with same set of conditions as above [Fig.2.4].

Percentage composition of the reaction product in various experiments was determined by analytical GLC based on peak areas. In order to eliminate the experimental error in calculating the percentage of each component from GLC data, a known mixture of various components was prepared and subjected to GLC analysis. The necessary correction was applied in each experiment for each component, in calculating the percentage composition.

#### G. Isolation of Products

Cyclohexanol and bi-2-cyclohexene-lyl were isolated

by preparative GLC from the reaction product of cyclohexene-H<sub>2</sub>O<sub>2</sub> experiment. [Aerograph model, column FFAP 30%, column temp. 175°C, H<sub>2</sub> flow rate 60 ml/min.]

1-Methylcyclohexanol, 2-methylcyclohexanone, 2-methylcyclohexanol [cis and trans isomers] allylic dimer of 1-methylcyclohexene and other allylic oxygenated products were isolated by preparative GLC from the pooled reaction products of various 1-methylcyclohexene-H<sub>2</sub>O<sub>2</sub> experiments. [Aerograph model; column FFAP 30%; column temp. 160°C; H<sub>2</sub> flow rate, 80 ml/min.].

#### H. Purification of Products

Various products obtained by preparative GLC were further purified by distillation before recording spectral data.

#### I. Spectral and other data

Abbreviations: IR - s - strong, m - medium, w - weak

<sup>1</sup>H NMR - s - singlet, d - doublet, t-triplet,  
c.a. - centred at.

Cyclohexanol: C<sub>6</sub>H<sub>12</sub> Mol. wt. - 100; b.p. 89-91°/11 mm  
GLC [Fig.2.4, peak No.1, RRT - 1]

IR (Fig.2.8): 3484(s), 3030(s), 1447(s), 1351(m),  
1333(w), 1282(w), 1250(w), 1222(w),  
1163(w), 1127(w), 1054(s), 1018(m),  
962(s), 917(w), 885(m), 855(w), 840(m),  
775(w), cm<sup>-1</sup>.



$^1\text{H}$  NMR (Fig.2.9): 1.5 [m, 10 protons methylene protons]  
 3.47 [m, 1 proton carbinol proton]  
 3.97 [s, 1 proton, exchanges with  
 $\text{D}_2\text{O}$  hydroxyl proton]

Mass:  $\text{M}^+$  at m/e 100, base peak at m/e 57; other major  
 peaks at m/e 82, 44, 67, 41, 71, 29, 56.

Bi-2-cyclohexen-yl [isomers]:  $\text{C}_{12}\text{H}_{18}$  Mol. wt. 162, b.p.  $100^\circ$   
 $110^\circ\text{C}$  (bath)/8 mm.

GLC [Fig.2.4, peak Nos.3 and 4, RRT 3.0  
 and 3.6 respectively]

IR: 2900(s), 1650 (w), 1468(m), 730(m)

$^1\text{H}$  NMR (Fig.2.10): 1.6 [m, 14 protons, 12 methylene and  
 2 methine proton]  
 5.5 [t, 4 protons, vinylic protons].

Mass (Fig.2.11):  $\text{M}^+$  at m/e 162, base peak at m/e 18;  
 other major peaks at m/e 133, 94, 91, 81,  
 80, 79, 67, 55, 41, 32, 28.

1-Methylcyclohexanol:  $\text{C}_7\text{H}_{14}\text{O}$  Mol. wt. 114; b.p.  $68-72^\circ/25$  mm.

GLC [Fig.2.5, peak No.1, RRT 1]

IR (Fig.2.12): 3471(s), 3030(s), 1435(m), 1366(m), 1250(m),  
 1199(w), 1163(m), 1115(m), 1032(w), 1002(w),  
 980(w), 962(s), 902(s), 885(w), 870(w),  
 848(m), 827(m), 712(w),  $\text{cm}^{-1}$ .

- <sup>1</sup>H NMR (Fig.2.13): 1.17 [s, 3 protons, tertiary methyl protons]  
 1.47 [broad s, 10 protons, methylene protons]  
 1.7 [s, 1 proton, exchanges with D<sub>2</sub>O, hydroxyl proton]

Mass: M<sup>+</sup> at m/e 114, base peak at m/e 57; other major peaks at m/e 68, 81, 96, 71, 55, 41, 43.

2-Methylcyclohexanone: C<sub>7</sub>H<sub>12</sub>O Mol.wt. 112; b.p. 88-90°C/20 mm  
 GLC [Fig.2.5, peak No.2, RRT 1.3]

IR (Fig.2.14): 3030(s), 1701(s), 1439(m), 1368(w), 1149(w),  
 1205(w), 1133(w), 1111(m), 1067(w), 1041(w),  
 980(w), 962(w), 878(w), 855(w), 801(w),  
 712(w), cm<sup>-1</sup>.

- <sup>1</sup>H NMR (Fig.2.15): 1.02 [d, 3 protons, secondary methyl protons]  
 1.9 [m, 9 protons, eight methylene and 1 methine protons]

Mass: M<sup>+</sup> at m/e 112, base peak at m/e 68; other major peaks at m/e 41, 55, 56, 69, 42, 53.

2-Methylcyclohexanol (cis and trans): C<sub>7</sub>H<sub>14</sub>O; Mol.wt. 114  
 b.p. 75-78°C/20 mm.  
 GLC [Fig.2.5, peak No.3, RRT 1.6].

This was a mixture of cis and trans isomers. This was confirmed by both IR [Fig.2.16 and 2.17 for cis and trans isomers respectively] and  $^1\text{H}$  NMR spectral data, which exhibits characteristic peaks of both isomers in IR and multiplets corresponding to carbinol proton in both conformations. From NMR integration curve for carbinol proton it was found to be cis and trans-isomers almost in equal amount.

IR (Fig.2.18): 3571(s), 3030(s), 1439(s), 1355(w), 1274(w), 1222(w), 1200(w), 1162(w), 1130(w), 1065(s), 1053(s), 1032(s) [characteristic of trans isomer]  
1020(s), 977(m), 943(w) [characteristic of cis isomer]  
 913(w), 901(w), 855(w), 842(w)  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (Fig.2.19): 1.00 [d, 3 protons, secondary methyl]  
 1.75 [m, 9 protons, eight methylene and one methine proton]  
 2.83 [s, 1 proton, exchanges with  $\text{D}_2\text{O}$  hydroxyl proton]  
 2.93 [m, 1/2 proton, carbinol proton in trans conformation, merges with

hydroxyl proton singlet, visible clearly after  $D_2O$  exchange].

3.5 [m 1/2 proton, carbinol proton in cis conformation].

Mass:  $M^+$  at m/e 114, base peak at m/e 57; other major peaks at m/e 81, 96, 68, 71, 55, 41, 43.

1-Methylcyclohexene allylic dimer:  $C_{14}H_{22}$ , Mol. wt. 190  
(Isomers) b.p. 130-40°C (bath)/8 mm.

GLC [Fig. 2.5, peak Nos. 4A and B, R.T. 2.47 and 2.7 respectively].

IR: 2820(s), 1650(w), 1355(m), 1380(w), 1155(w), 975(w), 330(w), 900(w), 810(w), 745(w)  $cm^{-1}$ .

$^1H$  NMR: 1.64 [s, 6 protons of two vinyl methyl group]  
1.77 [m, 14 protons, 12 methylene and 2 methine protons].  
5.05 [m, 2 protons, 2 vinyl protons]

Mass (Fig. 2.20):  $M^+$  at m/e 190 base peak at m/e 95, other major peaks at 189, 109, 105, 97, 96, 94, 93, 92, 91, 82, 80, 79, 78, 77, 67, 65, 55, 43, 41, 39, 28.

#### I. Authentic samples

1. 1-Methylcyclohexanol: 1-Methylcyclohexanol was prepared by Grignard reaction from methyl iodide (14.2 g), Mg (2.7 g)

and cyclohexanone (9.8 g).

Yield: 7.5 g, b.p. 74-75°C/30 mm.

2. trans-2-Methyl-cyclohexanol<sup>56</sup>: A solution of 2-methyl cyclohexanone (5.0 g) in dry ether (70 ml) and dry ethanol (80 ml) was added to liquid ammonia (400 ml), lithium (6.0 g) was added in small pieces over a period of 80 minutes under stirring. After the disappearance of blue colour [30 more minutes] ammonia was allowed to evaporate. The material obtained was diluted with ice-water mixture; acidified with dil. HCl [1:1, 200 ml] and extracted repeatedly with ether (75 ml x 4). Solvent was stripped off from the dried extracts and the residue distilled.

Yield: 4.0 g, b.p. 90-91°C/40 mm.

3. cis-2-Methyl-cyclohexanol<sup>56</sup>

To a solution of trans-2-methylcyclohexanol (5.7 g) in pyridine (70 ml) was added p-toluene sulfonyl chloride (19 g). White needles of pyridine hydrochloride separated after keeping the contents for 48 hours. It was poured into crushed ice (250 ml) and extracted repeatedly with ether (80 ml x 3). After stripping off solvent from the dried ether extracts, the residue was taken in a mixture of dimethyl formamide (250 ml) and water (5.5 ml) and heated on steam bath for 36 hours. The contents were cooled to 25°C poured into 600 ml crushed ice, saturated with sodium

chloride and extracted repeatedly with ether (250 ml x 3). Ether was stripped off and the residue refluxed with methanolic-KOH (10% 90 ml) for 4 hours. Methanol distilled out and the residue was extracted repeatedly with ether (75 ml x 4). Solvent stripped off from the dried ether extracts and residue distilled.

Yield 1.7 g, b.p. 78-80°C/22 mm.

#### 4. trans-1,2-Cyclohexanediol<sup>57</sup>

Hydrogen peroxide [30% 14 ml, .14 mole] was added to formic acid [88%, 60 ml, 1.37 moles] in a 1 litre three necked flask, equipped with a thermometer and motor driven stirrer. Freshly distilled cyclohexene [8.2 g, 0.1 mole] was added slowly from a dropping funnel over a period of 20-30 minutes. Temperature of the reaction mixture was maintained between 40-45°C by ice cooling and controlled rate of addition. Reaction mixture was maintained at 45°C for 1 hour after all the cyclohexene has been added and then it was allowed to stand overnight at room temperature.

The formic acid and water were removed by distillation from a steam bath under reduced pressure, an ice cold solution of sodium hydroxide [8 g] in water (15 ml) was added in small portions (temp. maintained below 45°C), to the viscous mixture of diol and its formates. The alkaline solution was warmed to 45°C and extracted thoroughly with

ethyl acetate (7 x 35 ml) at 45°C. Solvent was removed and the crude product (melting in the range 90-98°C) was distilled at 120-5°C at 4 mm of Hg. Yield 7.8 g (m.p. 101.5 - 103°C).

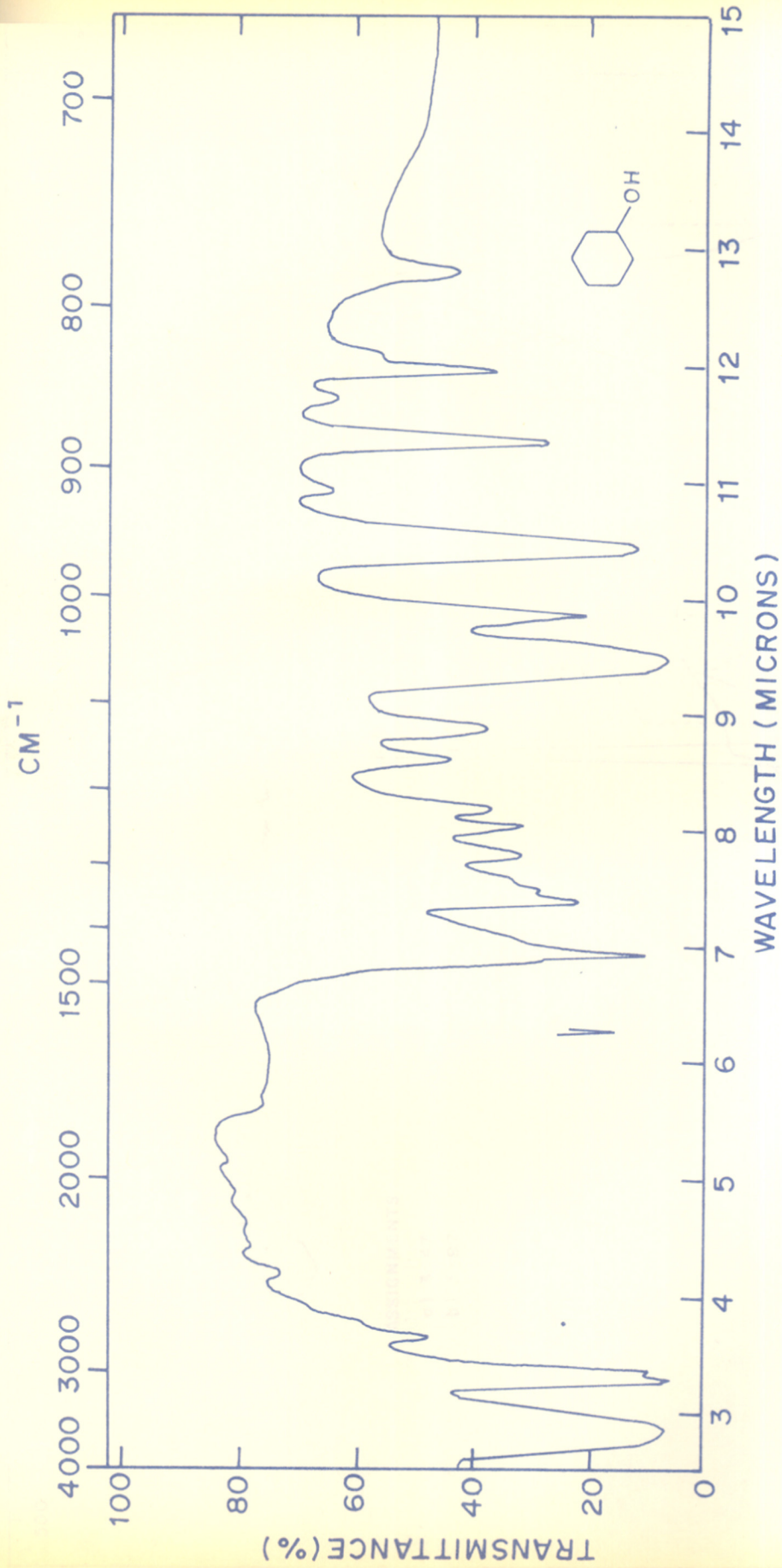
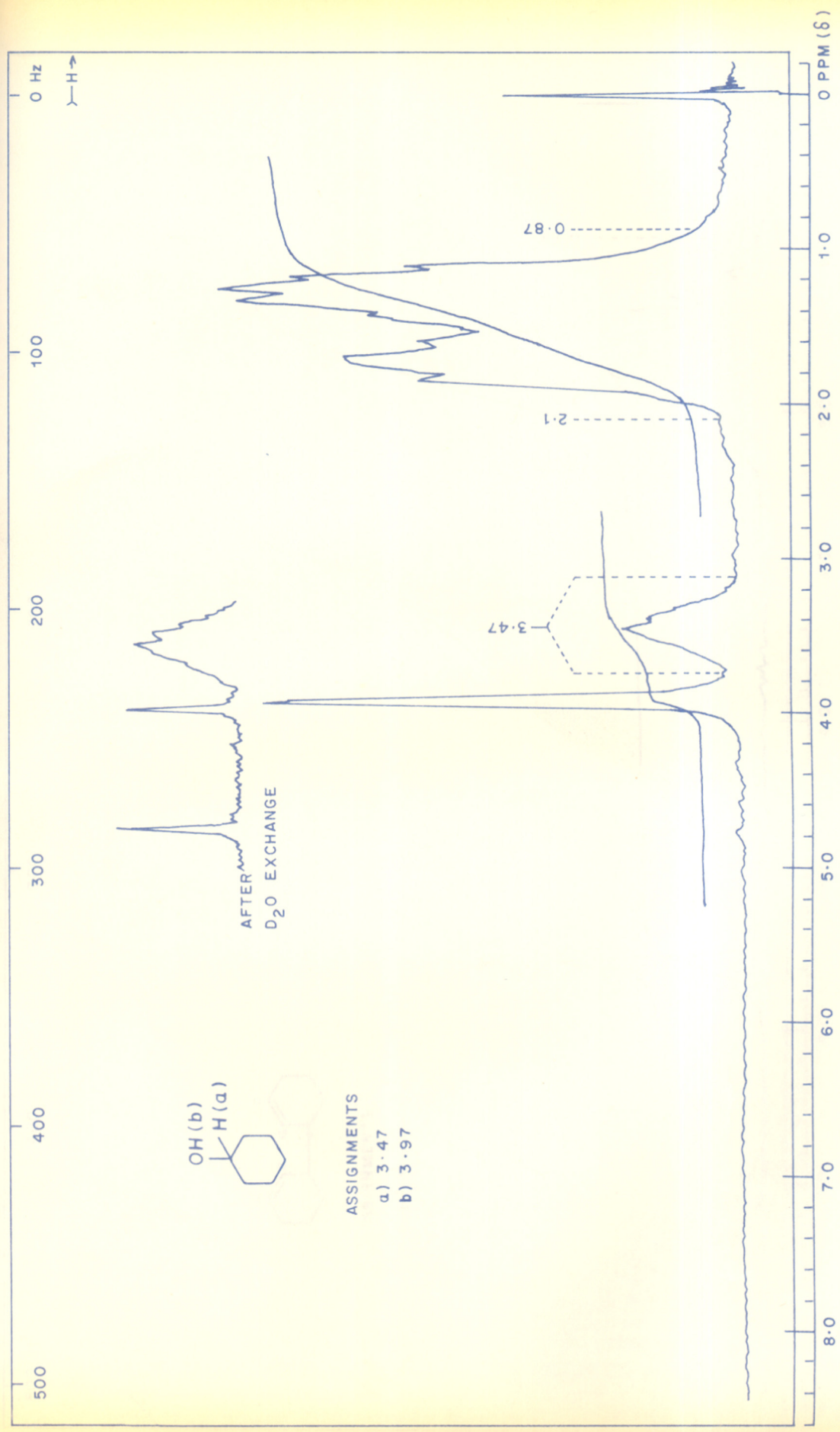


