CHAPTER II

Aluminosilicates-Induced Oxirane Rearrangements

ALUMINOSILICATES-INDUCED OXIRANE REARRANGEMENTS

Abstract —— Rearrangements of $3\alpha,4\alpha$-epoxycarene and $2\alpha,3\alpha$-epoxypinane with aluminosilicates (molecular sieve zeolites) are described. In view of the results described here, it is concluded that most of the products originated *via* carbonium ion.

ALUMINOSILICATES-INDUCED OXIRANE REARRANGEMENTS

1. INTRODUCTION

As an extension of the earlier work on alumina and silica gel-induced oxirane rearrangements,[1] the action of aluminosilicates (synthetic molecular sieve zeolites) on 1,2-epoxides have been investigated. The present chapter describesthese results.

Molecular sieve zeolites are crystalline alumino-silicates composed of silicon and aluminum atoms and may be represented by a general formula,

$$Mx/v\ (AlO_2)_x\ (SiO_2)_y\ zH_2O$$

where M is a cation with valency v and x, y, z are numbers of aluminium and silicon atoms and water molecules per unit cell.

In 1756, Baron Cronstedt discovered the mineral and named it zeolite. McBain[2] recognised the importance of these minerals and coined the term "molecular sieves" for materials which have the ability to separate molecules on the basis of size. In 1930, Barrer[3] began systematic investigations of these materials and pointed out the molecular sieving properties of the zeolites and their use in the separation of polar and nonpolar compounds.

1.1. Structure of zeolites

The structure of zeolites consists of simple arrangement of silica-alumina tetrahedra in a definite form. The tetrahedra are arranged at the corners of a truncated octahedron (or sodalite cage) which contains eight hexagonal faces and six square faces. In the structure of zeolite type A, the octahedra are linked in a cubic array by cubes on the square faces.

The arrangement of tetrahedra in the frame work structures of faujasite and in the synthetic zeolites type X is basically similar to that in A type. The frame work of X zeolite consists of a tetrahedral arrangement of the truncated octahedra, joined at the octahedral faces through hexagonal prisms. The free diameter of the hexagonal prism is 2.2 A^o and that of octahedron (orβ-cage) is 6.6 A^o. Fig. 1 shows a diamond type arrangement of the sodalite cages in the X-type zeolite. This arrangement permits the sodalite unit (volume 160 A^o) to enclose a large supercavity. Thus, three types of cages are present in the X-type zeolite: the faujasite cage is enclosed by sodalite

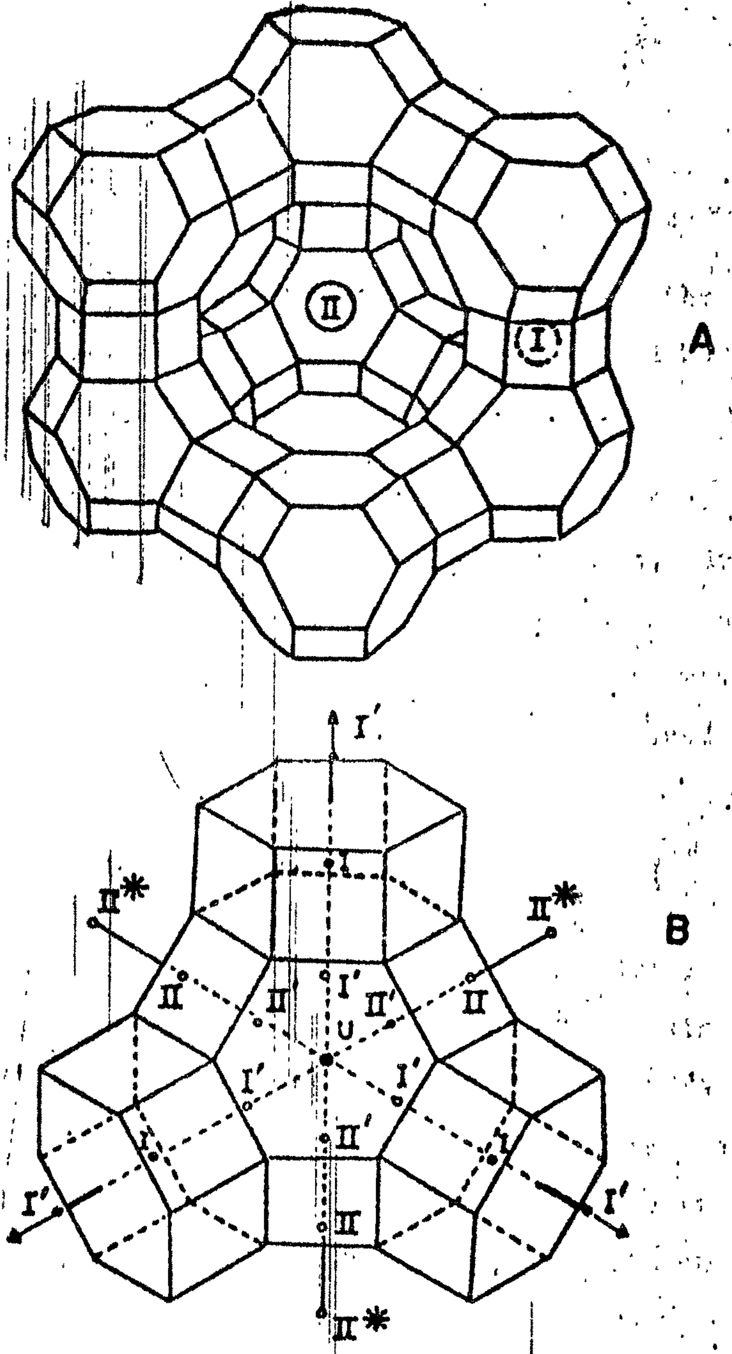


FIG.—1 A- PERSPECTIVE VIEW OF PART OF THE FAUJASITE STRUCTURE.
I AND II ARE THE CATION SITES

B- IDEALIZED PROJECTION OF SODALITE UNIT WITH CATION SITES cages linked together by hexagonal prism faces. Six sodalite units are linked together by hexagonal faces to form six membered (sodalite) rings and four such sodalite rings delineate the faujasite activity. These six membered sodalite rings contain twelve oxygen atoms. The internal diameter of faujasite cavity is 12.5 A^{o} and its volume is about 850 A^{o}.

1.1.1. Unit cell composition

The unit cell of zeolite A consisting of $12AlO_4$ and $12SiO_4$ is represented by the formula:

$$Na_{12}(AlO_2)_{12}\,(SiO_2)_{12}\cdot 27H_2O$$

The unit cell composition of type X zeolite is represented by

$$Na_{86}\,(AlO_2)_{86}\,(SiO_2)_{106}\cdot 264\,H_2O$$

1.1.2. Cation sites

The excess negative charge on the aluminium tetrahedra is balanced by a monovalent, divalent or multivalent cations. The cation may occupy different positions in the zeolite.