FIG. 2-8 IR SPECTRUM OF CYCLOHEXANOL





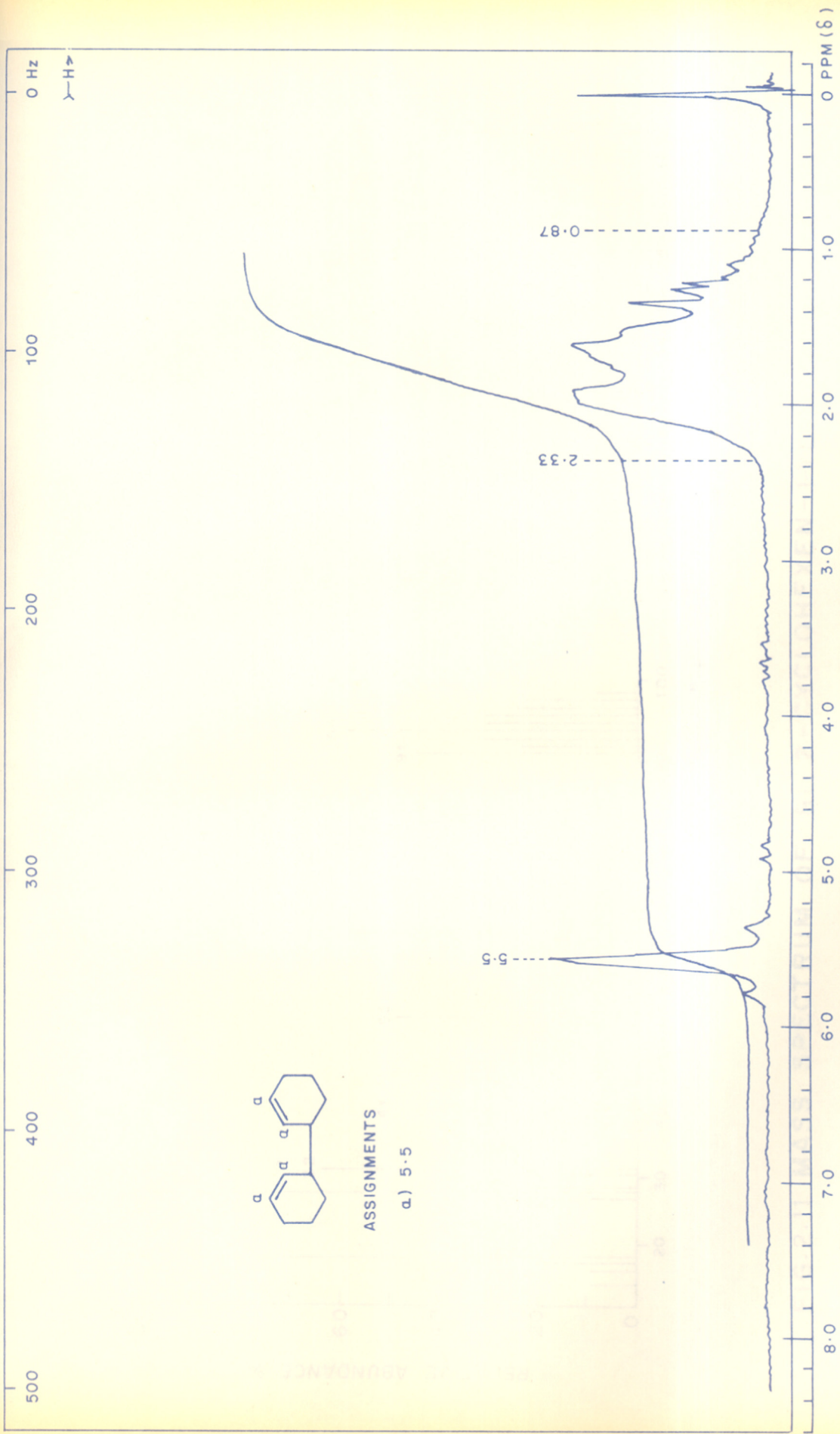


FIG. 2.10  $^1\text{H}$  NMR SPECTRUM OF Bi-2-CYCLOHEXEN-1-YL

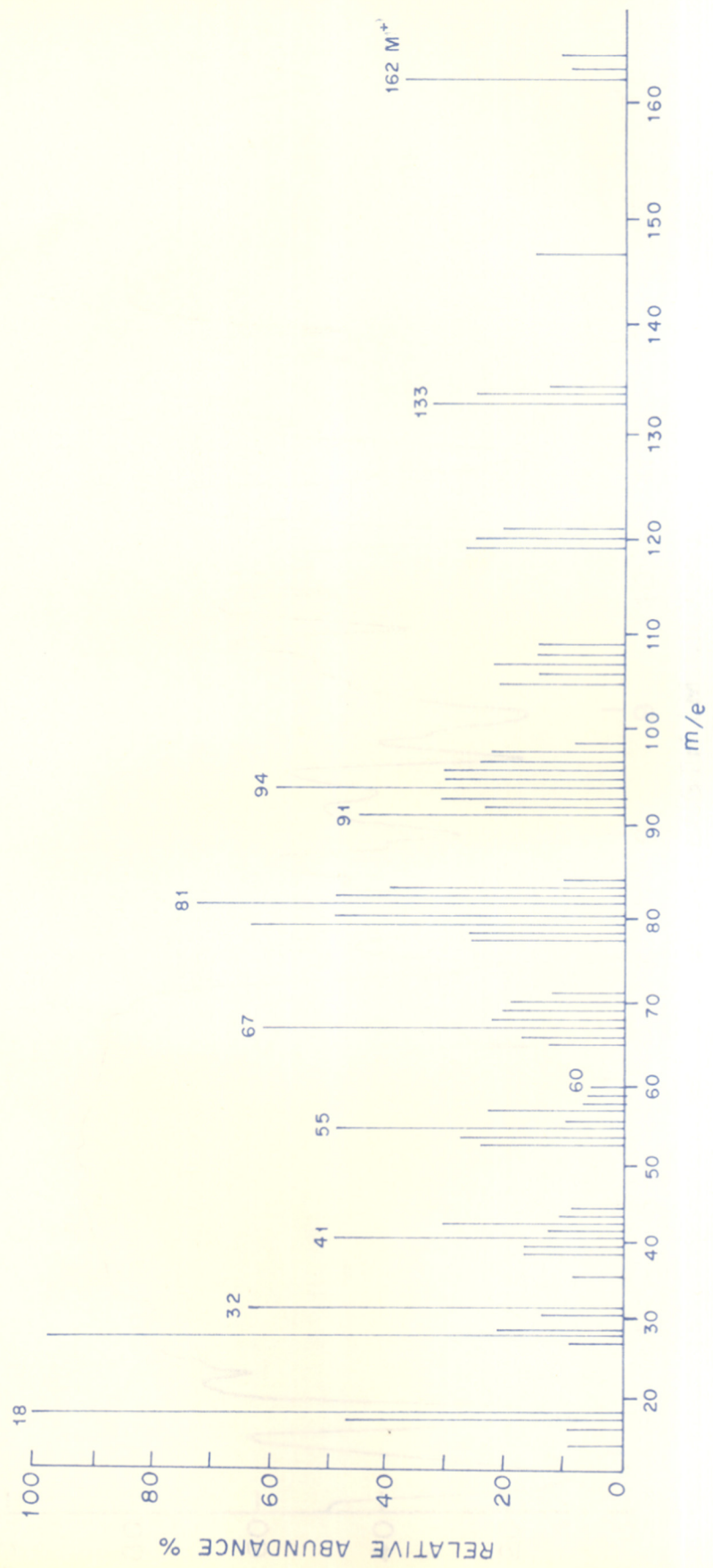


FIG.2.11 MASS SPECTRUM OF BI-2-CYCLOHEXEN-1-YL

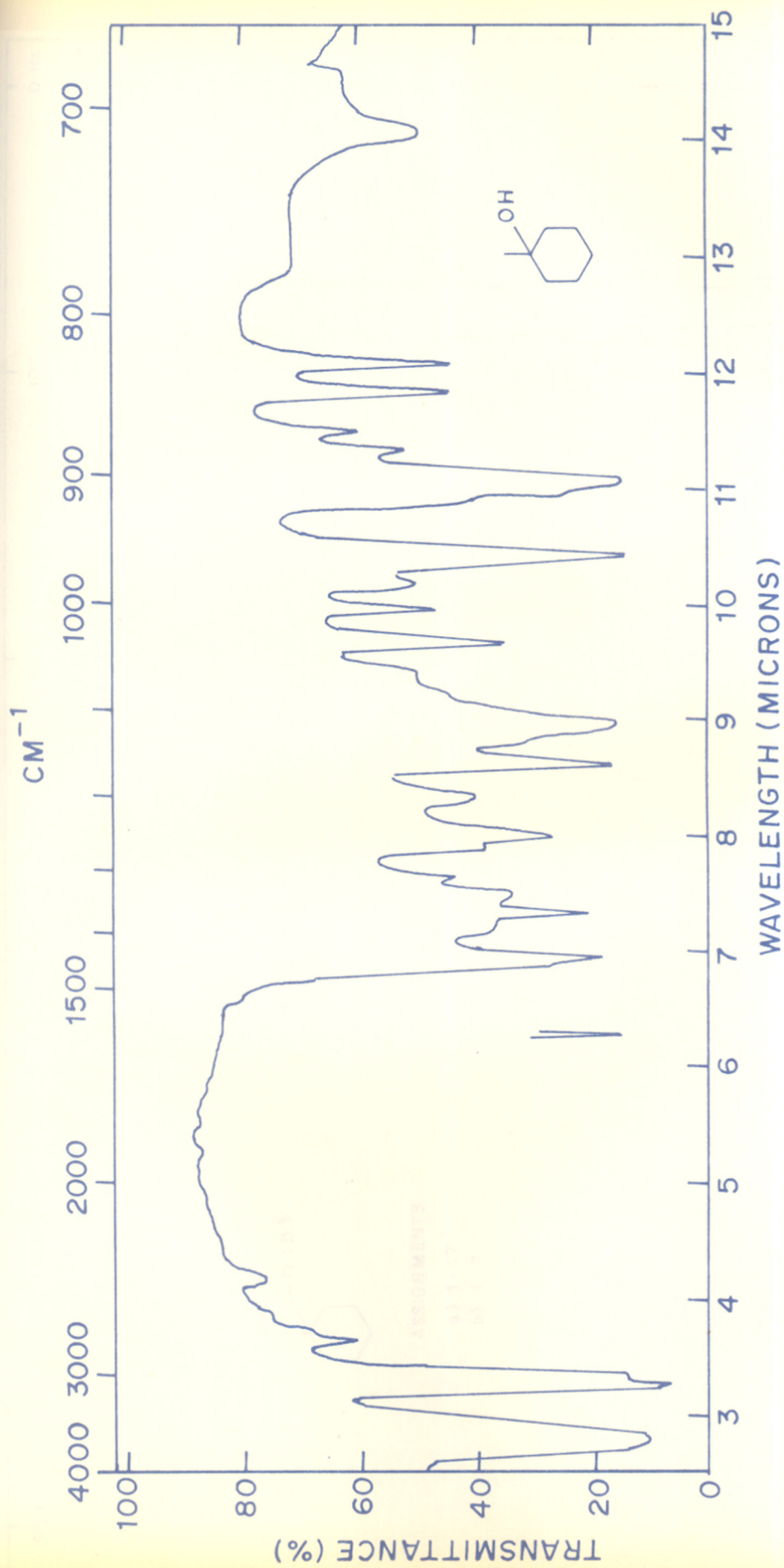
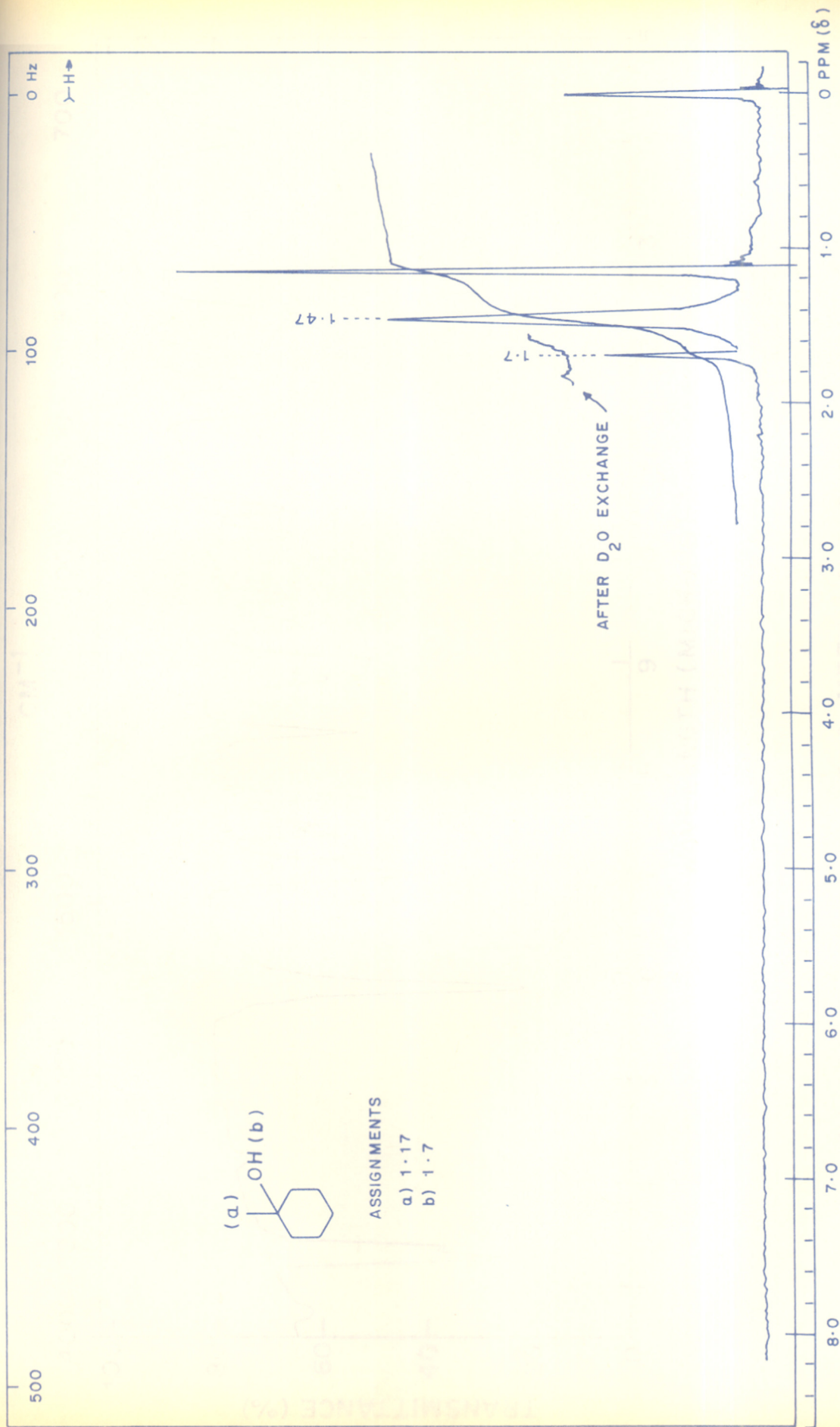


FIG. 2.12 IR SPECTRUM OF 1-METHYLCYCLOHEXANOL

FIG-2.13  $^1H$  NMR SPECTRUM OF 1-METHYLCYCLOHEXANOL

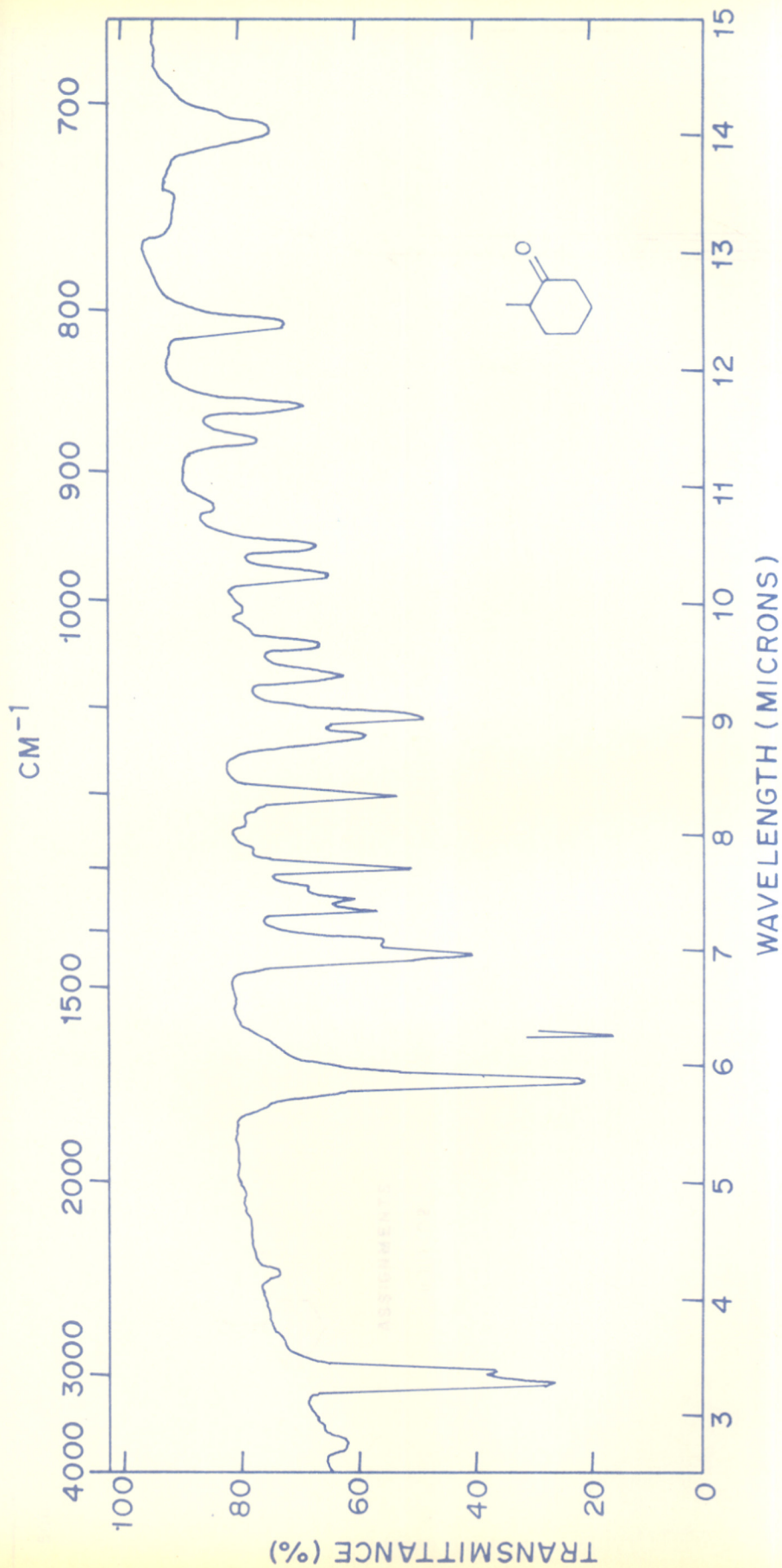
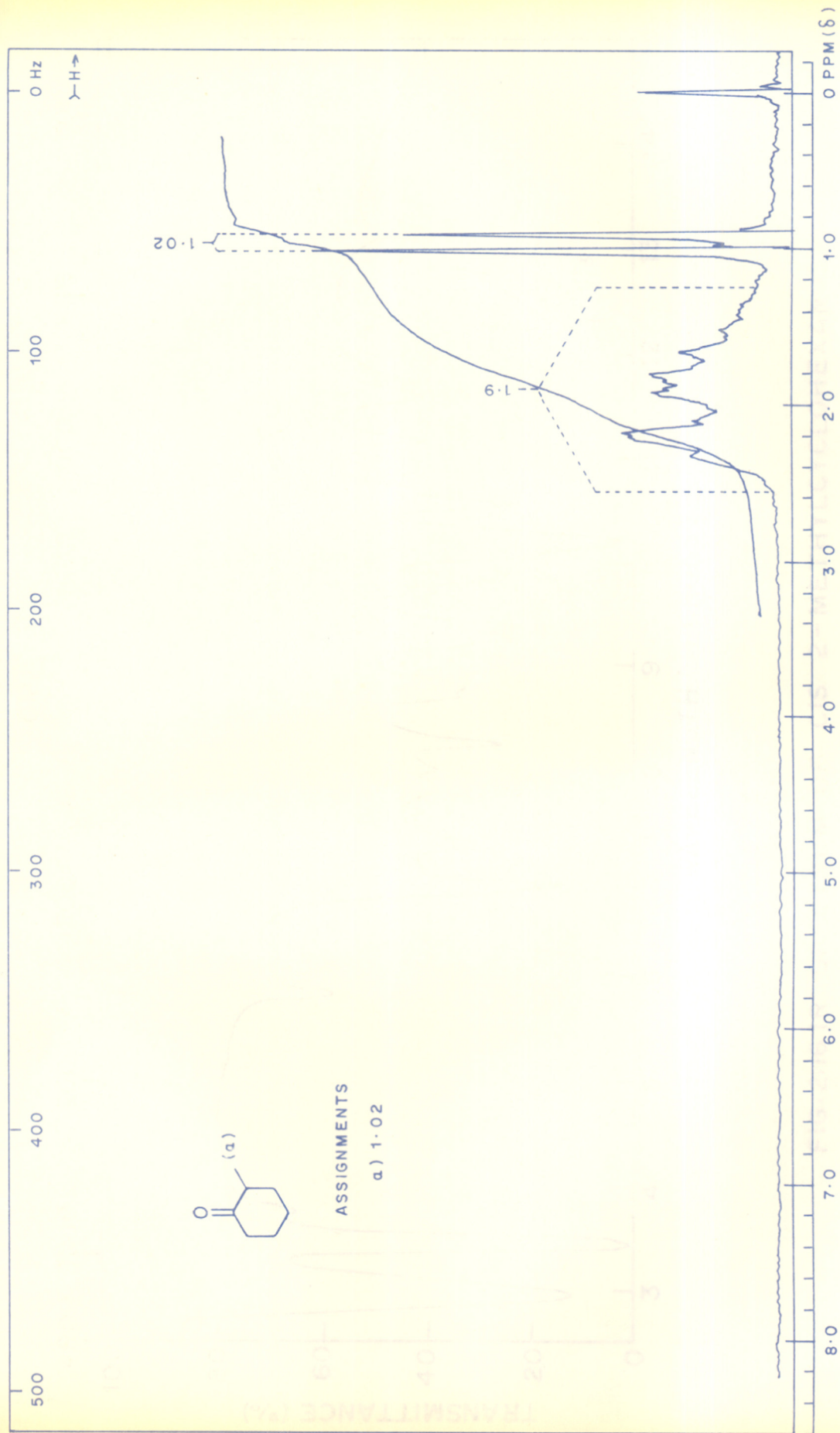


FIG-2.14 IR SPECTRUM OF 2-METHYLCYCLOHEXANONE

FIG.2.15  $^1\text{H}$  NMR SPECTRUM OF 2-METHYLCYCLOHEXANONE

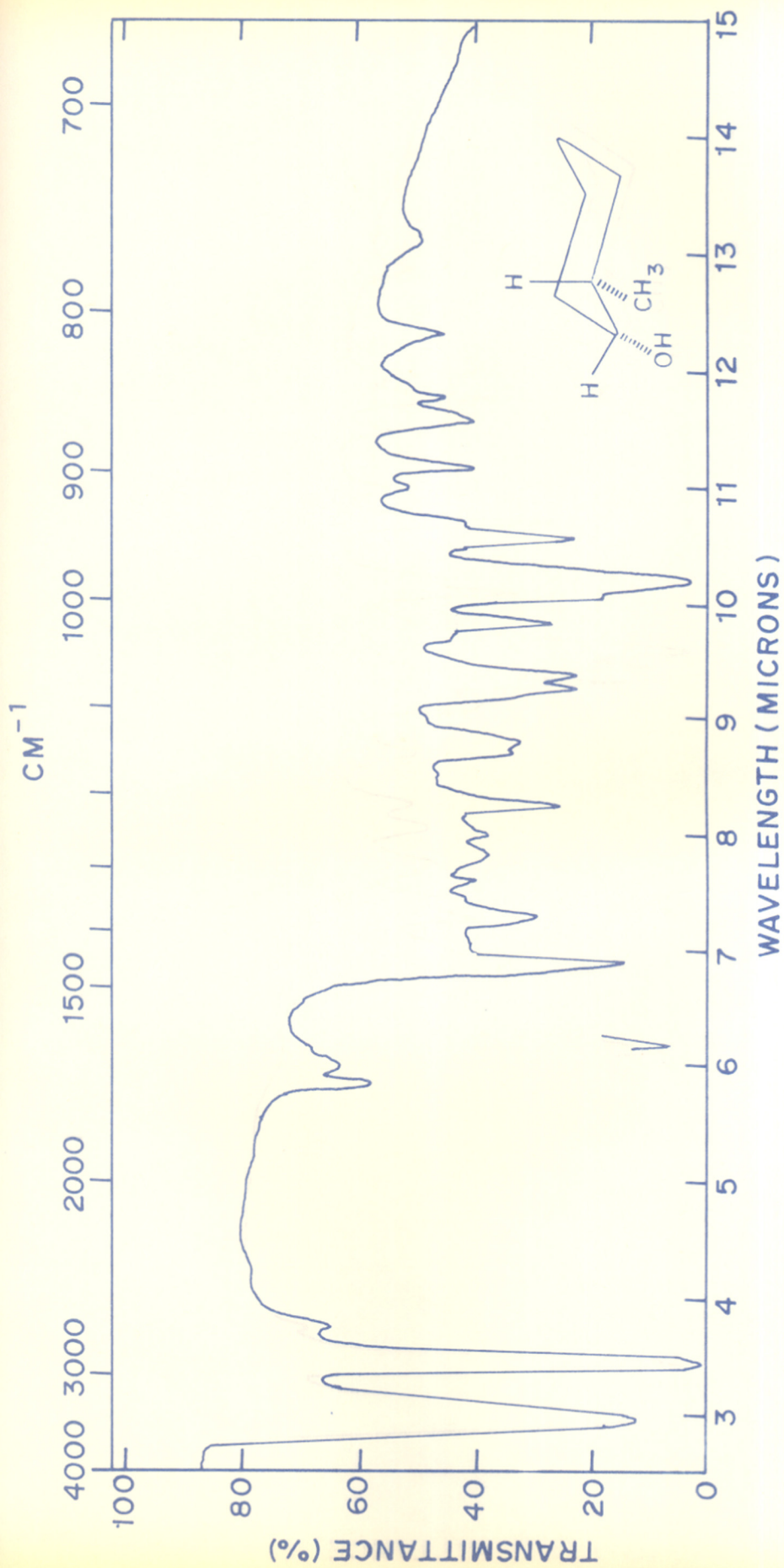


FIG. 2.16 IR SPECTRUM OF CIS 2-METHYLCYCLOHEXANOL



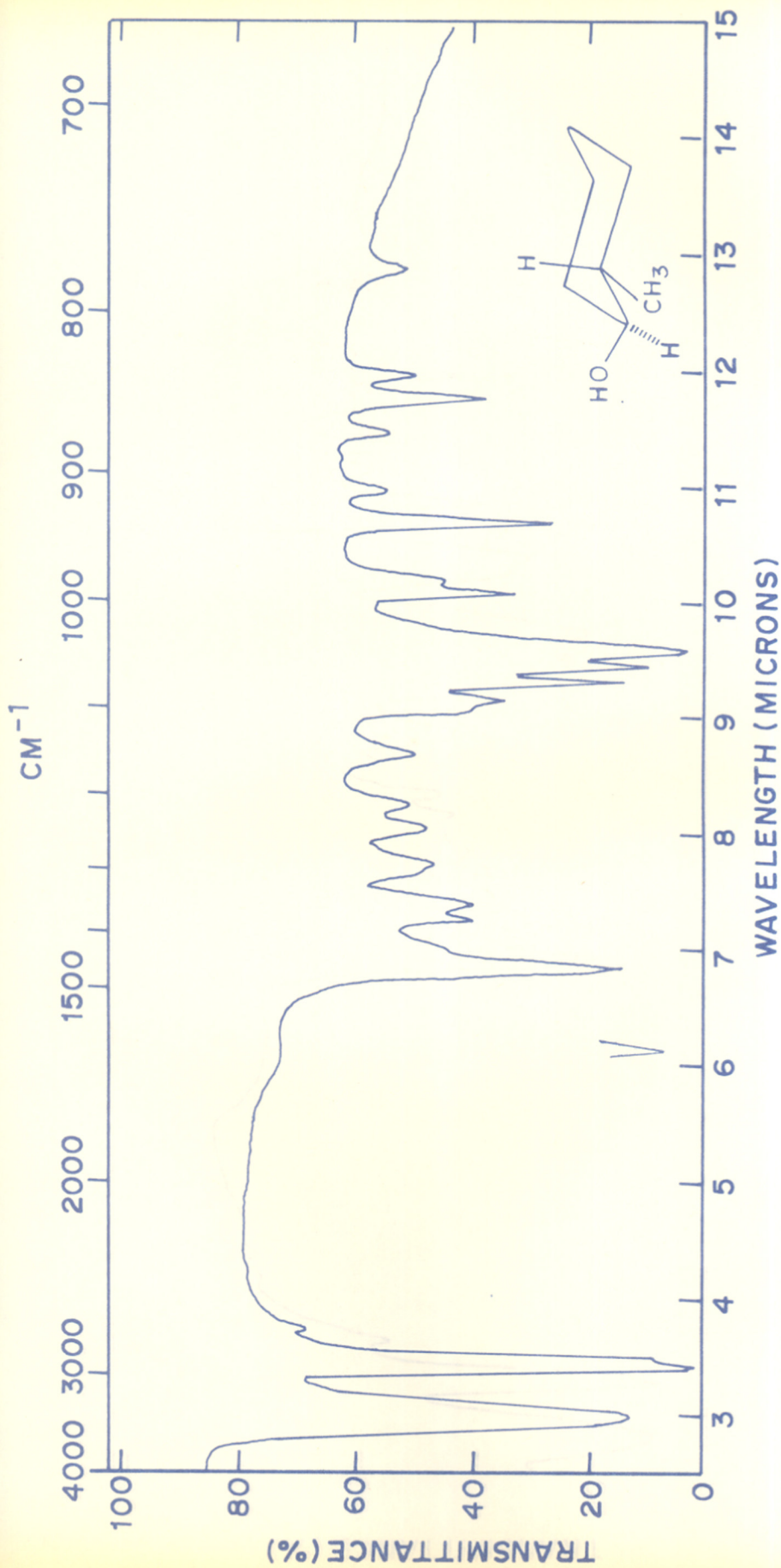


FIG-2.17 IR SPECTRUM OF TRANS 2-METHYLCYCLOHEXANOL

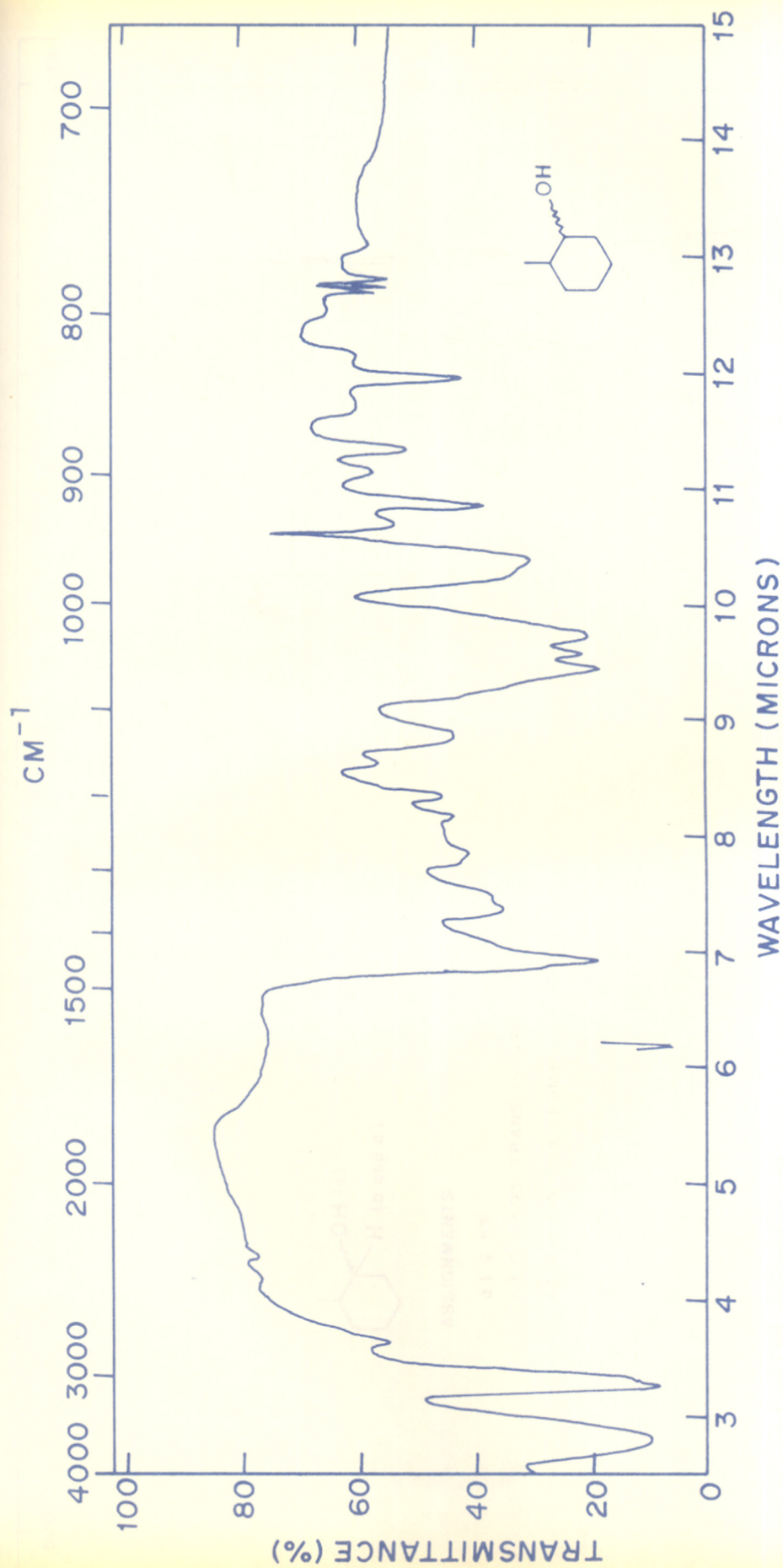


FIG. 2.18 IR SPECTRUM OF 2-METHYLCYCLOHEXANOL

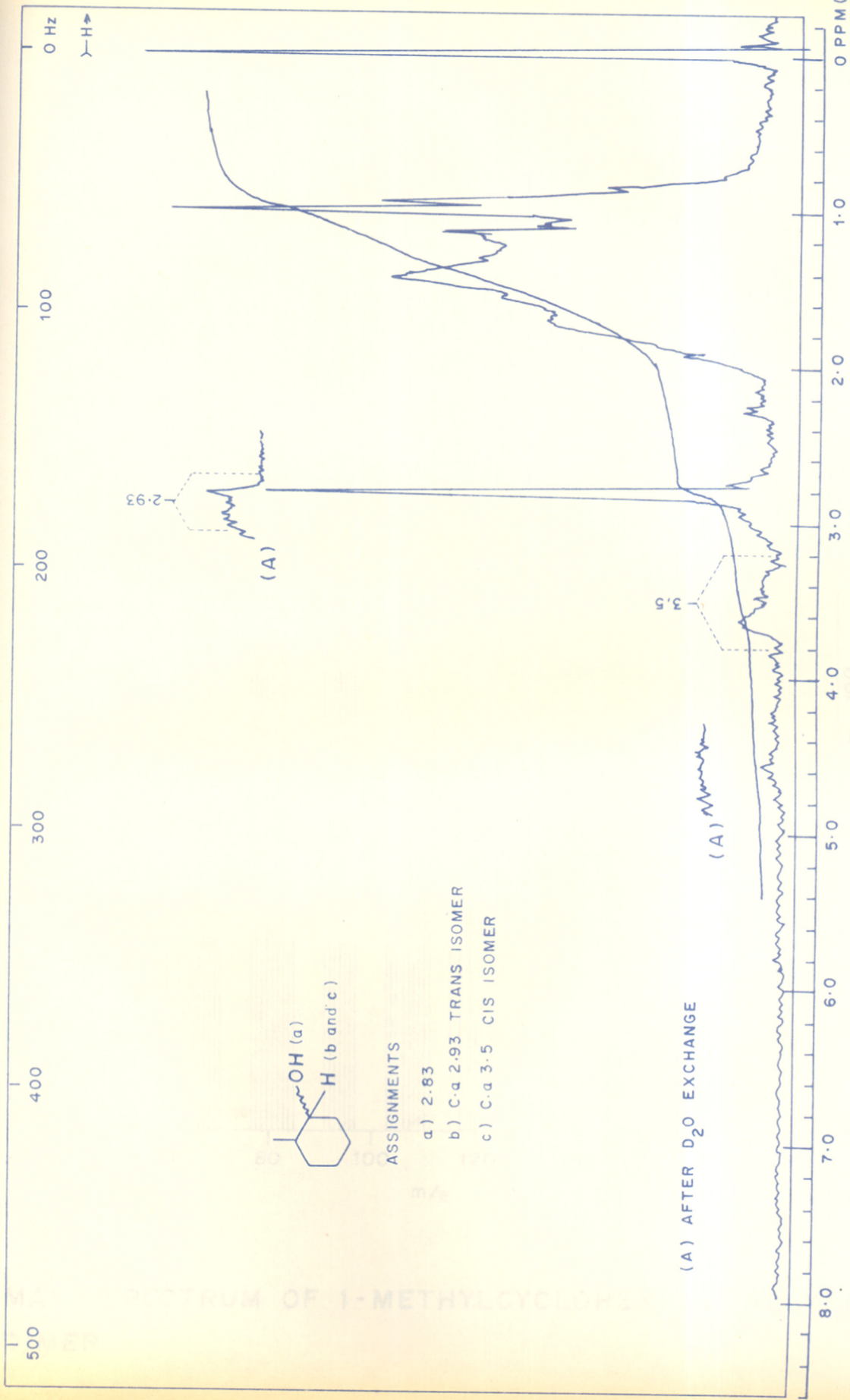


FIG. 2.19  $^1H$  NMR SPECTRUM OF 2-METHYLCYCLOHEXANOL

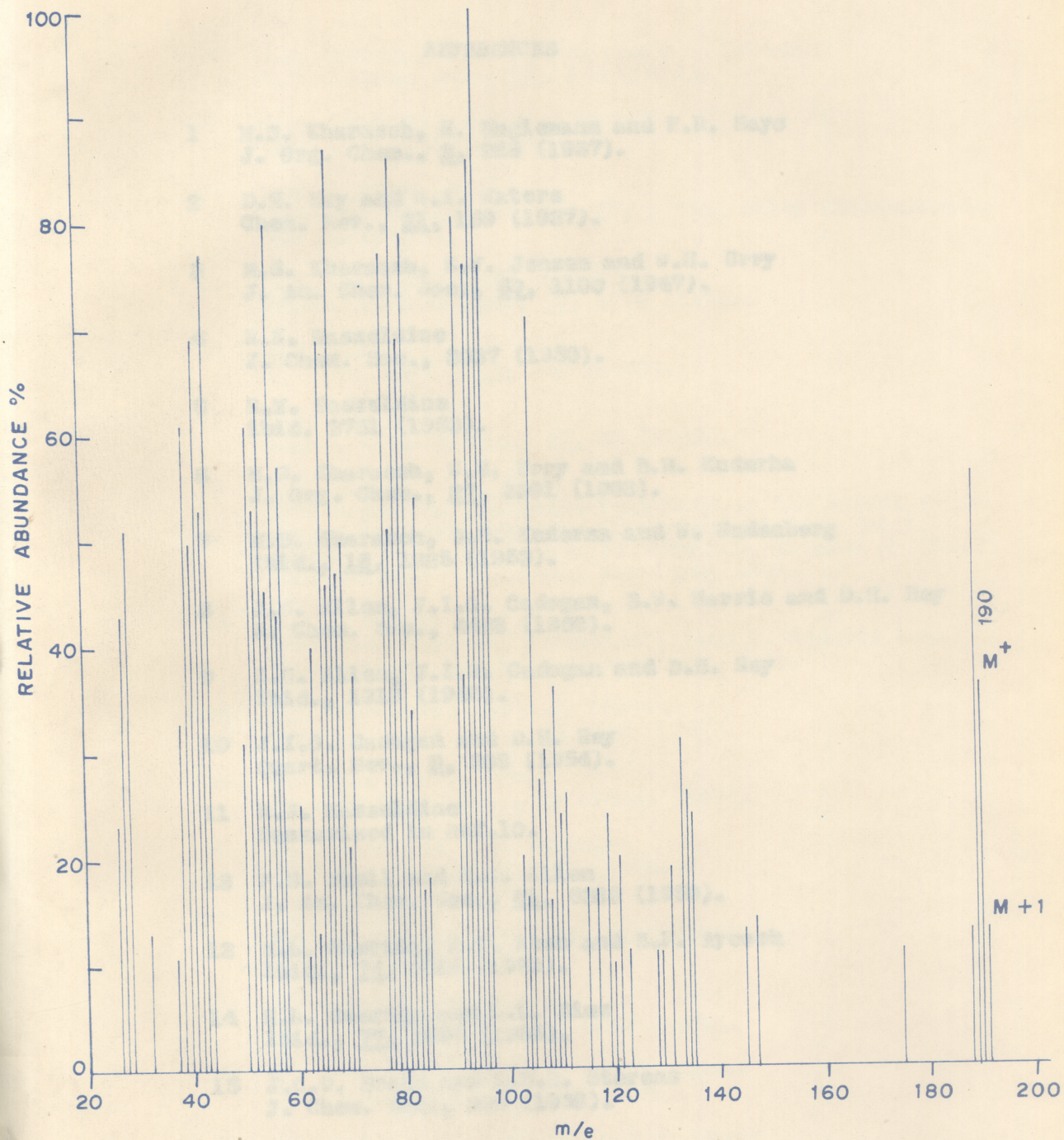


FIG. 2.20 MASS SPECTRUM OF 1-METHYLCYCLOHEXENE ALLYLIC DIMER

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CHAPTER III  
PHOTOINDUCED HYDROXYLATION OF OTHER  
ALICYCLIC OLEFINS

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The work on the photo-induced hydroxylation of olefins has been extended to cycloheptene, 1-methylcycloheptene and cyclooctene with a view to study the effect of the ring size on the process.

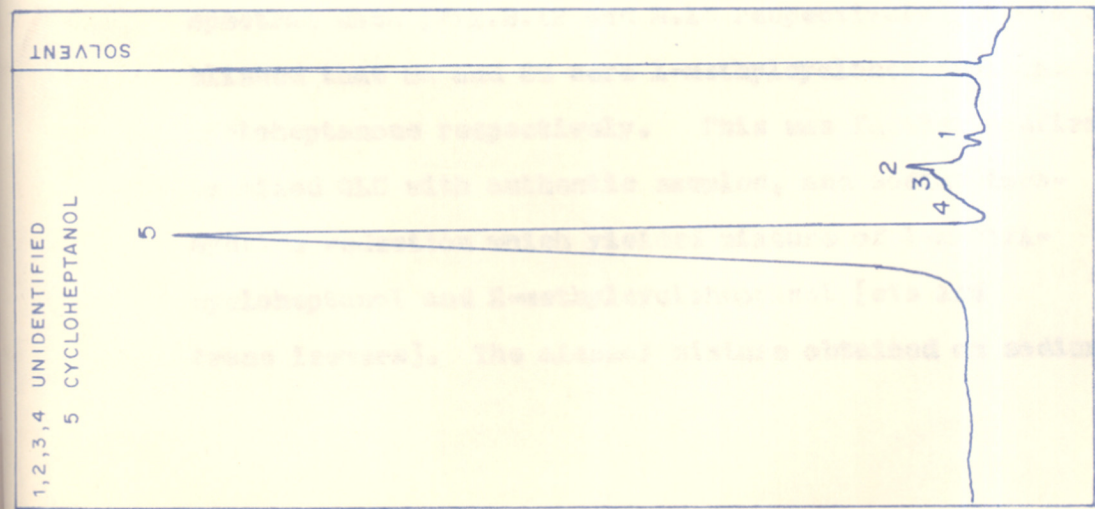
### Results

#### 1. Cycloheptene-Hydrogen peroxide

A solution of cycloheptene and hydrogen peroxide in acetonitrile was irradiated till the disappearance of  $H_2O_2$ . Acetonitrile was removed on waterbath at reduced pressure, and the material obtained was distilled to give a colourless liquid. GLC analysis [Fig.3.1] of this material revealed one prominent product (90%). This was isolated in pure form by preparative GLC, using carbowax column, and was characterized as cycloheptanol from its spectral data in comparison with that of the authentic sample. It was further confirmed by chromic acid oxidation to cycloheptanone. The rest of the 10% material could not be investigated since it was a complex mixture.

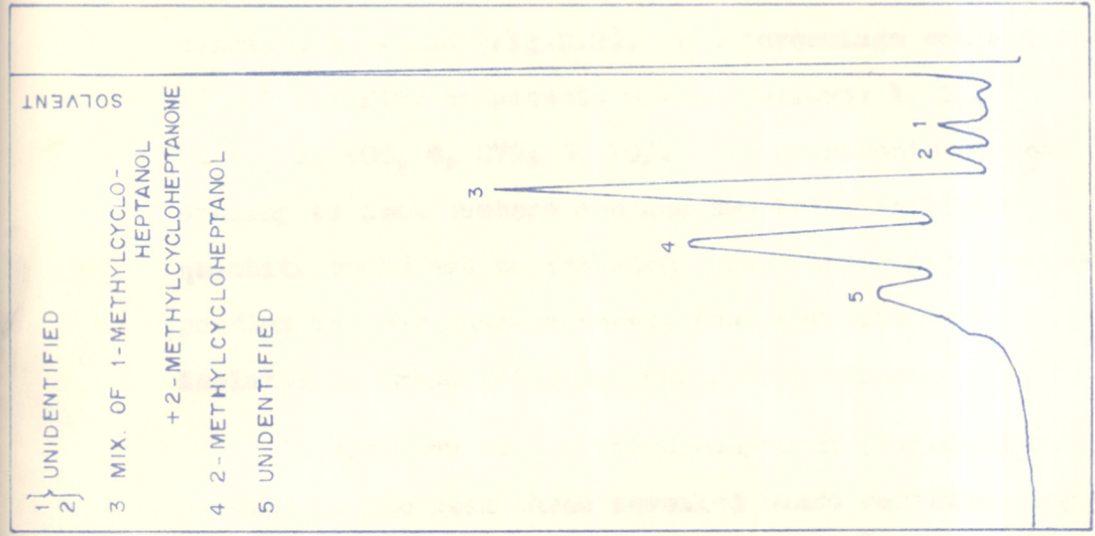
#### 2. 1-Methylcycloheptene-Hydrogen peroxide

A solution of 1-methylcycloheptene and hydrogen peroxide was irradiated in acetonitrile till the disappearance of  $H_2O_2$ . The reaction product obtained after



GLC OF CYCLOHEPTENE-H<sub>2</sub>O<sub>2</sub> REACTION PRODUCT

FIG. 3.1



GLC OF 1-METHYLCYCLOHEPTENE H<sub>2</sub>O<sub>2</sub> REACTION PRODUCT

FIG. 3.2

the usual work-up was found to be a mixture of five components by GLC [Fig.3.2]. The percentage composition of all the five components was as follows: 1, 3%; 2, 2%; 3, 48%; 4, 37%; 5, 10%. The components corresponding to peak numbers one and two being in minor quantity could not be isolated. The components corresponding to peak numbers three, four and five were isolated by preparative GLC using FFAP column.