Earlier, three types of sites were generally recognised i.e., type S_I, located in the hexagonal prisms between the sodalite units, type S_{II} located in the open six-membered faces on the sodalite unit and type S_{III} located on the walls of the cavity. Fig. 1 shows the basic sodalite unit and the position of most of these sites in the X-type zeolite.

1.2. Ion-exchange properties

The cations can be replaced by other univalent, divalent or multivalent ions by percolation, hydrothermal, fusion or vapour phase treatment.[4] Rees[5] and Sherry[6] have published comprehensive reports on ion-exchange in zeolites.

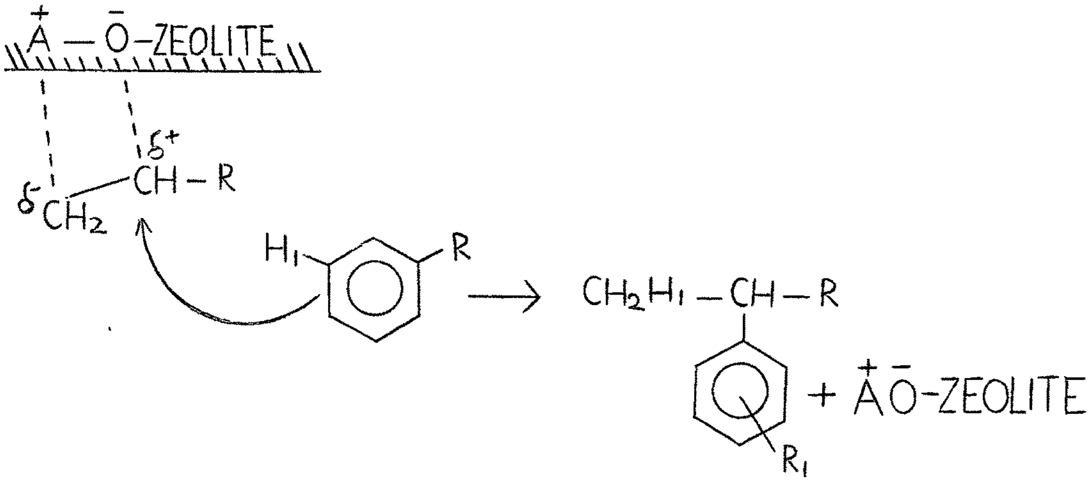
Ion exchange is found to have profound effect on various cation-oxygen bond lengths. Occupancy of site I by small univalent, divalent or trivalent cations increases the free diameter of the six-membered oxygen rings at the expense of the free diameter of the six-membered oxygen rings in the hexagonal prism joining the sodalite cages.[5]

2. Previous work

Although the subject of synthetic crystalline aluminosilicates (molecular sieve zeolites) catalysis is only twenty years old, an extensive body of literature already exists. The summary of the earlier work, particularly acid catalysed reactions is adumbrated here in order to provide a background for the present work.

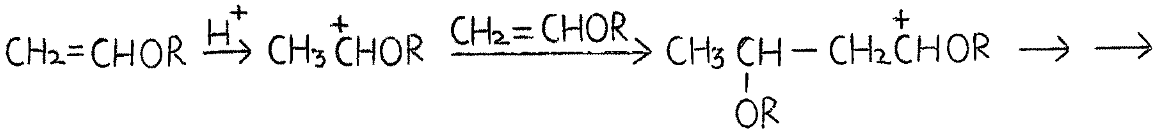
2.1. Friedel-Craft alkylation

A considerable body of literature exists concerning the Friedel-Craft alkylation using convensional protonic acids, proton donor-promoted Lewis acids, and many acidic oxides and mixed oxides as catalyst.[7] A recent study demonstrated that a number of crystalline aluminosilicates are versatile catalysts for a wide variety of alkylation reactions.[8] Modified faujasites, REX, REY and HY have shown the broadest application, although Cax, Nax and H-Mordenite were useful in some cases. The acid catalysed alkylation of aromatics with olefins proceeds by capture of the olefin-derived carbonium ion by the nucleophilic aromatic ring.



2.2. Polymerization

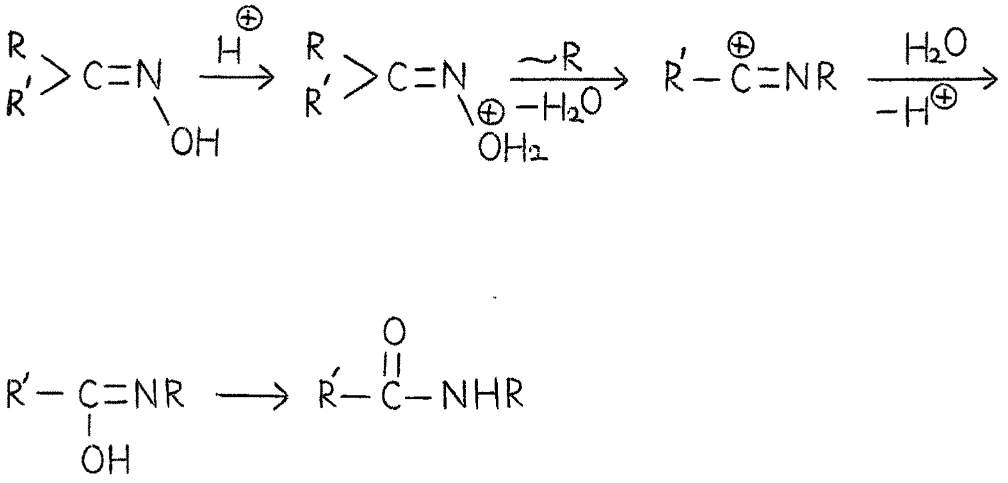
In the acid catalysed condensation of olefins, a carbonium ion formed by substrate protonation is captured by unprotonated substrate to form a new carbonium ion. Barrer and Oei[9] exposed hydrogen mordenite, activated at 360°C, to vapours of *n*-butyl vinyl ether at 22-50°C. A low polymer composed of ~10 monomer units formed. The polymerization rate was enhanced by previously adsorbed water upto level of one added water per calculated Bronsted acid site, and a cationic polymerization mechanism proceeding through carbonium ions stabilized by the α-alkoxy group was suggested.



$$CH_2{=}CHOR \xrightarrow{H^+} CH_3\overset{+}{C}HOR \xrightarrow{CH_2=CHOR} CH_3\underset{OR}{\underset{|}{CH}}-CH_2\overset{+}{C}HOR \longrightarrow \longrightarrow$$