IR spectrum of the third component [Fig.3.3] corresponding to the peak three revealed bands corresponding to ketone [ $1701\text{ cm}^{-1}$ ] and hydroxyl [ $3663\text{ cm}^{-1}$ ] functions, as ketoalcohol was not expected in the reaction product, this component was checked for its purity on different columns, and it was found that it resolved further into two components namely 3A (51%) and 3B (49%) when subjected to GLC analysis of QF1 column [Fig.3.4]. The material was subjected to GC-Mass analysis using QF1 column. From mass spectral data [Fig.3.12 and 3.15 respectively] it was established that 3A and 3B were 1-methylcycloheptanol and 2-methylcycloheptanone respectively. This was further confirmed by mixed GLC with authentic samples, and sodium borohydride reduction which yielded mixture of 1-methylcycloheptanol and 2-methylcycloheptanol [cis and trans isomers]. The alcohol mixture obtained on sodium

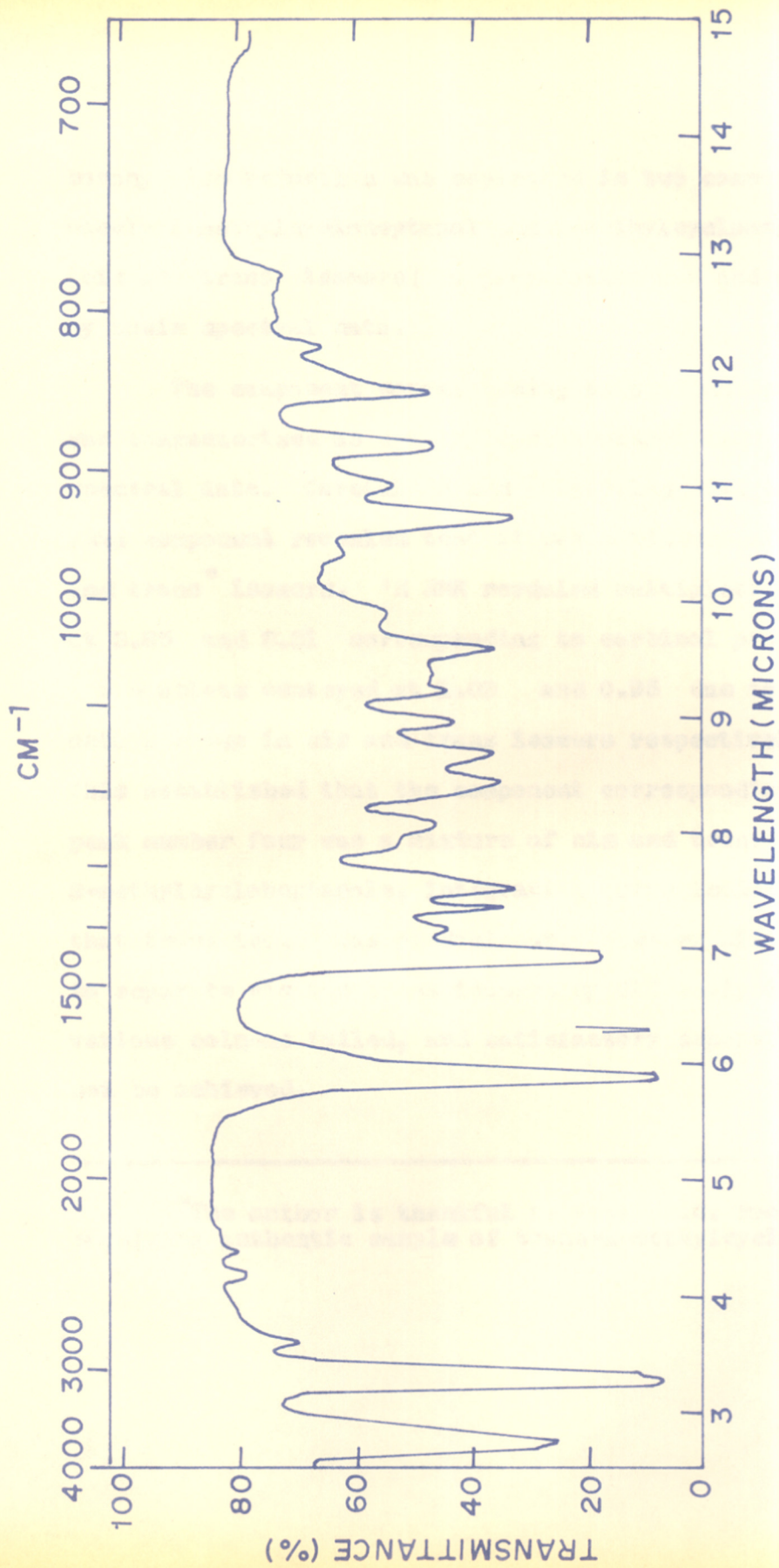


FIG.3.3 IR SPECTRUM OF COMPONENT CORRESPONDING TO PEAK No.3 IN FIG. 3.2

borehydride reduction was separated in two components namely 1-methylcycloheptanol and 2-methylcycloheptanol [cis and trans<sup>\*</sup> isomers] by preparative GLC and characterized by their spectral data.

The component corresponding to peak number four was characterized as 2-methylcycloheptanol from its spectral data. Careful <sup>1</sup>H NMR [Fig.3.14] analysis of this component revealed that it was a mixture of cis and trans<sup>\*</sup> isomers. <sup>1</sup>H NMR revealed multiplets centered at 3.85 and 3.31 corresponding to carbinol proton and two doublets centered at 1.03 and 0.95 due to secondary methyl group in cis and trans isomers respectively<sup>1</sup>. This established that the component corresponding to peak number four was a mixture of cis and trans 2-methylcycloheptanols, integration curve indicated that trans isomer was predominant. However all the attempts to separate cis and trans isomers by GLC analysis using various columns failed, and satisfactory separation could not be achieved.

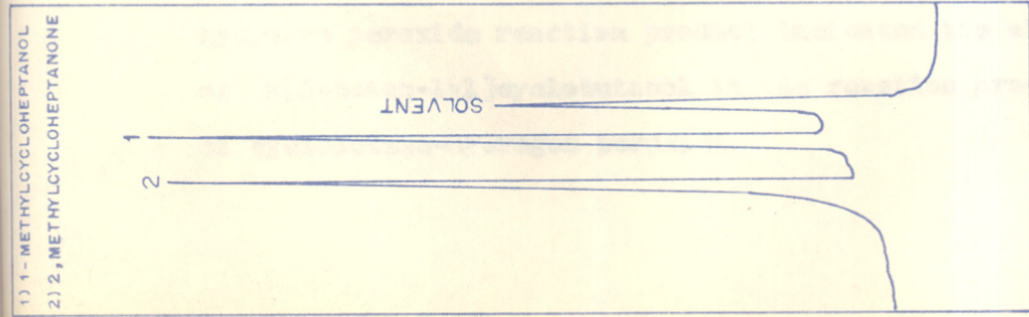
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<sup>\*</sup>The author is thankful to Prof. H.C. Brown for supplying authentic sample of trans-2-methylcycloheptanol.

The component corresponding to peak number five could not be obtained in sufficiently pure form for further investigation, due to its relatively small percentage in total reaction mixture. However the  $^1\text{H}$  NMR of this component indicated presence of olefinic protons indicating that it may be some allylic product.