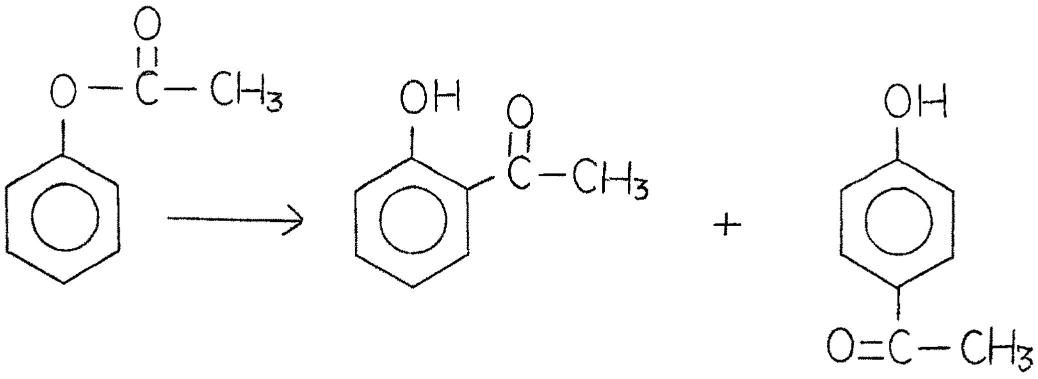
2.3. Beckmann rearrangement

Landis and Venuto[10] described the conversion of the oximes of acetophenone, acetone and cyclohexanone to N-methylacetamide, acetamilide (with a trace of N-methylbenzamide), and ε-caprolactum, respectively, over a variety of acid zeolites. Hy catalyst was most effective for this transformation. Based on analogies to the normal acid-catalysed rearrangement,[11] the authors proposed the following mechanism, the key competitive steps being the migration of the anti-alkyl group to an electron defficient nitrogen centre in a protonated oxime and β-seission of this same intermediate.



2.4. Fries rearrangement

An efficient analog of the Fries rearrangement[11] was reported over REX at 100-200° in which phenyl-acetate was

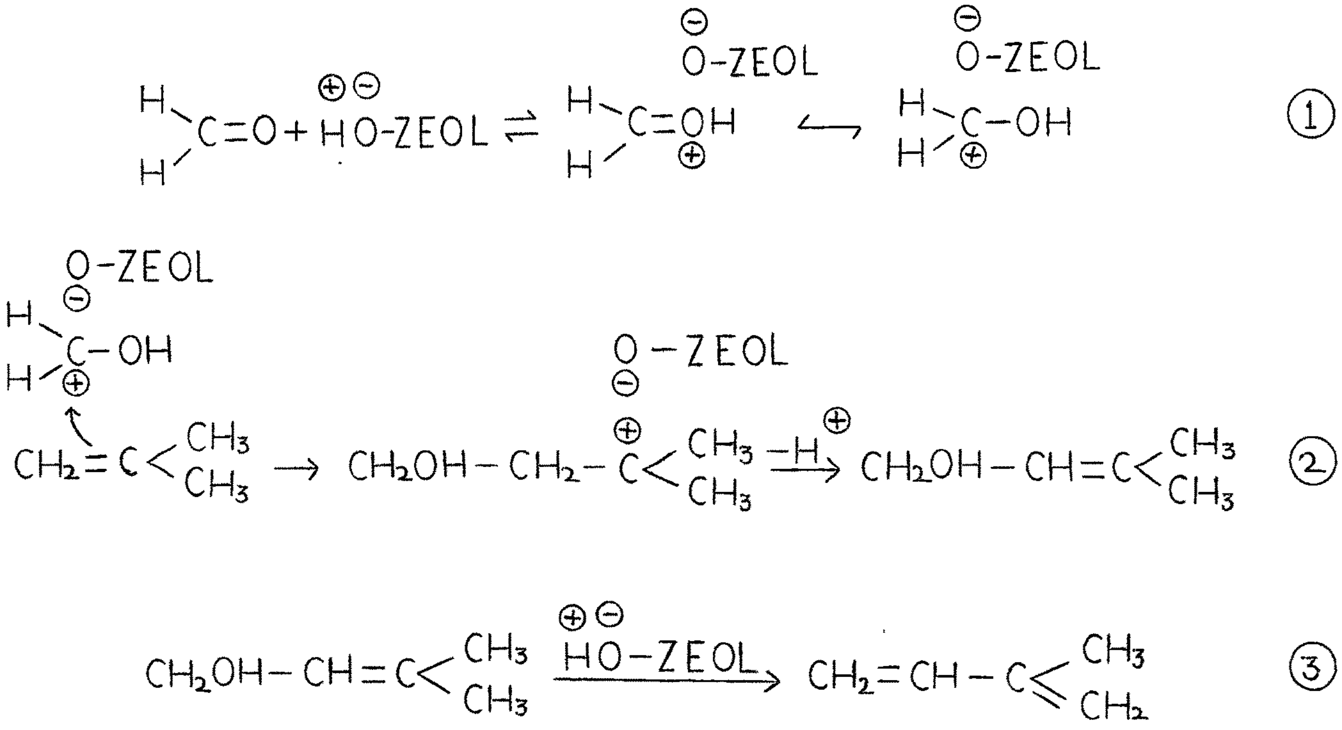


I II

rearranged to a mixture of phenolic ketones (I) and (II). The ratio of (II) to (I) was 3.36 at 204°; at 90°, (II) was the only product. In the reaction of phenyl acetate over $AlCl_3$,[13] para isomer is favoured at lower temp. (25°) and the ortho isomer, at higher ones (165°).

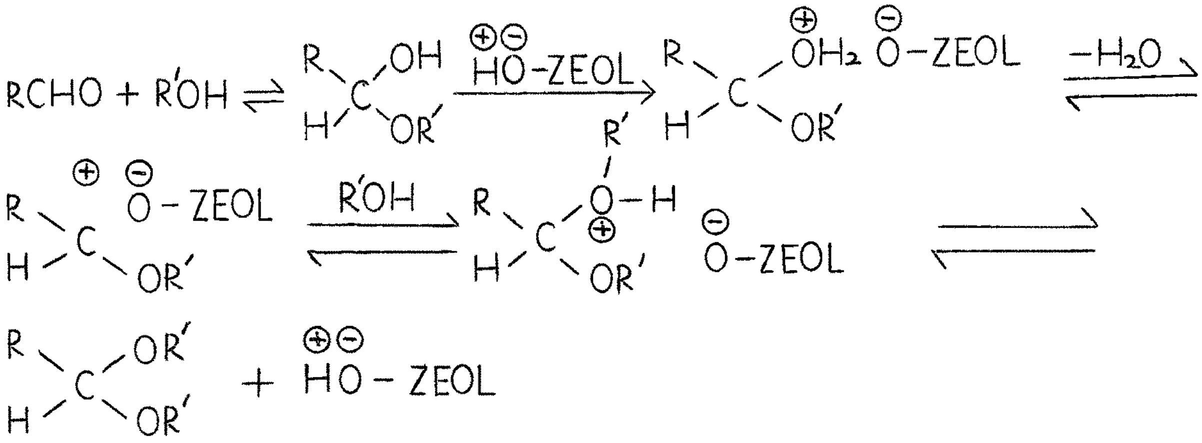
2.5. Prins reaction

In the presence of isobutene, formaldehyde over H-mordenite at 300° gave isoprene in an apparent heterogeneous version of Prins reaction.[14] A carbonium ion-type reaction scheme, involving a Prins reaction (step 1,2) and a subsequent dehydration rearrangement (step 3), explains the formation of isoprene.