### 3. Cyclooctene - Hydrogen peroxide

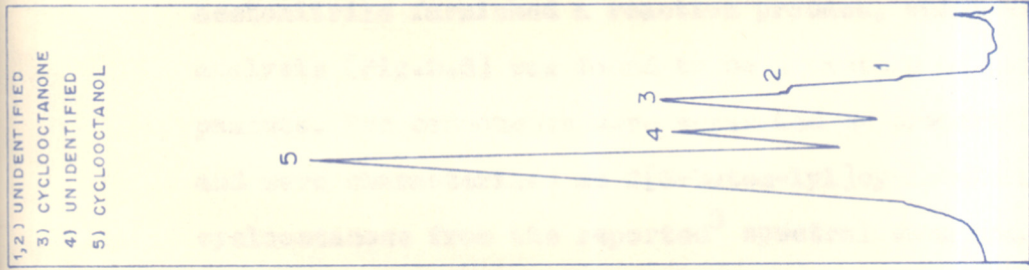
The reaction product obtained from the irradiation of the solution of cyclooctene and hydrogen peroxide in acetonitrile revealed a complex GLC pattern [Fig.3.5a], consisting of 5 components. The component corresponding to peak number 5 [78%] was characterized as cyclooctanol, after separating on preparative GLC and comparing its spectral data with those of that authentic sample. The close retention time of other four components prohibited their separation on preparative GLC. However the total reaction mixture was separated in two parts on preparative GLC; part one containing components corresponding to peak numbers one to four and part two containing component corresponding to peak number five [established as cyclooctanol]. The IR spectrum of part one exhibited band corresponding to ketone function [ $1710\text{ cm}^{-1}$ ]. Mixed GLC of total reaction mixture with authentic sample of cyclooctanone [Fig.3.5b] suggested that the component corresponding



GLC OF 3rd COMPONENT

IN FIG.3.2

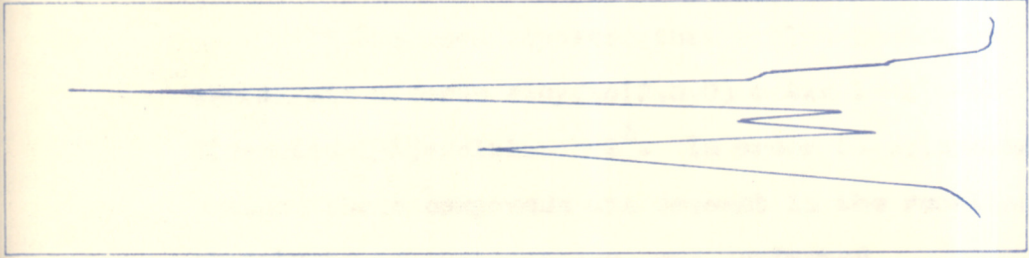
FIG. 3.4



GLC OF CYCLOOCTENE-H<sub>2</sub>O<sub>2</sub>

REACTION PRODUCT

FIG. 3.5 (a)

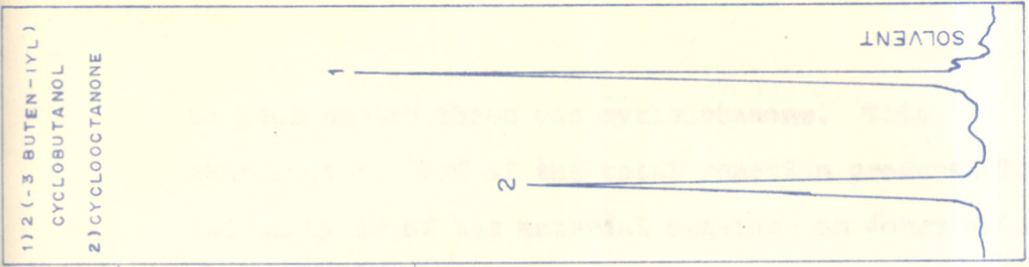


GLC OF CYCLOOCTENE

H<sub>2</sub>O<sub>2</sub> REACTION PRODUCT

+ CYCLOOCTANONE

FIG. 3.5 (b)



GLC OF CYCLOOCTANONE

PHOTOLYSIS

FIG. 3.6



to peak number three was cyclooctanone. This constituted 13% of the total reaction product. The GLC analysis of the material obtained on Jones oxidation showed that the major peak corresponding to cyclooctanol has been changed into the peak corresponding to cyclooctanone.

It has been reported that cyclooctanone on photolysis affords bicycle[3,3,0] octan-1-ol<sup>2</sup> and 2[3-buten-1yl]cyclobutanol<sup>3</sup>. In order to determine whether these compounds are present in the reaction mixture, photolysis of cyclooctanone was performed.

#### 4. Photolysis of cyclooctanone

Cyclooctanone after 11 hours of irradiation in acetonitrile furnished a reaction product, which after GLC analysis [Fig.3.6] was found to be a mixture of two components. The components were separated by preparative GLC and were characterized as 2[3-buten-1yl]cyclobutanol and cyclooctanone from the reported<sup>3</sup> spectral data and comparison of spectral data with that of the authentic sample of cyclooctanone respectively. However, the mixed GLC of 2[3-buten-1yl]cyclobutanol and cyclooctene-hydrogen peroxide reaction product indicated the absence of 2[3-buten-1yl]cyclobutanol in the reaction product of cyclooctene-hydrogen peroxide.

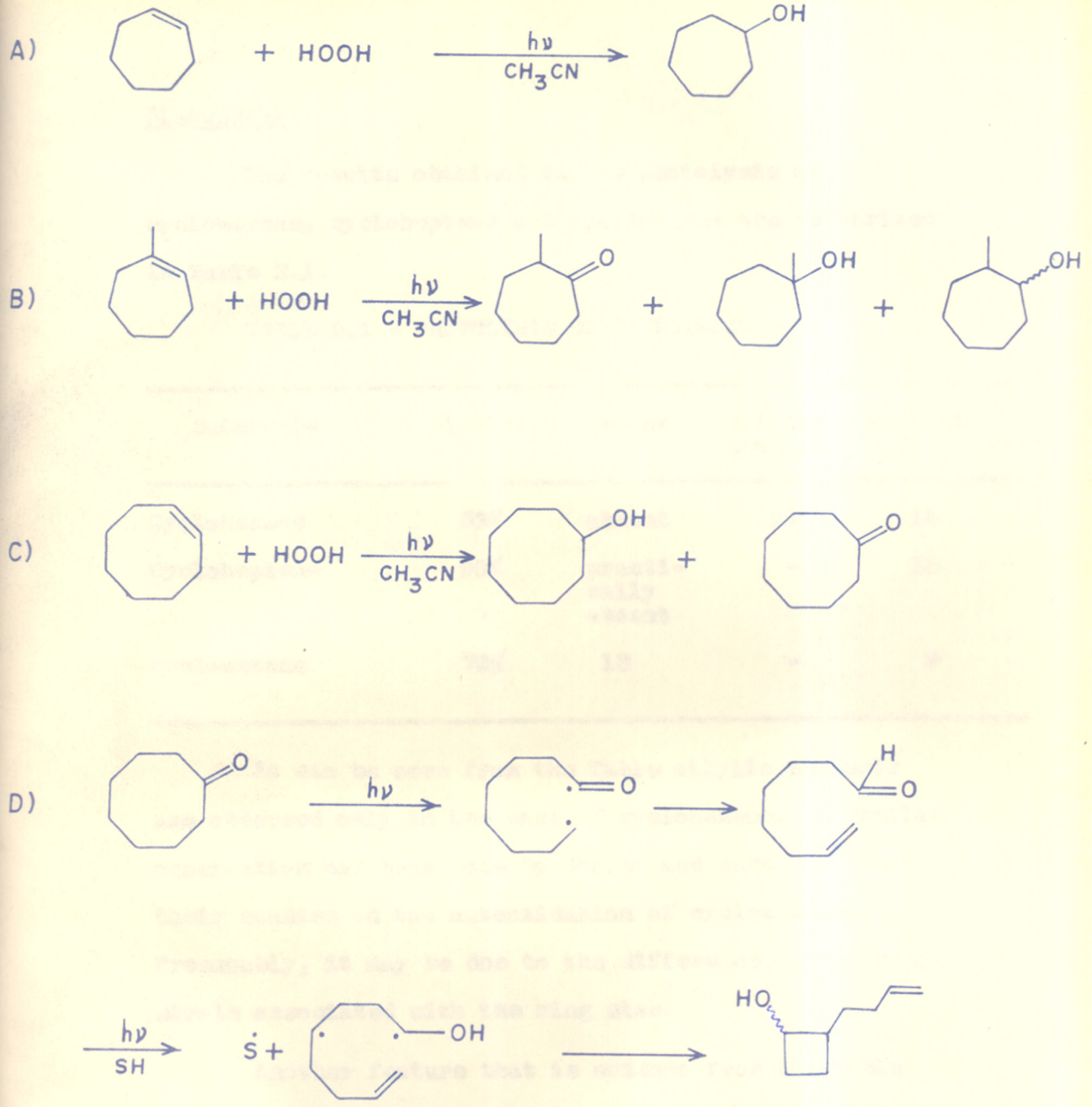


FIG. 3.7 PHOTOLYSIS PRODUCTS OF :-

- A) CYCLOHEPTENE
- B) 1-METHYLCYCLOHEPTENE

DISCUSSION

The results obtained in the photolysis of cyclohexene, cycloheptene and cyclooctene are summarized in Table 3.1.

TABLE 3.1 - PHOTOLYSIS OF CYCLOALKENES

Substrate	Alcohol	Ketone	Allylic products	Unidentified
Cyclohexene	53%	absent	29%	18
Cycloheptene	90%	practically absent	-	10
Cyclooctene	78%	13	-	9

As can be seen from the Table allylic products are observed only in the case of cyclohexene. A similar observation has been made by Sharma and Sukh Dev<sup>4</sup> in their studies on the autooxidation of cycloalkenes. Presumably, it may be due to the difference in the ring strain associated with the ring size.<sup>5,6</sup>

Another feature that is evident from the Table is that appreciable quantity of ketone is formed only in the photolysis of cyclooctene, presumably this is due to the I strain factor<sup>5,6</sup> which makes the transformation of

a  $sp^3$  carbon to a  $sp^2$  carbon particularly facile in the case of 8-membered rings.

The formation of 2[3-buten-yl]cyclobutanol is depicted in Fig.3.7 as suggested by Sung Moon and Howard Behm<sup>3</sup>.

The results of the photolysis of 1-methylcyclohexene and 1-methylcycloheptene are presented in Table 3.2.

It may be noticed that the ketone percentage is more in the larger ring size presumably due to the I strain factor<sup>5,6</sup>.

In this series also the allylic product is more in the six membered ring system.

TABLE 3.2 - PHOTOLYSIS OF 1-METHYL CYCLOALKENES

Substrate	Tertiary alcohol	2-Methyl cyclic ketone	Secondary alcohol	Allylic product	Unidentified.
1-Methylcyclohexene	19%	4%	38%	36%	3.00%
1-Methylcycloheptene	24.5%	23.5%	37%	Unestimated < 10% (grouped with unidentified)	15%

## E X P E R I M E N T A L

See Chapter 2 for 'General remarks'.

A. GLC: The reaction products obtained from (1) cycloheptene- $H_2O_2$  and (2) cyclooctene- $H_2O_2$  were analyzed on Aerograph model A-350-B using 6' x 1/4" aluminium column packed with 20% carbowax-20M adsorbed on chromosorb W of 60-80 mesh.

Preparative GLC of these reaction products was carried out on the same model using a 10' x 3/8" aluminium column packed with 30% carbowax-20M adsorbed on chromosorb W of 30-60 mesh.

Analytical GLC of (3) 1-Methylcycloheptene- $H_2O_2$  experiment was carried out on the same model using FFAP 20% and QF1 [5% silicon QF1 adsorbed on chromosorb W 60-80 mesh in aluminium column 12' x 1/4"] analytical columns.

Preparative GLC of this experiment was carried out on the same model using 30% FFAP preparative column.

GC/Mass analysis of the third component of this experiment was carried out on 3% QF1 column [using 6' glass column] using AEI-M.S.-30 GC-MS model.

Analytical GLC of (4) Cyclooctanone experiment was

carried out on Aerograph model using 10' x 1/4" aluminium column with 20% diethylene glycol polysuccinate, "P" packed on chromosorb W of 60-80 mesh. Preparative GLC was carried out on the same model using 10' x 3/4" aluminium column packed with 30% "P" on chromosorb W of 30-60 mesh.

**B. Materials:** Cycloheptene was prepared by dehydration of cycloheptanol [from Koch-Light Laboratories Ltd., England] using phosphoric acid and purified by distilling the olefin over sodium before use.

1-Methylcycloheptene was prepared by dehydrating 1-methylcycloheptanol using iodine. The alcohol was prepared by Grignard reaction of cycloheptanone and methyl iodide. The olefin was distilled over sodium before use.

Cyclooctene and cyclooctanone were obtained from Koch-Light Laboratories Ltd., England and M/s Fluka respectively.

### C. General procedure for irradiation

A mixture of olefin [0.15 mole] and hydrogen peroxide [0.015 mole, 88-90%] in acetonitrile [300 ml] was irradiated using 450 Watts Hanovia high pressure mercury lamp, till the disappearance of  $H_2O_2$  [checked by KI-acetic acid]. Generally this required 7-8 hours. For irradiation assembly see Chapter 2. Solvent was stripped off along with unreacted olefin and final material was distilled under

reduced pressure [90-180°C/10-1 mm of Hg].

I. Cycloheptene-H<sub>2</sub>O<sub>2</sub>:

A mixture of cycloheptene [14.2 g i.e. 0.15 mole] and hydrogen peroxide [0.5795 g, 88% i.e. 0.015 mole] in acetonitrile [300 ml] was irradiated till the disappearance of H<sub>2</sub>O<sub>2</sub> [checked after 1/2 hour interval after 5 hours of irradiation]. This required 7 hours. The reaction product was transferred to distillation assembly and solvent was removed along with unreacted olefin; residual reaction product was distilled under reduced pressure over a range of 90-180°C at 1-10 mm of Hg pressure. The receiver flask was kept cool at 0°C in ice bath to prevent evaporation of low boiling components at high vacuum.

Yield → 2.19 g.      conversion 64.00%

Similarly run experiments with same molar amounts of hydrogen peroxide and olefin in acetonitrile gave following results.

II. 1-Methylcycloheptene-H<sub>2</sub>O<sub>2</sub>

Reaction period 7.5 hours

Yield .. 2.52 g      conversion 65.6%

III. Cyclooctene-H<sub>2</sub>O<sub>2</sub>

Reaction period 7.5 hours

Yield .. 1.39 g      conversion 36.2%

IV. Cyclooctanone

Cyclooctanone [1.87 g i.e. .015 mole] in acetonitrile



[300 ml] was irradiated for eleven hours and worked up as usual. The reaction product was distilled under reduced pressure 74-90°C/12 mm.

Yield .. 0.52 g.

V. Jones oxidation of cycloheptanol<sup>7</sup>

Cycloheptanol [0.570 g] was taken in dry ether (40 ml) at 0°C (ice bath). To this solution was added Jones reagent (2 ml) under N<sub>2</sub> atmosphere and stirred for 15 min. It was diluted with ice cold water (50 ml) and extracted with ether (50 ml x 3) washed with water and dried (Na<sub>2</sub>SO<sub>4</sub>). After removal of solvent crude cycloheptanone was obtained which was distilled (0.521 g, b.p. 100-120°C(bath)/20 mm).

VI. NaBH<sub>4</sub> reduction of 1-methylcycloheptanol.

2-methylcycloheptanone mixture

The alcohol-ketone mixture (0.850 g) was dissolved in ether (30 ml) and methanol (100 ml) and to it was added NaBH<sub>4</sub> (0.185 g) in one lot. This solution was stirred at room temp. for 2 hours. Acetic acid (1 ml) was added and the solvent was distilled. Ice-cold water (50 ml) was added, and the reaction product extracted with ether (100 ml x 3). The combined ether extract was washed with brine, water and dried (Na<sub>2</sub>SO<sub>4</sub>). Solvent removed and crude material was distilled [100-120°C(bath)/10 mm] 0.830 g.

#### D. Analysis of the products

The reaction products of various experiments were subjected to GLC analysis. Particulars of various columns are given earlier under the heading (A) GLC. Only the product composition is given below.

##### I. Cycloheptene-H<sub>2</sub>O<sub>2</sub>

Cycloheptanol (90%), others (10%).

##### II. 1-Methylcycloheptene-H<sub>2</sub>O<sub>2</sub>

1-Methylcycloheptanol (Peak 3A → 24.5%),  
2-Methylcycloheptanone [Peak 3B → 23.5%], 2-Methylcycloheptanol (cis + trans) [Peak 4 → 37%] and others [15%].

##### III. Cyclooctene - H<sub>2</sub>O<sub>2</sub>

Cyclooctanol [78%], cyclooctanone [13%] and other [9%].

##### IV. Cyclooctanone

2(3-buten-yl) cyclobutanol (43%) and cyclooctanone unreacted (57%).

#### E. Isolation of the products

Various components of different experiment were isolated using preparative GLC as described earlier under the heading (A) GLC.

#### F. Purification of the products

All the products obtained from preparative GLC were further purified by distillation before recording the

spectral data.

#### G. Characterization of the products

The compounds isolated from various reaction products as described above were characterized from their spectral data and comparison with authentic samples.

#### H. Spectral and other data

Cycloheptanol:  $C_7H_{14}O$ , Mol. wt. 114, b.p. 98-104/20 mm  
[GLC Fig.3.1, Peak 5, RRT 2.3]

IR (Fig.3.8): 3450(s), 2995(s), 1475(s), 1300(w),  
1205(w), 1120(w), 1040(s), 975(w),  
920(w),  $cm^{-1}$ .

$^1H$  NMR (Fig.3.9): 1.57 [broad s, 12 protons, methylene protons], 2.1 [s, 1 proton, exchanges with  $D_2O$  hydroxyl proton], 3.77 [m, 1 proton, carbinol proton.]

Mass:  $M^+$  at m/e 114 base peak at m/e 57, other major peaks at m/e 68, 81, 41, 55, 96, 44, 67.

1-Methylcycloheptanol:  $C_8H_{16}O$ , Mol. wt. 128, b.p. 82-84°/  
20 mm.

[GLC Fig.3.2 Peak 3 RRT 2.2]

Fig.3.4 Peak 1 RRT 1.0]

IR (Fig.3.10): 3272(s), 2857(s), 1460 (s), 1370(m),  
1282(w), 1250 (w), 1198(m), 1127(m),  
1053(m), 943(m), 926 (m), 893 (m), 833(w),  $cm^{-1}$ .

- $^1\text{H}$  NMR (Fig.3.11): 1.17 [s, 3 protons, tertiary methyl group protons]  
 1.53 [broad s, 12 protons, methylene protons]  
 1.80 [s, 1 proton, exchanges with  $\text{D}_2\text{O}$ , hydroxyl proton].

Mass (Fig.3.12):  $\text{M}^+$  at  $m/e$  128 base peak at  $m/e$  71 other major peaks at  $m/e$  43, 58, 113, 85, 18, 28.

2-Methylcycloheptanol:  $\text{C}_8\text{H}_{16}\text{O}$ , Mol. wt. 128, b.p. 88-90°/10 mm.

GLC Fig.3.2 Peak 4 R.T 3.3.

IR (Fig.3.13): 3571(s), 3030(s), 1449(m), 1351(w), 995(m), 962(w),  $\text{cm}^{-1}$ .

- $^1\text{H}$  NMR: (Fig.3.14): 0.95 [d, corresponding to secondary methyl of trans isomer] } 3 protons  
 1.03 [d, corresponding to secondary methyl of cis isomer] }  
 1.4 [s, 1 proton, exchanges with  $\text{D}_2\text{O}$  hydroxyl proton]  
 1.57 [broad s, 11 protons, 10 methylene and 1 methine proton].  
 3.31 [s due to carbinol proton corresponding to trans isomer. ] 1 proton  
 3.85 [s due to carbinol proton corresponding to cis isomer] ]

2-Methylcycloheptanone:  $C_8H_{14}O$ , Mol. Wt. 126, b.p.  
80-85°/10 mm.

[GLC Fig.3.2 Peak 3 RRT 2.2

Fig.3.4 Peak 2 RRT 2.4]

Mass (Fig.3.15):  $M^+$  at m/e 126, base peak at 95, other  
major peaks at m/e 41, 68, 18, 84, 112,  
28 and 97.