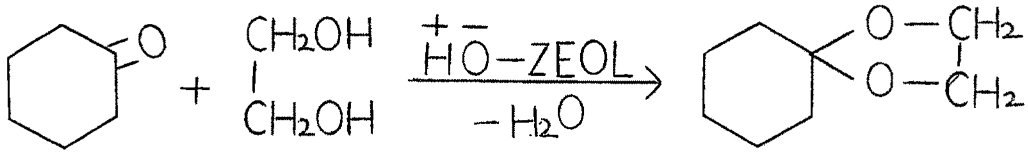


2.6. Acetal and ketal formation

In the presence of excess of alcohol, acidic zeolites at 30^{0} converted aldehydes slowly to the corresponding ketals. The reaction undoubtedly proceeds through formation of the hemiacetals, followed by acid catalysed etherification of the hemiacetal by excess alcohol. A possible mechanism is illustrated here.

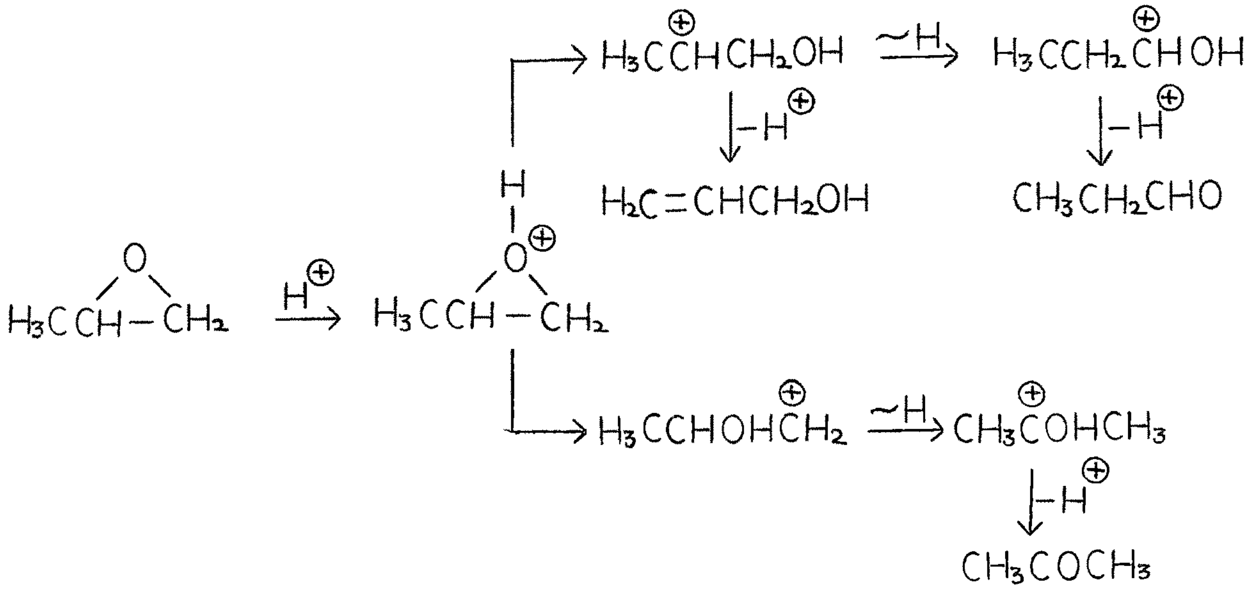


Both aldehydes and ketones react with 1,2-glycols in the presence of zeolite catalysts, preferably with continuous removal of water, to form cyclic acetals or ketals. For example, cyclohexanone reacts with ethylene glycol in the presence of H-mordenite, HY or REY forming 1,4-dioxaspiro (4.5) decane.[15]



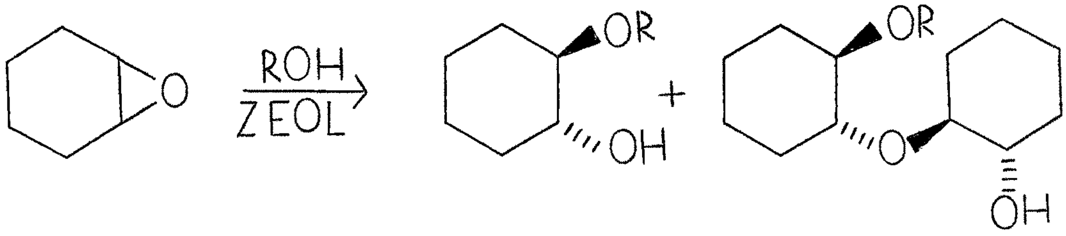
2.7. Epoxide transformation

Isomerization: Epoxides are isomerized to the corresponding aldehydes, ketones or alcohols using a variety of crystalline aluminosilicates as catalysts.[16] In the specific case of propylene oxide,[17] the major product was propionaldehyde, accompanied by small amounts of acetone and traces of allylic alcohol. More active and more acidic catalysts were less selective to the aldehyde. The gross mechanism by analogy to reactions in solution, is probably as shown, with the hydride shift possibly being concerted with ring opening; however, the detailed factors involving the direction of ring-opening are not clear.



Hydration of ethylene oxide: High activity of both Linde A- and faujasite-type aluminosilicates has been reported in the hydration of ethylene oxide to ethylene glycol.[18] Representative data are shown in Table 1. Reactions in both the gas and liquid phase have been demonstrated, although greatest selectivity against aldehyde formation is evident in liquid phase reactions at low temperatures.

An aluminosilicate molecular sieve zeolite has recently been used for catalytic alcoholysis of cyclohexene oxide, giving a mixture of 1,2-cyclohexanediol derivative (1) and dicyclohexyl ether (2).[19]



(1) (2)

TABLE 1 - Hydration of Ethylene Oxide over zeolite

Catalyst	C_2H_4O/H_2O	Temp. °C	Glycol in product (w%)
Linde 4A	0.1	93	35.6
		238	25.2
Linde 5A	0.1	96	19.1
		238	23.4
NaX	1.0	93	16.7
CaX	0.1	17	29.3
		96	23.8

3. PRESENT WORK

The general title "Organic Reactions in a Solid Matrix" has been chosen to report on organic reactions occurring on a solid surface (in a solid matrix), the latter besides holding the substrate (e.g., by adsorption or by clathrate/molecular complex formation, or by a readily reversible chemical reaction) also provides nearby, a suitable reaction centre. A solvent, when employed, acts essentially as a dispersing vehicle.

From the previous observations, it is clear that oxiranes, regardless of their degree of substitution and carbon-skeletal features, are quite sensitive[1,20] to active alumina at ambient temperatures and, in general, four different types of reactions have been observed:[1d]

(i) Transformation into allylic alcohol

(ii) Hydration to <u>trans</u>-glycol

(iii) Isomerisation to carbonyl compounds

(iv) Typical carbonium ion rearrangements

With trisubstituted 1,2-epoxides, generally reactions (ii) and (iii) are not very significant. Modified alumina[1g] suppresses reaction (iv) and transformation to allylic alcohols reaction (i) becomes the dominant pathway with trialkyl-substituted 1,2-epoxides.