Cyclooctanol:  $C_8H_{16}O$ , Mol. Wt. 128, b.p. 99-103°/16 mm.

[GLC Fig.3.5 Peak 3 RRT 1.6]

IR(Fig.3.16): 3200(s), 2810 (s), 1480(s), 1455 (s),  
1365(m), 1300(m), 1125(w), 1100(w),  
1060(s), 995(s), 930(w), 900(w),  $cm^{-1}$ .

$^1H$  NMR (Fig.3.17): 1.6 [broad s, 14 protons, methylene  
proton]

3.4 [s, 1 proton exchanges with  $D_2O$ ,  
hydroxyl proton]

3.78 [m, 1 proton, carbinol proton].

Mass:  $M^+$  at m/e 128, base peak at m/e 59, other important  
peaks at m/e 69, 85, 43, 84, 57, 72, 56,  
95, 110.

Cyclooctanone:  $C_8H_{14}O$ , Mol. Wt. 126, b.p. 74-78°/12 mm.

[GLC Fig.3.5 Peak 1 RRT 1.00

Fig.3.6 Peak 2 RRT 3.8]

IR (Fig.3.18): 2895(s), 1700(s), 1480(m), 1460(m),  
 1425(w), 1340(w), 1220(w), 1160(w),  
 1110(w), 1080(w), 980(w), 860(w),  
 842(w),  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (Fig.3.13): 1.7 [c.a. m, 10 protons, methylene  
 protons away from keto group]  
 2.37 [c.a. m, 4 protons, methylene  
 protons near keto group]

Mass:  $\text{M}^+$  at m/e 126, base peak at m/e 55, other major  
 peaks at m/e 41, 99, 82, 84, 42, 98, 111.

2-(3-Buten-1-yl) cyclobutanol:  $\text{C}_8\text{H}_{14}\text{O}$ , Mol.wt. 126, b.p.  
 95-105° (bath)/10 mm.

[GLC Fig.3.6 Peak 1 RRT 1.0]

IR (Fig.3.20): 3502(s), 3030(s), 1639(s), 1445(s), 1316(m),  
 1220(w), 1163(w), 1111-1031 (broad),  
 990(w), 900(s), 833(w)  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (Fig.3.21): 1.7 [c.a. m, 9 protons, 4 ring methy-  
 lenes 4 sidechain methylenes and  
 1 ring methine proton].  
 2.97 [s, 1 proton, exchanges with  $\text{D}_2\text{O}$   
 hydroxyl proton]  
 3.93 [c.a.2doublet of triplet, 1 proton  
 carbinol proton]

5.00 [c.a. m, 2 protons secondary vinyl  
protons]

5.83 [c.a. m, 1 proton, tertiary vinyl  
proton]

Mass:  $M^+$  at  $m/e$  126, base peak at  $m/e$  57, other major  
peaks at  $m/e$  67, 41, 98, 54, 55, 82,  
44 and 39.

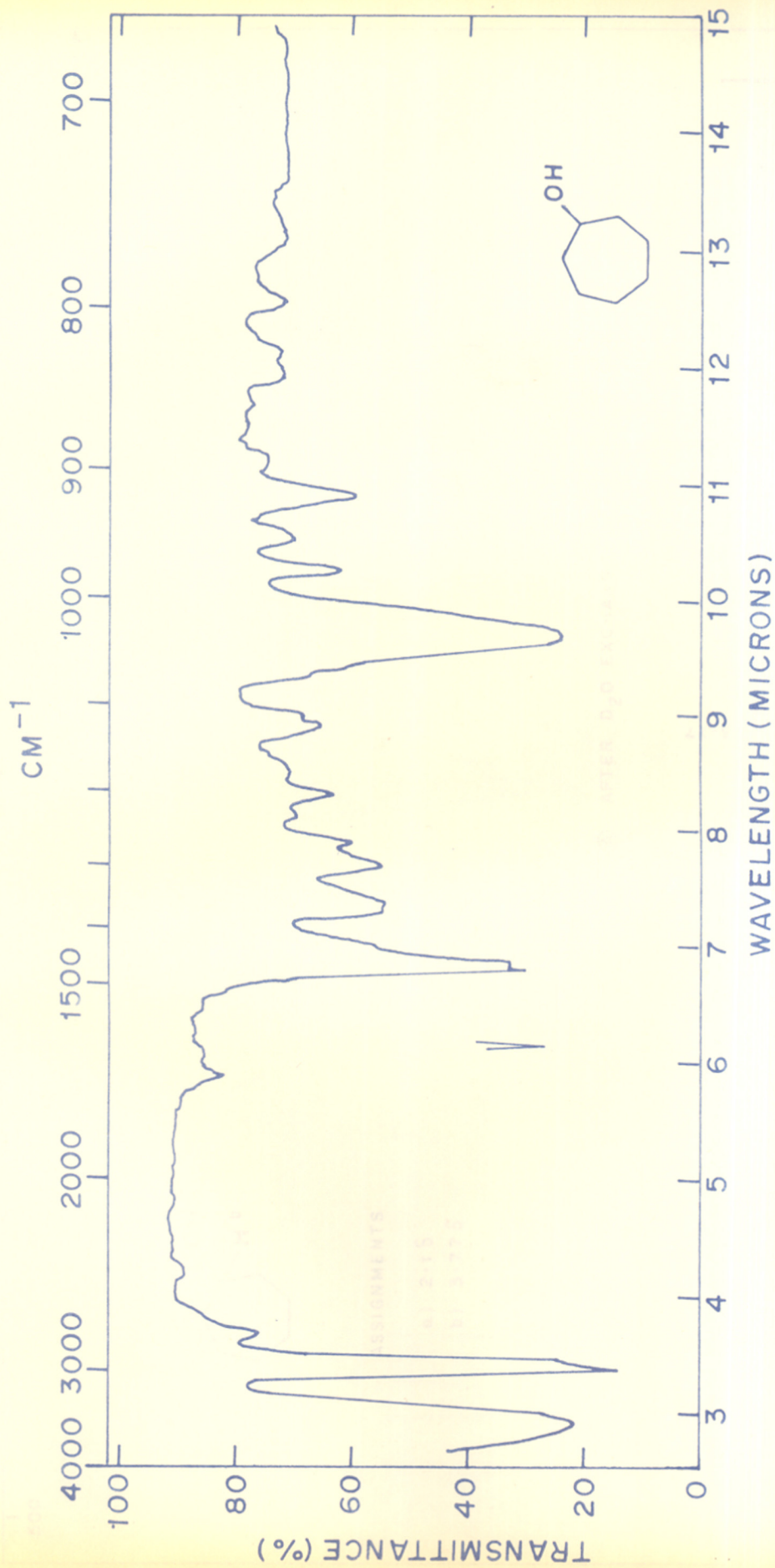
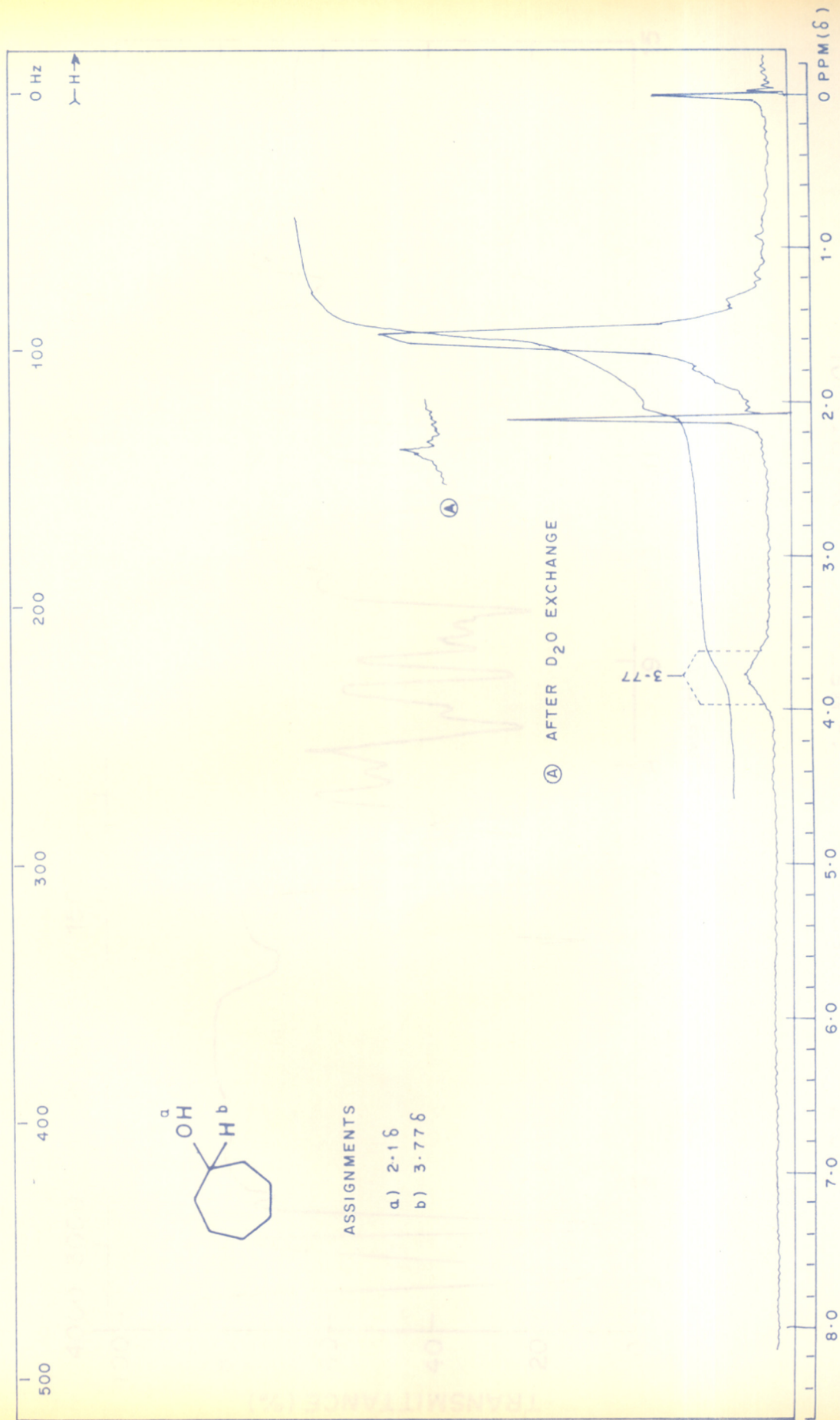