Likewise, it has also been reported[1e] that carbonium ion rearrangement constitute the chief pathway open to oxirane ring isomerisation in a silica gel matrix. The present work was undertaken to see the ambivalent behaviour of aluminosilicates (molecular sieve zeolites type 4A and 13X) towards oxiranes. Crystalline aluminosilicates (molecular sieves) are typically obtained in the sodium form and the sodium ions in aluminosilicates (type 4A and 13X) were next ion-exchanged with different ions (e.g. NH_4^+, Li^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Fe^{3+}, CO^{2+} and Ni^{2+}). The behaviour of resulting modified molecular sieves towards oxiranes derived from two olefins, e.g. (+)-Δ^3-carene and (+)-α-pinene have been investigated and are reported in this Chapter.

3.1. Reaction conditions

In order to optimise the reaction conditions for complete conversion of epoxide (+)-Δ^3-carene oxide) to the rearranged products, various parameters (e.g., substrate/aluminosilicate ratio, time period) have been studied. Table 2 represents the result of such a study.

As a result of this work, the following conditions were

TABLE 2 - Rearrangement of (+)-3α,4α-epoxycarene effect of substrate-aluminosilicate ratio*

No.	Aluminosilicate -epoxide ratio (w/w)	Temp. °C	Time (hr)	Unchanged epoxide I (%)	Product distribution(% by GLC)++			
					hydrocarbons II,III,IV,V	aldehyde VI	Ketones VII, VIII	alcohols IX, X
1.	10	30-35	12	48.0	13.0	22.5	9.5	6.5
			24	33.0	17.0	30.5	10.0	8.0
2.	15	30-35	12	11.0	25.0	40.0	13.0	10.0
			24	4.0	24.0	44.0	14.0	12.5
3.	25	30-35	3	3.0	24.0	47.0	12.5	12.0
			6	0.5	23.0	49.0	14.0	10.0

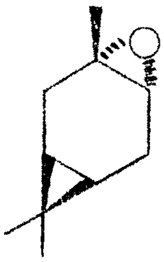
* Aluminosilicate (molecular sieve type 4A; activated at 120-130° for 6 hr).

++ Total recovery: 75%.

considered most suitable for this transformation and were employed through-out the subsequent work with other substrates: Temperature of activation; 120-130°/6 hr; substrate aluminosilicate ratio: 1:25 (w/w); solvent: Hexane, 30 ml for 25 g of aluminosilicate; reaction temperature: Room temp. (25-35°); Reaction time: 6 hr.

3.2. Effect of Cation-modified Molecular Sieves on Oxiranes

Under the standard reaction conditions described above, (+)-3α,4α-epoxycarane was totally transformed to different products viz., hydrocarbons (II, III, IV and V), bicyclic aldehyde (VI), caranones (VII and VIII) and allylic alcohols (IX and X). It was next decided to study the effect of various ion-exchanged aluminosilicates on the product distribution of epoxide rearrangement. Table 3 summarises the results of preparation of various ion-exchanged aluminosilicates and percentage of exchange. Table 4 displays the effect of these aluminosilicates on carene oxide. From Table 4 it is clear that HA form gives the maximum of carbonium ion rearranged product (aldehyde VI, 54%) and SrA form gives the maximum of isomerised product (caranones VII and VIII), hence three forms of aluminosilicates (4A, HA and SrA) have been selected for final study and for similar reason 13X, HX and SrX also (see Tables 5 and 6).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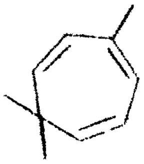
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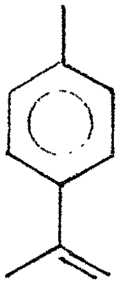
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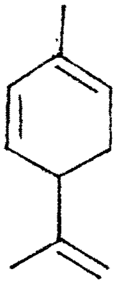
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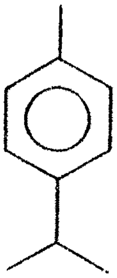
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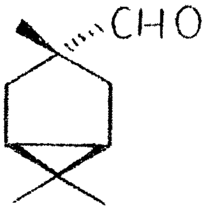

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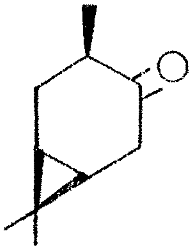

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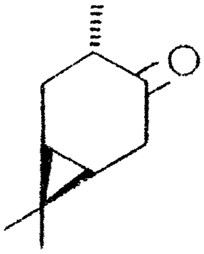

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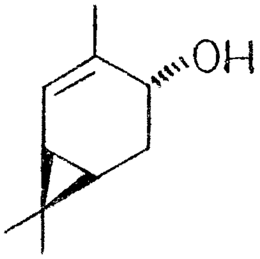

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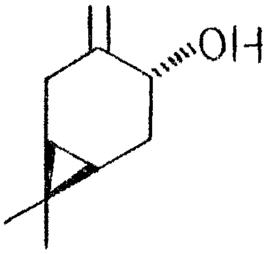

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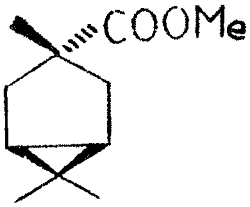

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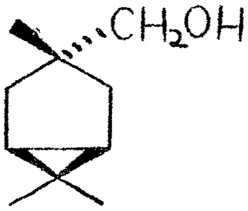

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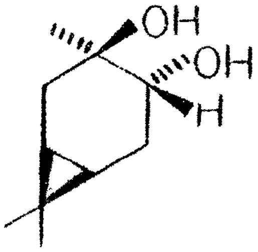

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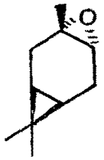
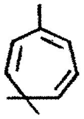
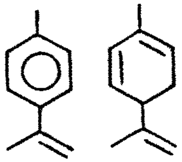
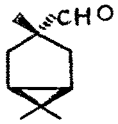
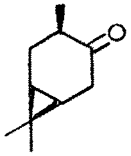
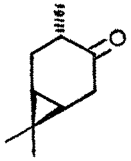
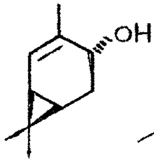
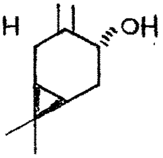
TABLE 3 - Ion-exchange of Zeolites

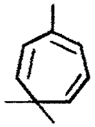
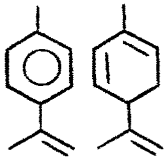
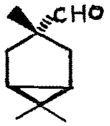
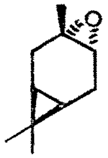
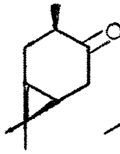
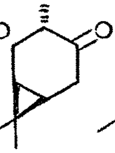
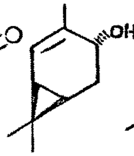
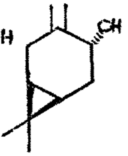
No.	Zeolite	Salt	Solution concentration	Temp. °C	% exchange
1.	4A	-	-	-	-
2.	HA	NH_4OH	5%	30-35	17
3.	LiA	$LiCl.H_2O$	molar	30-35	41
4.	KA	KCl	molar	30-35	60
5.	MgA	$MgCl_2.6H_2O$	molar	30-35	55
6.	CaA	$CaCl_2$	molar	30-35	59
7.	SrA	$SrCl_2.6H_2O$	molar	30-35	64
8.	FeA	$FeCl_3.6H_2O$	molar	30-35	28
9.	COA	$COCl_2.6H_2O$	molar	30-35	38
10.	NiA	$NiCl_2.6H_2O$	molar	30-35	19

TABLE 4 - Rearrangement of (+)-3α,4α-epoxycarane
Effect of Cation-exchange

No.	Alumino-silicates (zeolite)	Unchanged epoxide	Product composition (%)$^{+}$									
		I	increasing RRT									
												
			II	III + IV	V	U	VI	U	VII	VIII	IX	X
1.	4A	0.5	14.0	4.0	5.0	1.0	49.0	-	3.0	11.0	2.5	7.5
2.	HA	-	15.0	5.0	3.0	0.2	54.0	-	2.0	12.0	2.0	4.0
3.	LiA	2.0	3.5	2.5	2.0	2.0	48.0	-	12.0	18.0	5.0	3.0
4.	KA	20.0	12.0	6.5	1.5	2.0	42.0	-	1.9	6.5	4.0	3.0
5.	MgA	-	4.0	3.5	6.0	-	45.0	-	9.0	24.0	3.5	4.5
6.	CaA	2.0	2.0	2.0	9.0	-	27.0	-	12.5	36.0	-	9.0
7.	SrA	1.0	3.0	3.5	10.0	1.0	20.0	-	10.5	38.0	3.5	9.0
8.	FeA	6.5	6.0	5.0	9.0	6.0	48.0	3.0	6.5	8.0	1.0	1.0
9.	CoA	6.5	2.0	2.0	5.5	6.0	26.0	4.0	13.0	22.0	3.5	9.5
10.	NiA	1.5	1.5	2.0	5.5	2.5	40.5	-	7.5	25.0	1.5	12.5

$^{+}$ Total recovery: 70-80%
U = Unidentified.

TABLE 5 - Rearrangement of (+)-3α,4α-epoxycarane*

No.	Alumino-silicates	Total product recovery (%,w/w)	Product distribution (%, GLC)+										
			RRT: 1.00	1.13	1.39	2.34	2.52	2.78	3.21	4.34	4.78	6.60	7.73
													
			II	III+IV	V	IVI	U	I	U	VII	VIII	IX	X
1.	4A	78	14.0	4.0	5.0	49.0	-	0.5	-	3.0	11.0	2.5	7.5
2.	HA(17)	81	15.0	5.0	3.0	54.0	-	0.2	-	2.0	12.0	2.0	4.0
3.	SrA(64)	76	4.0	2.0	13.0	22.0	-	0.5	-	8.0	35.0	2.0	10.
4.	13X	84	13.0	2.0	34.0	16.0	8.0	9.0	6.0	9.0	2.0	0.5	0.
5.	HX(11)	86	19.0	1.0	43.0	15.0	6.0	6.0	2.0	6.5	1.0	-	-
6.	SrX(50)	74	2.5	4.0	2.0	53.0	4.0	5.5	1.0	4.5	12.5	0.5	8.

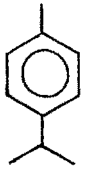
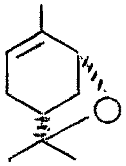
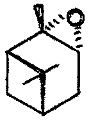
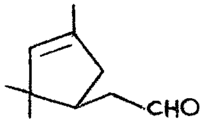
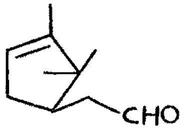
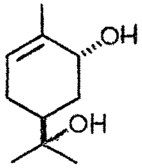
* Room temp. (30-35°); reaction time: 6 h

\+ Column: Al column, 580 x 0.3 cm; support, 60-80 mesh Chromosorb W; stationary phase 10% carbowax 20M; carrier gas H_2

U = Unidentified

In paranthesis % of exchange are given.

TABLE 6 - Rearrangement of (+)-2α,3α-epoxypinane*

No.	Alumino-silicates	Total product recovery (%,w/w)	Product distribution (%, GLC)							
			RRT: 1.00	1.25	1.62	2.00	2.25	2.62	3.18	8.25
			 V	 XV	 XIV	 XVI	U	 XVII	U	 XVIII
1.	4A	75	10.0	4.5	0.5	18.0	1.0	50.0	2.0	12.0
2.	HA	70	8.0	6.0	0.4	18.5	2.0	53.0	2.5	8.0
3.	SrA	71	11.0	16.0	0.5	21.0	2.0	44.0	3.0	2.5
4.	13X	67	9.0	3.0	-	9.0	1.0	44.0	3.0	29.0
5.	HX	72	11.0	5.0	0.2	15.0	1.5	40.0	3.0	22.0
6.	SrX	72	8.0	4.5	-	15.5	1.0	42.0	2.5	25.0

* Room temp. (30-35^{0}); reaction time: 6 h

U = Unidentified

3.3. Results

The behaviour of the oxides derived from the following olefins, was investigated: (+)-Δ^3-carene and (+)-α-pinene.

(+)-3α,4α-Epoxycarane,[1c] on exposure to aluminosilicate type 4A furnished a product (recovery 78% on wt. basis) which was shown by GLC to consist eight main components having RRT of 1.00, 1.13, 1.39, 2.34, 4.34, 4.78, 6.6 and 7.73 (GLC Fig. 2) and various components were separated by preparative GLC and identified by its spectroscopic* (IR, PMR) and other properties. Results are enumerated in Table 7.

GLC component 1 (RRT = 1.00) was recognised from its spectral characteristic (PMR, IR; Figs. 3 & 4) as 3,7,7-trimethyltropilidene[21] (II), the spectral data agreeing well with that reported in literature[22,1e]. GLC component 2 (RRT = 1.13) was revealed from its PMR spectrum to be a mixture of III and IV (see Experimental). GLC component 3 (RRT = 1.39 was easily recognised as p-cymene (V).