FIG. 3.8 IR SPECTRUM OF CYCLOHEPTANOL



FIG. 3.9 <sup>1</sup>H NMR SPECTRUM OF CYCLOHEPTANOL

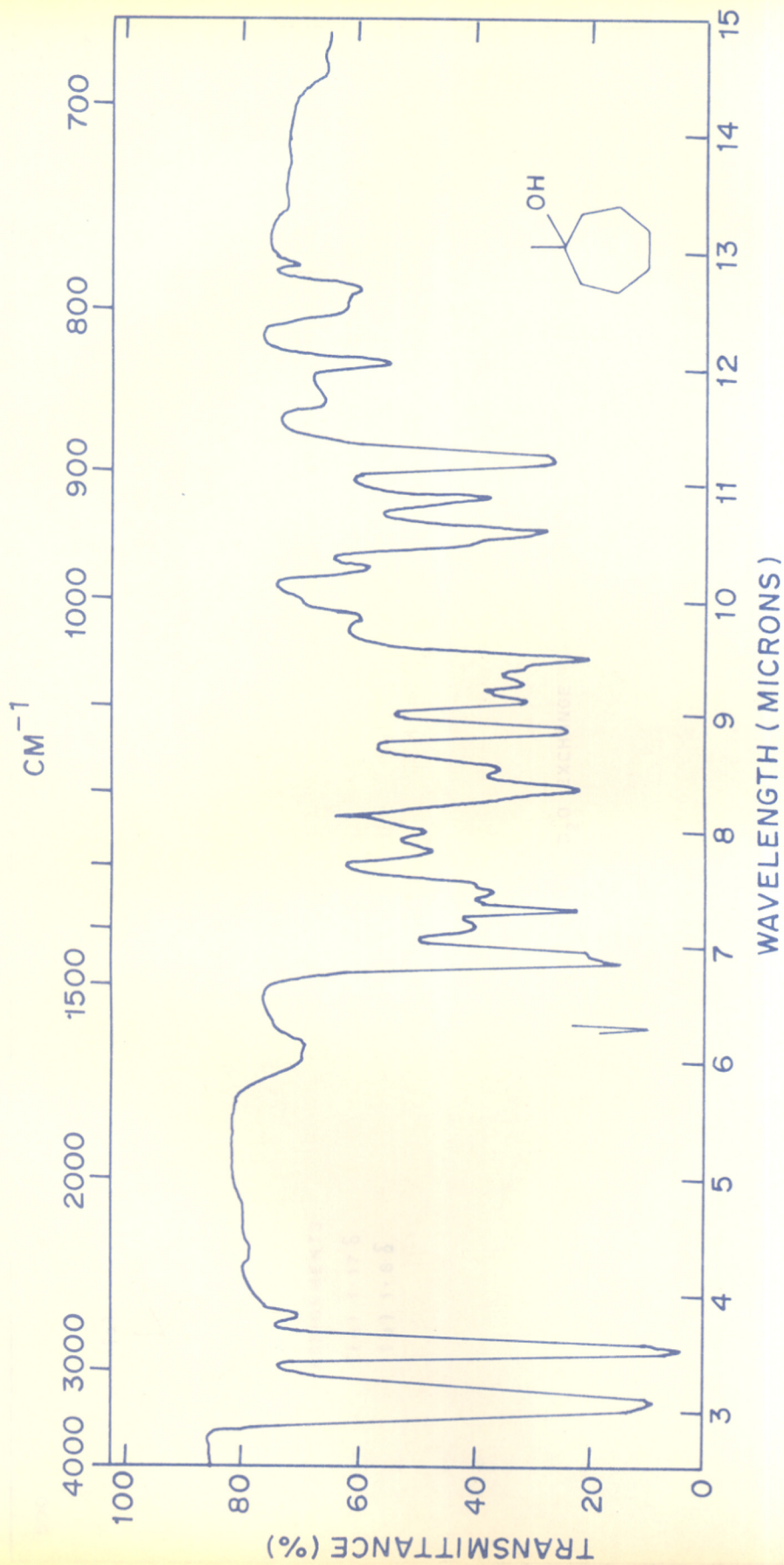


FIG. 3.10 IR SPECTRUM OF 1-METHYLCYCLOHEPTANOL

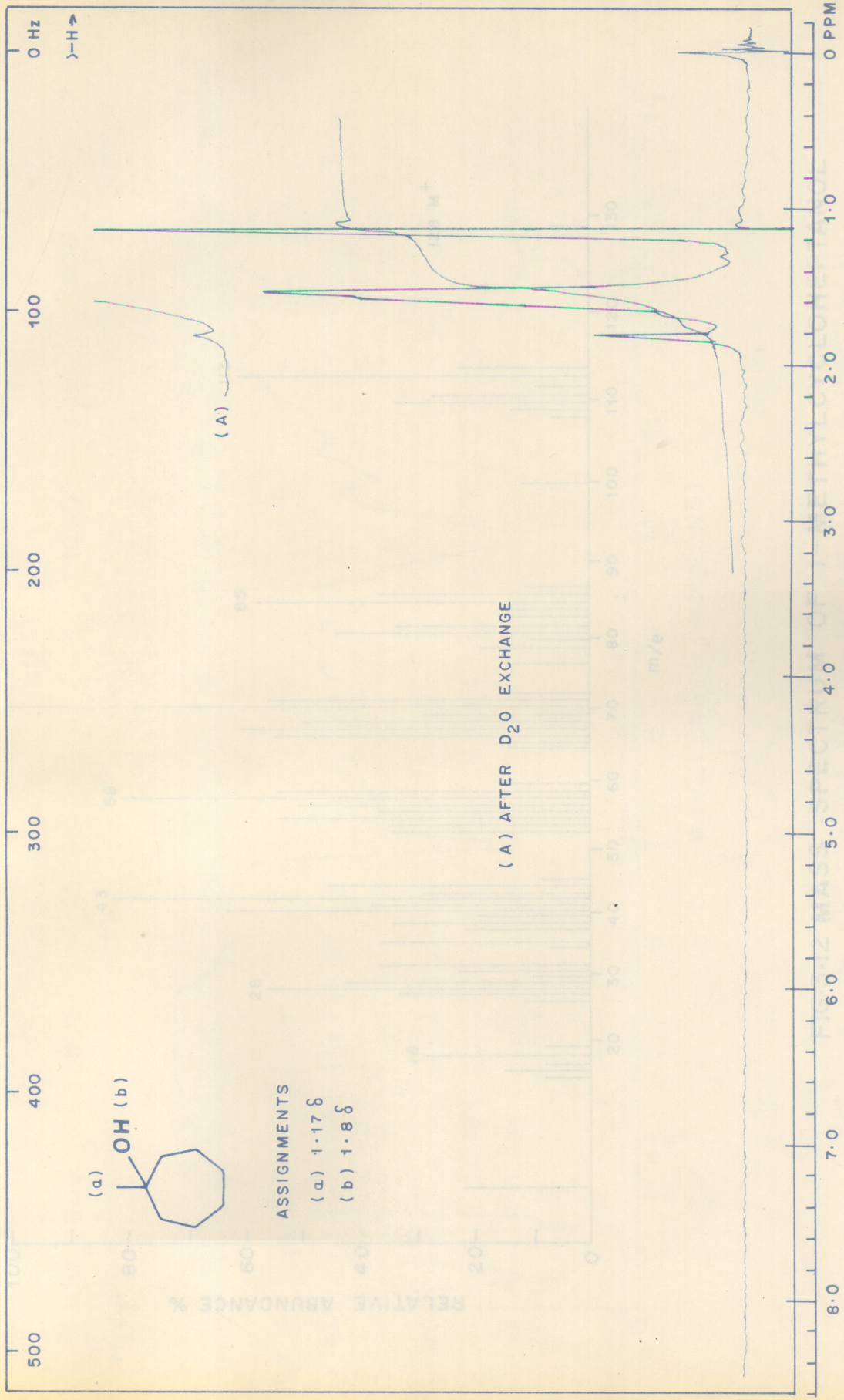


FIG. 3.11 <sup>1</sup>H NMR SPECTRUM OF 1-METHYLCYCLOHEPTANOL

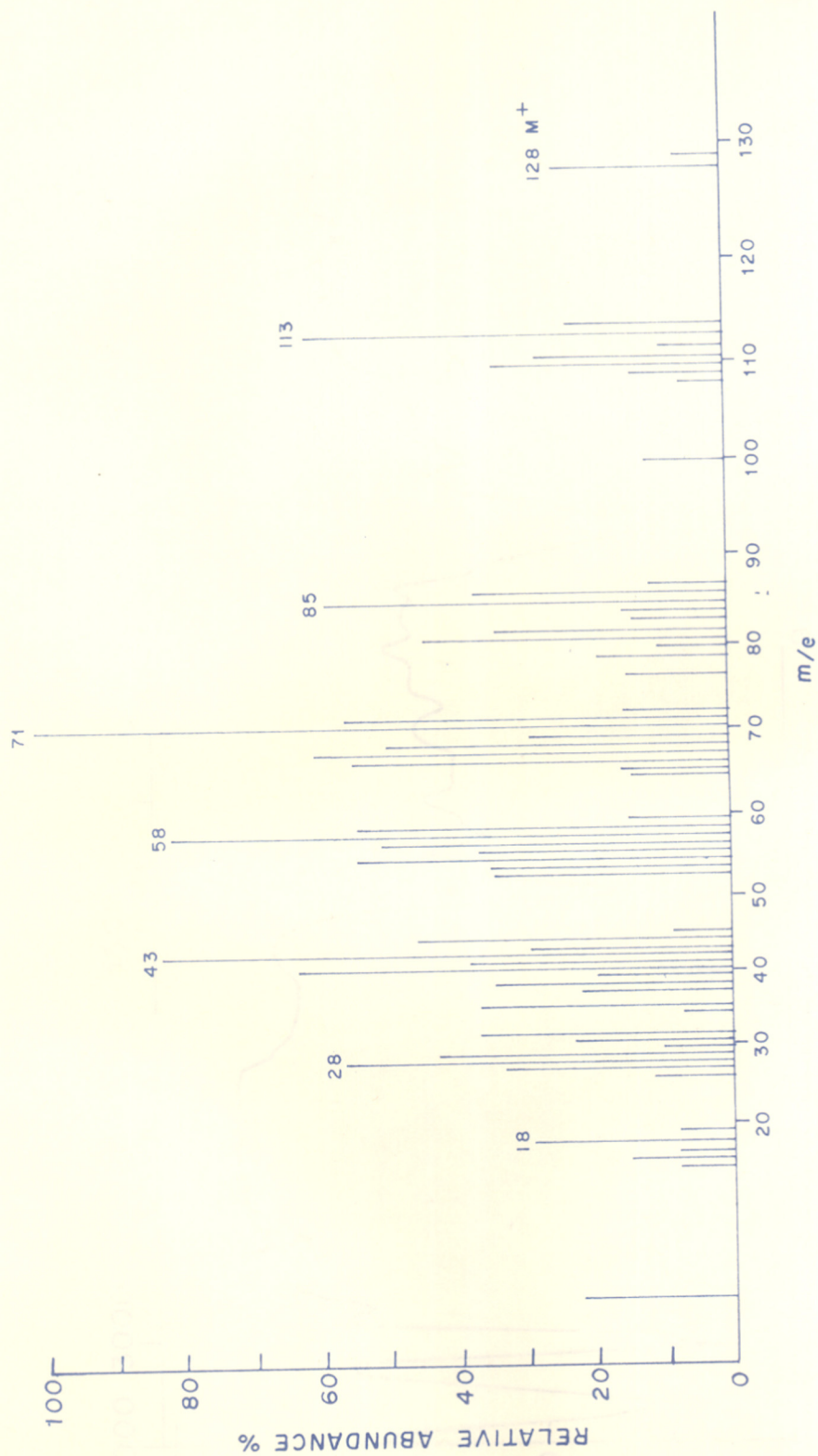


FIG.3.12 MASS SPECTRUM OF 1-METHYLCYCLOHEPTANOL

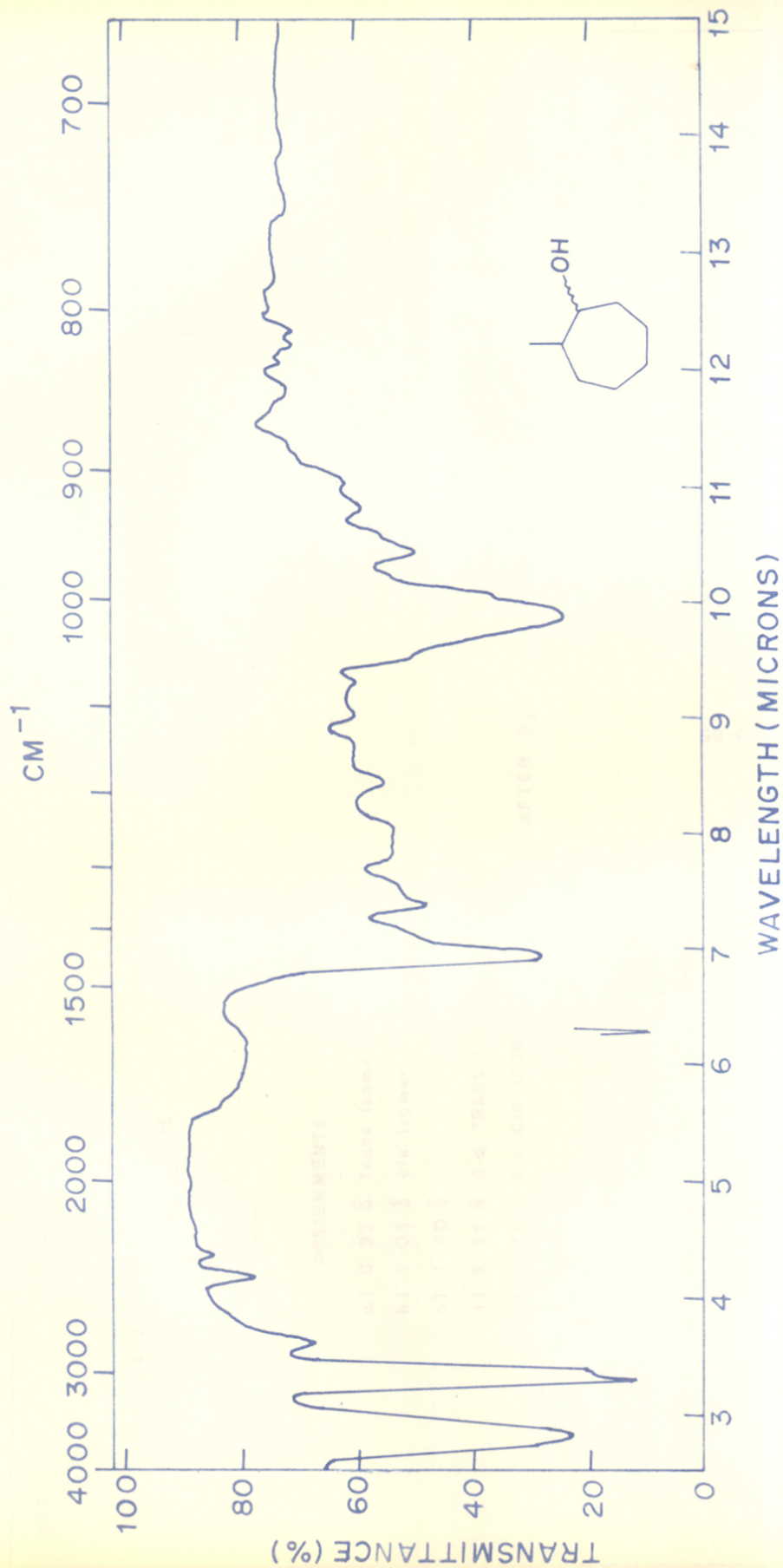


FIG. 3.13 IR SPECTRUM OF 2-METHYLCYCLOHEPTANOL

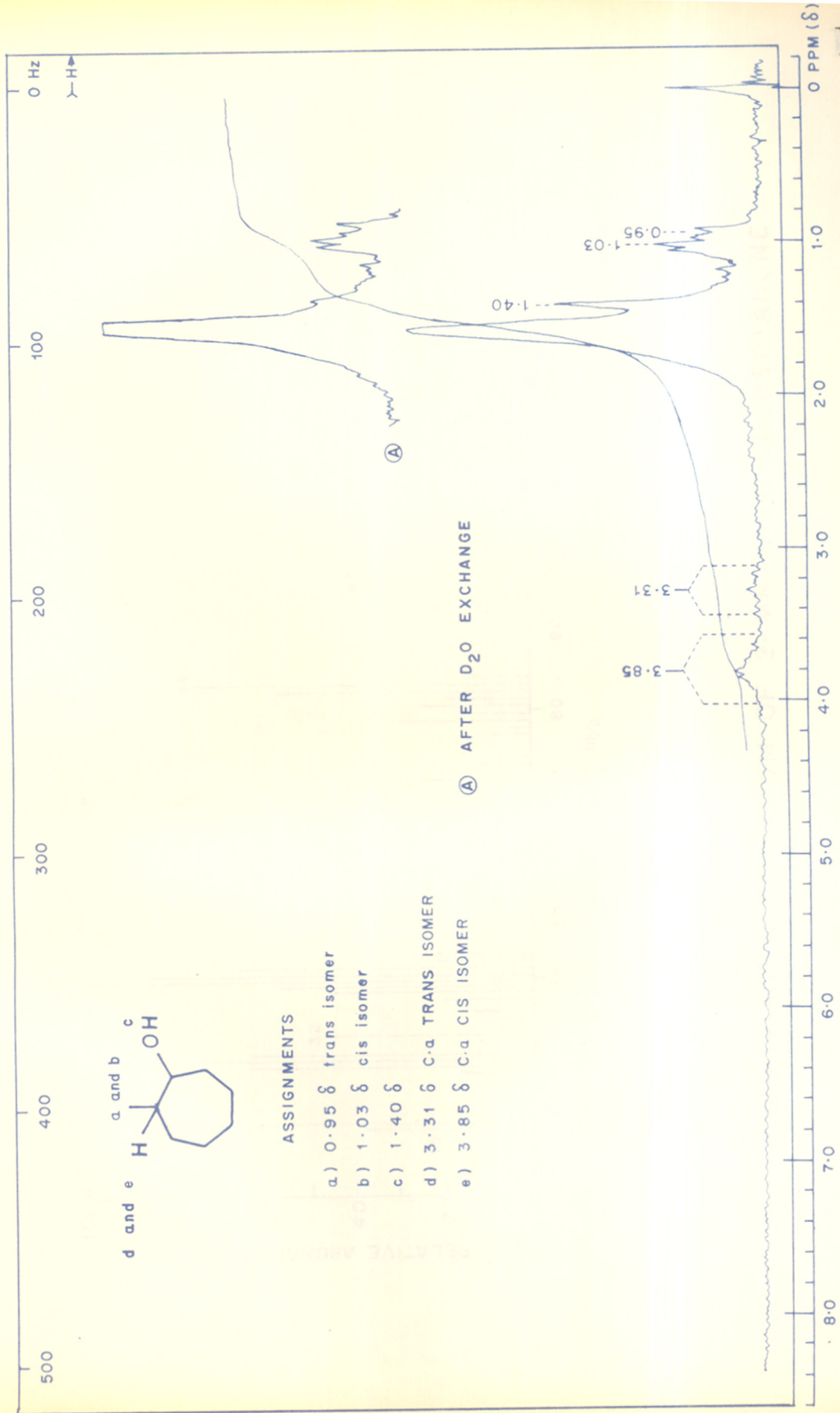


FIG. 3-14 <sup>1</sup>H NMR SPECTRUM OF 2-METHYLCYCLOHEPTANOL

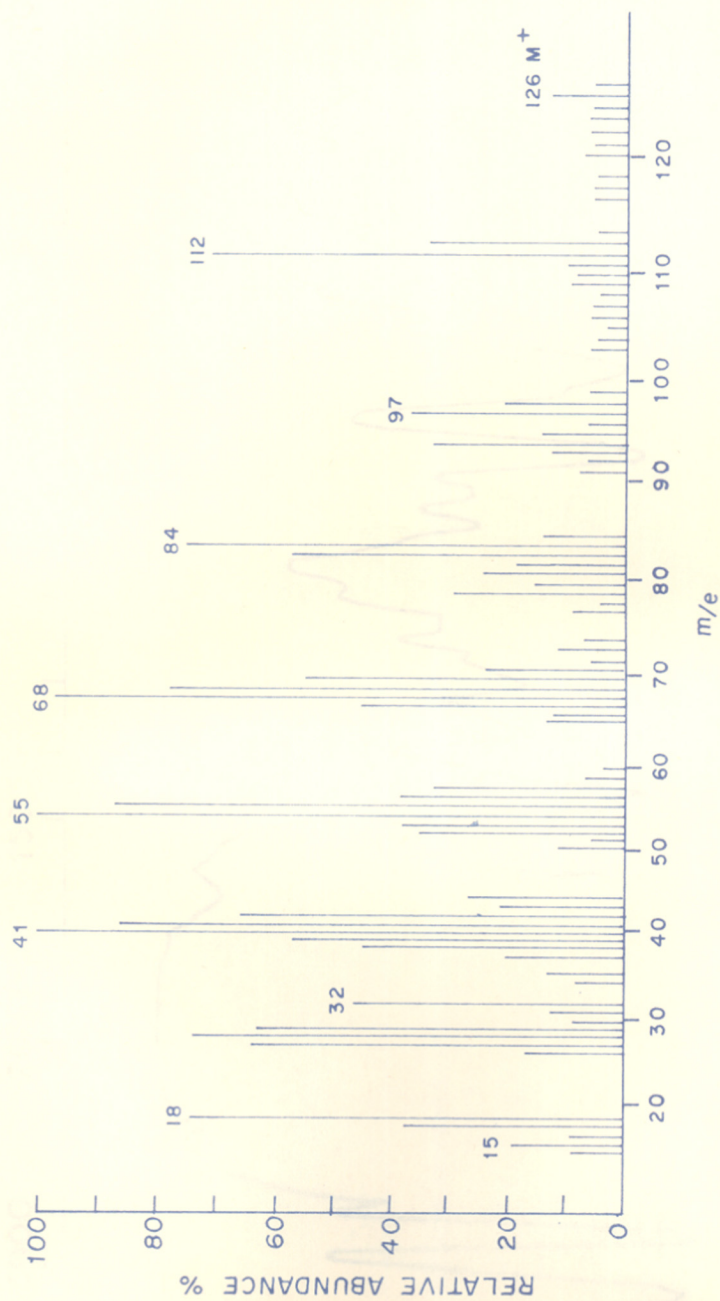


FIG. 3.15 MASS SPECTRUM OF 2-METHYLCYCLOHEPTANONE

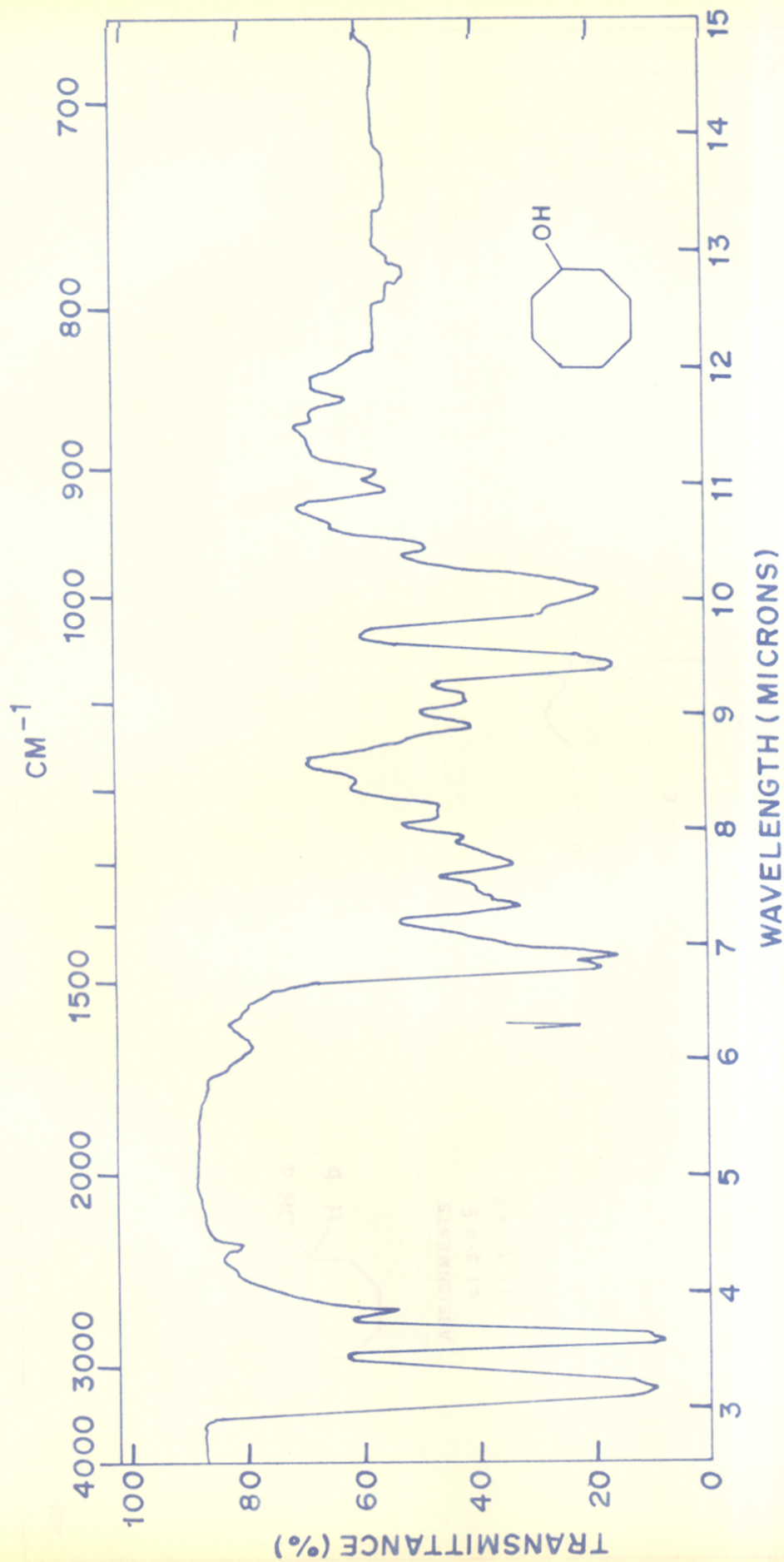