The major product of epoxycarane-aluminosilicate (type 4A) reaction (GLC component 4, RRT = 2.34) was readily

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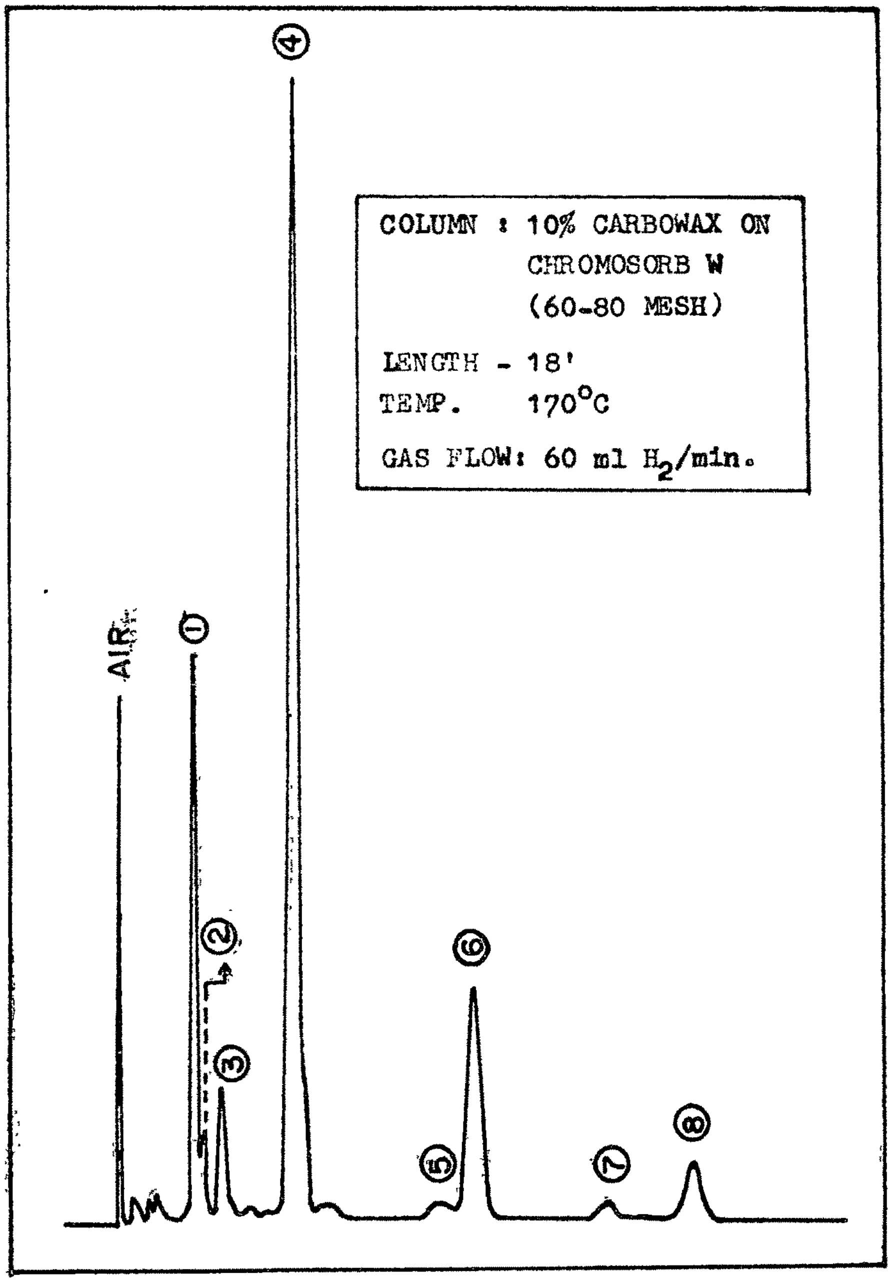
* For spectral assignments, see "Experimental".



COLUMN : 10% CARBOWAX ON CHROMOSORB W (60-80 MESH)

LENGTH - 18'
TEMP. 170°C

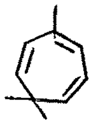
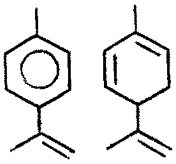
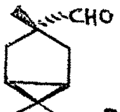
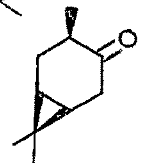
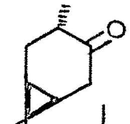
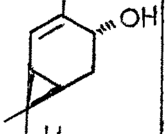
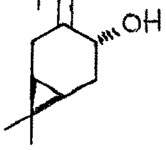
GAS FLOW: 60 ml H_2/min.

Fig.2: GL CHROMATOGRAPH OF REARRANGED PRODUCTS OF 3,4-EPOXYCARANE OVER ZEOLITE (4A)

IDENTIFICATION

① 3,7,7-TRYMETHYLTROPILIDENE ② III + IV ③ p-CYMENE
④ ALDEHYDE VI ⑤ ISOCARANONE ⑥ CARANONE
⑦ ALCOHOL IX ⑧ ALCOHOL X

TABLE 7 - Products from rearrangement of Δ^3-Carene oxide

GLC component	Relative retention time (RRT)	Product		Name	PMR Fig. No.	IR Fig. No.	GLC Fig. No.
		Structure No.	Actual structure				
1	1.00	II		3,7,7-trimethyltropilidene	3	4	2
2	1.13	III+IV		III- -p-dimethylstyrene IV-1,5,8(9)-p-menthatriene			
3	1.39	V		p-Cymene			
4	2.34	VI		3,6,6-Trimethyl-3-formylbicyclo-[3.1.0] hexane	5	6	
5	4.34	VII		Isocaranone	11	12	
6	4.78	VIII		Caranone	13	14	
7	6.6	IX		Δ^4-Carene-3α-ol	15	16	
8	7.73	X		$\Delta^{4(10)}$-Carene-3α-ol	17	18	