FIG. 3.16 IR SPECTRUM OF CYCLOOCTANOL



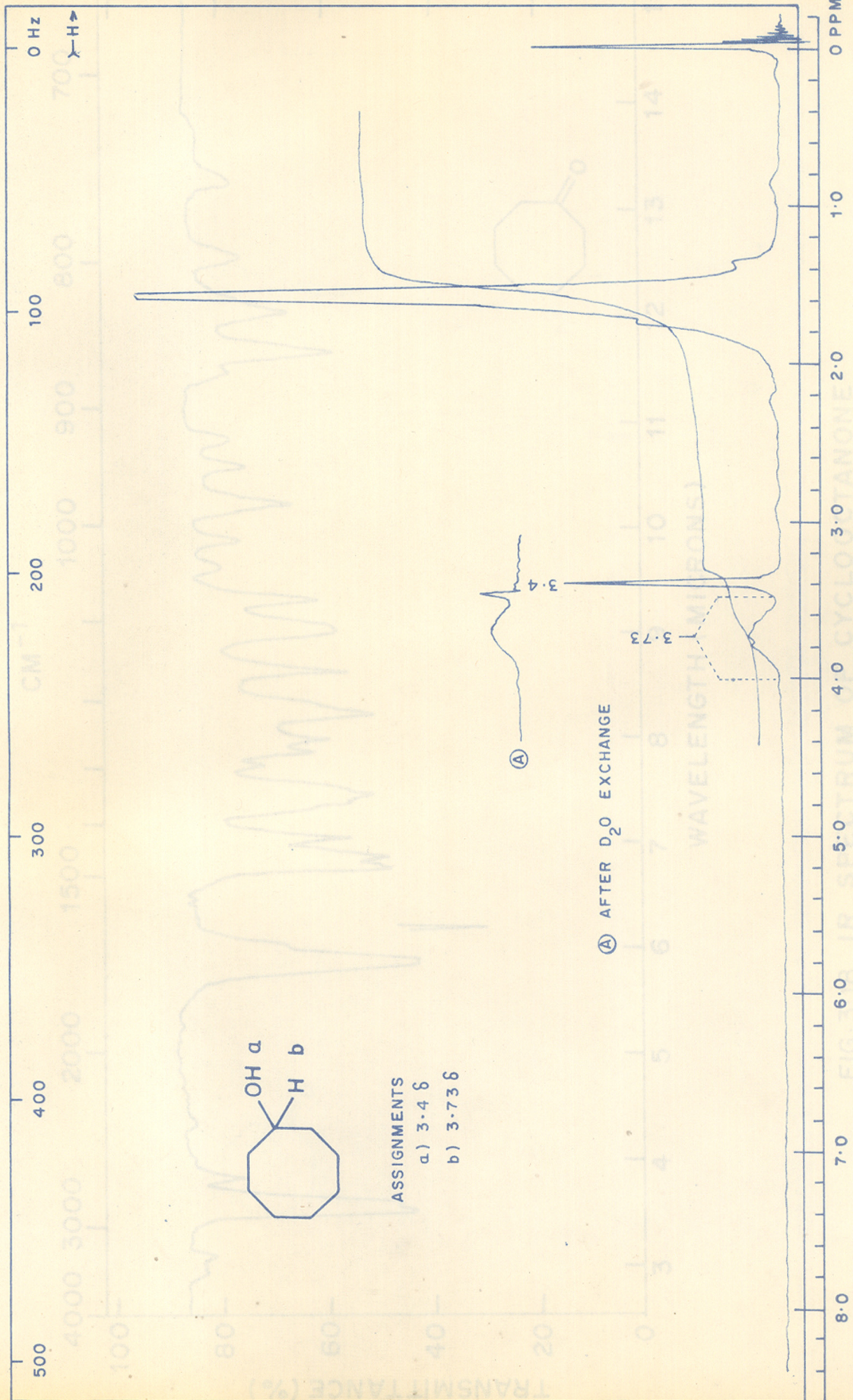


FIG. 3-17  $^1\text{H}$  NMR SPECTRUM OF CYCLOOCTANOL

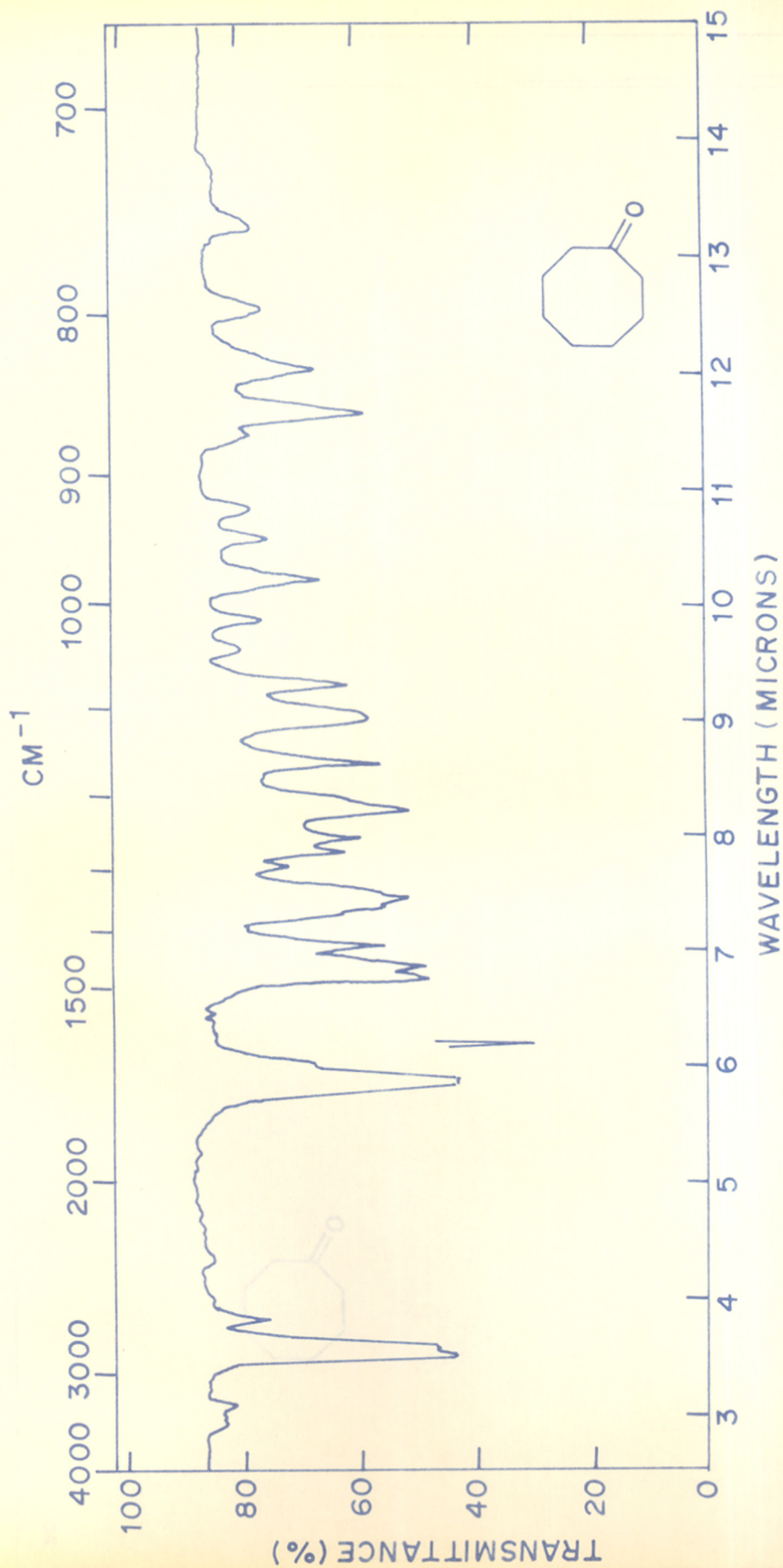


FIG. 3-18 IR SPECTRUM OF CYCLOOCTANONE

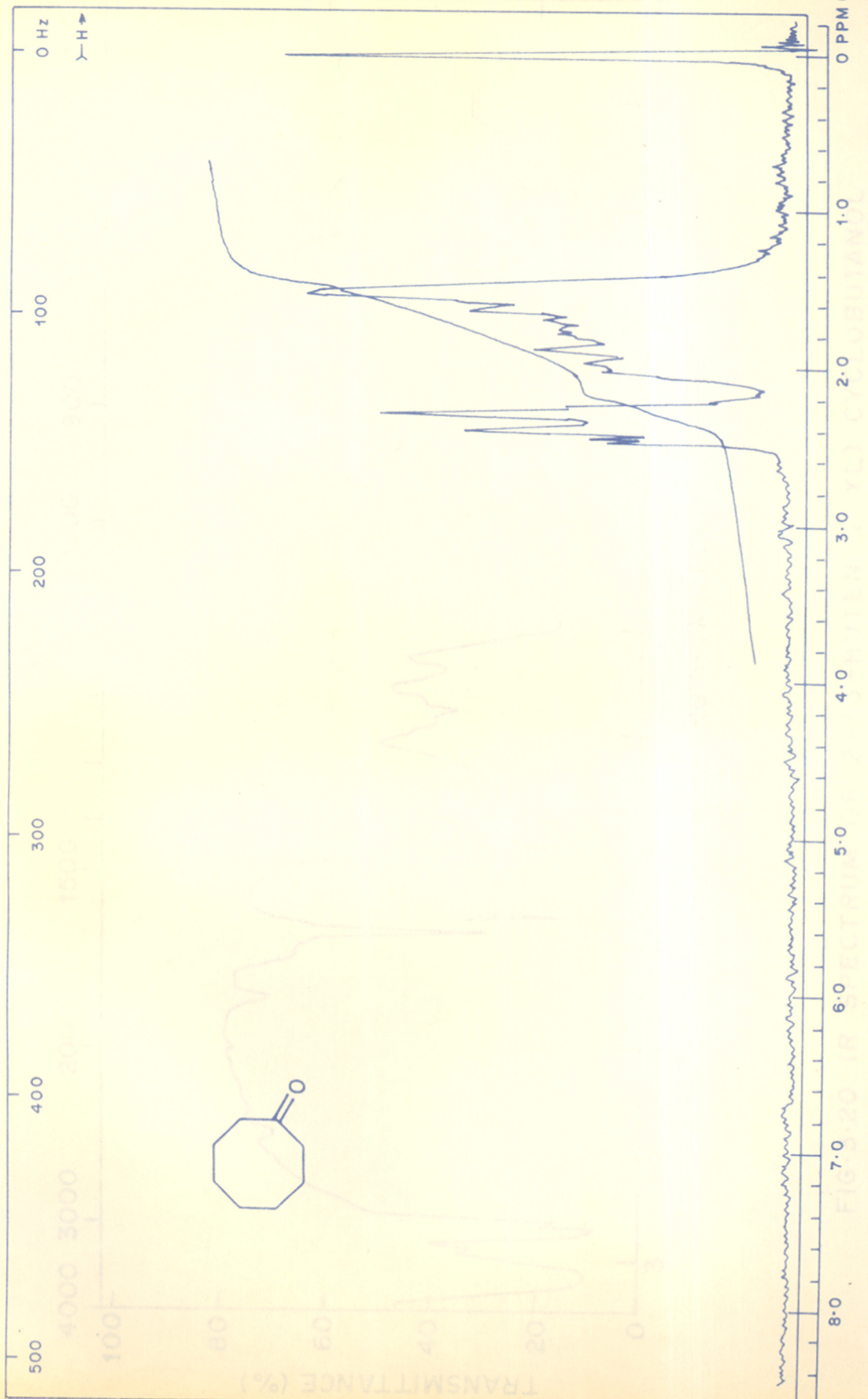


FIG. 3.19  $^1\text{H}$  NMR SPECTRUM OF CYCLOOCTANONE

FIG. 3.20 IR SPECTRUM OF 2-METHYLCYCLOOCTANONE

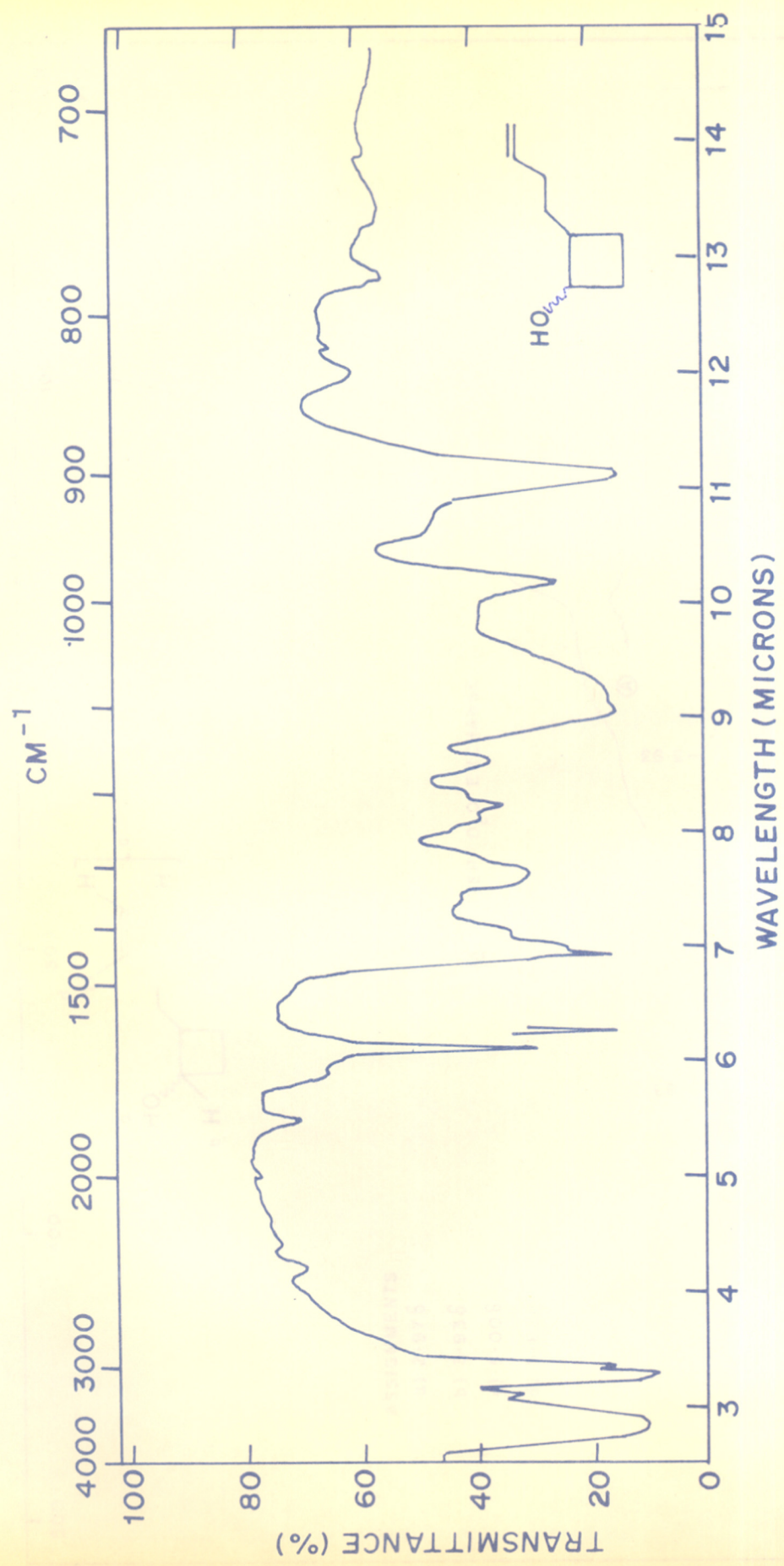
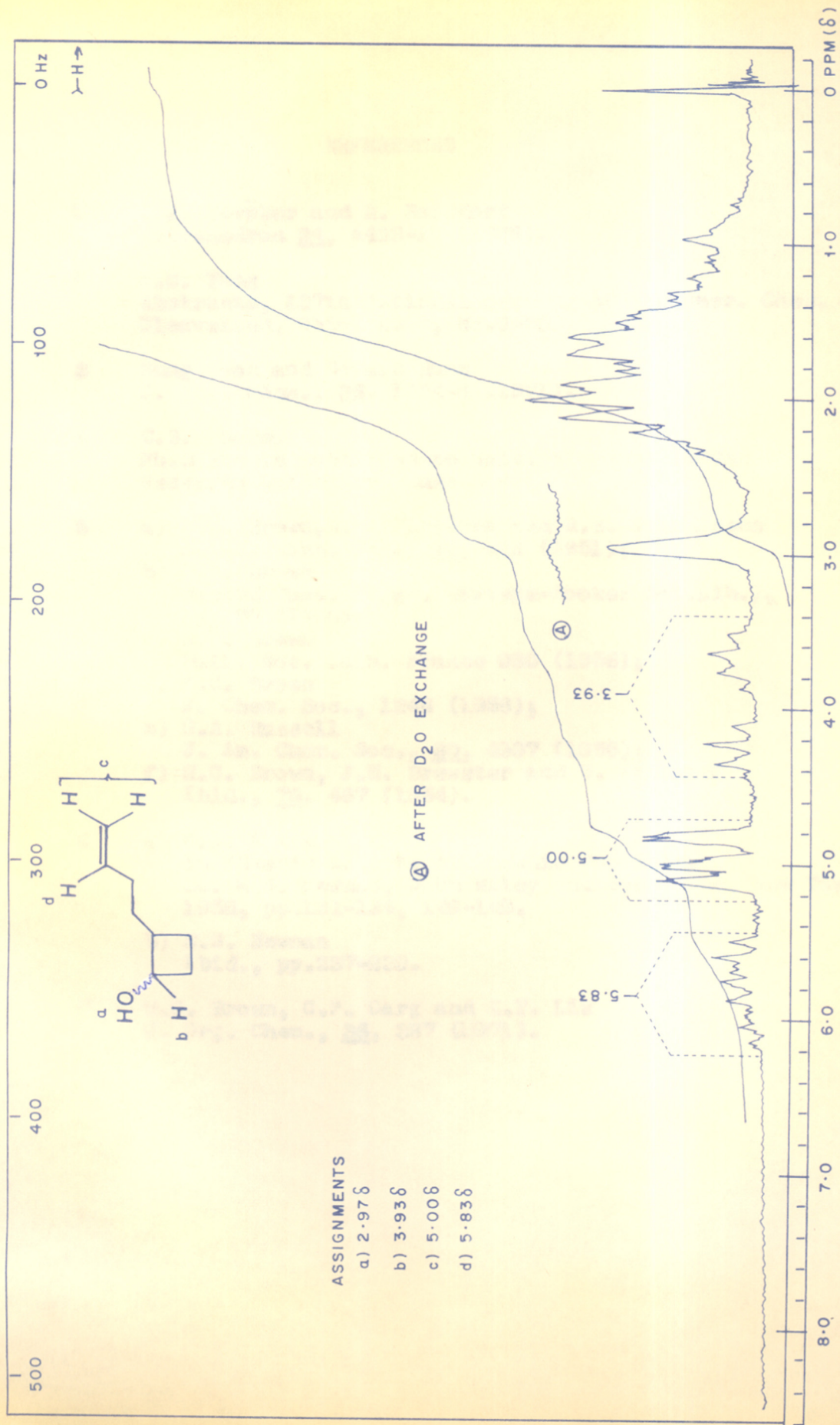


FIG. 3.20 IR SPECTRUM OF 2-(3-BUTEN-1-YL) CYCLOBUTANOL

FIG. 3.21  $^1\text{H}$  NMR SPECTRUM OF 2-(3-BUTEN-1-YL) CYCLOBUTANOL

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NCL, Poona 8

*(R. G. Kulkar)*  
(R. G. KULKAR)

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