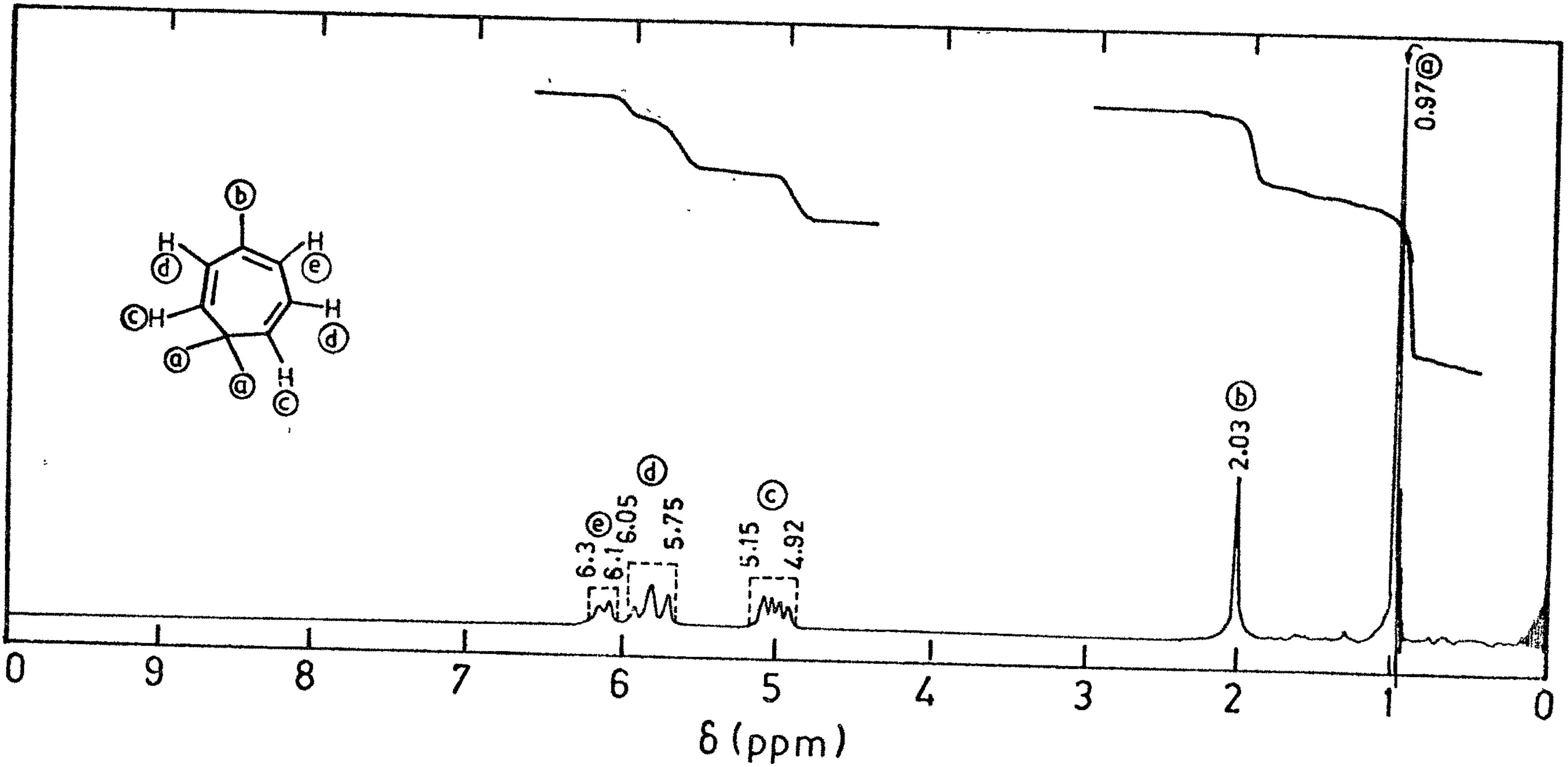


FIG. 3 - PMR SPECTRUM OF 3,7,7-TRIMETHYL TROPILIDENE (II).

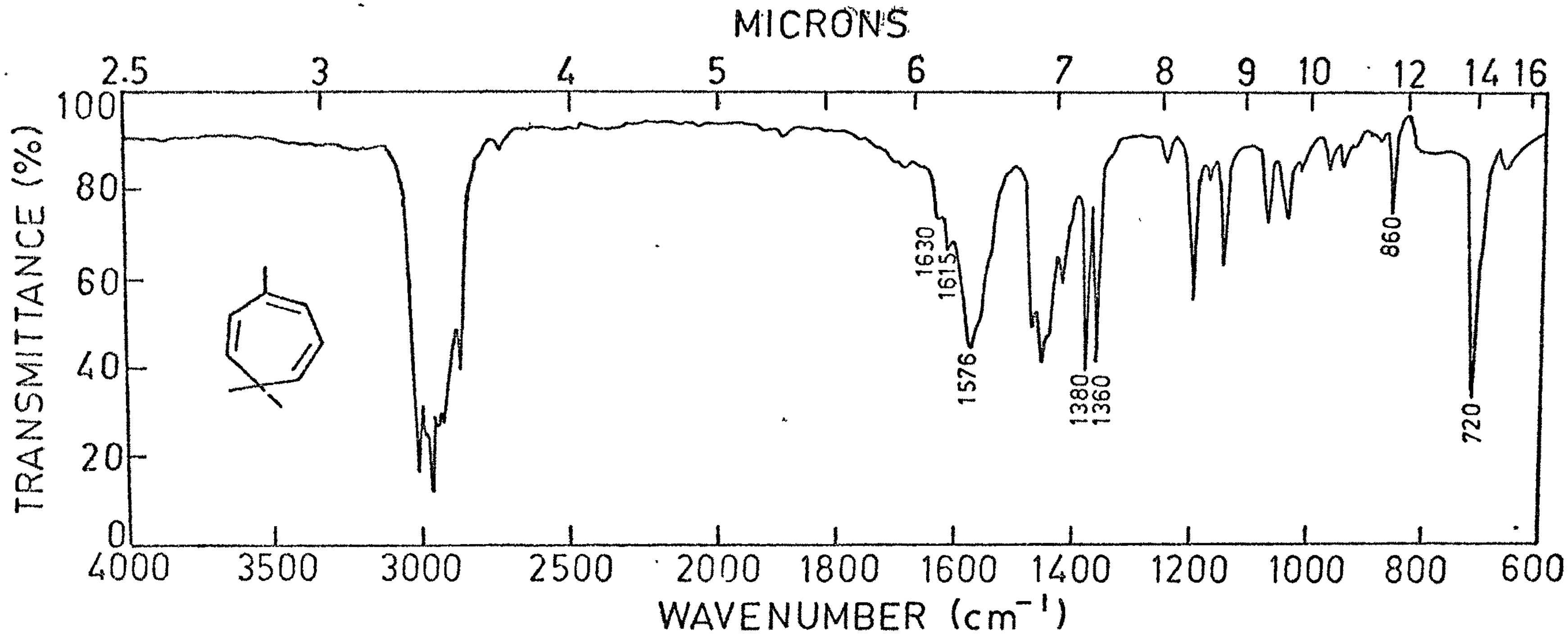


FIG. 4-IR SPECTRUM OF 3,7,7-TRIMETHYL TROPILIDENE (II).

reçognised as a knwon[23,1e] bicyclic aldehyde (VI) from its physical constants and spectral data (PMR, IR; Figs. 5 and 6). Its characterisation was completed by preparation of its semicarbazone, oxidation (Ag_2O) to the corresponding acid and comparison of the derived methyl ester XI[1e] (PMR, IR; Figs. 7 and 8) with authentic sample, and reduction to 3,6,6-trimethyl-3-carbinol[3.1.0] hexane XII[1e] (PMR, IR; Figs. 9 and 10).

GLC component 5 with RRT = 4.34 was identified as isocaranone VII (PMR, IR; Figs. 11 and 12). GLC component 6 (RRT = 4.78) revealed from its PMR, IR (Figs. 13 and 14) to be caranone VIII; the spectrum was compared with the spectra of isocaranone and caranone recorded by Sukh Dev et al.[1e] as well as with that of an authentic sample of isocaranone and caranone.[24]

GLC component 7 (RRT = 6.60) was recognised as Δ^4-carene-3α-ol[25] IX from its spectroscopic characteristics (PMR, IR; Figs. 15 and 16). GLC component 8 (RRT = 7.73) was essentially $\Delta^{4(10)}$-carene-3α-ol X[25] (PMR, IR; Figs. 17 and 18) and compares well with the reported data.[1e]

(+)-2α,3α-Epoxypinane, XIV,[1c] on treatment with zeolite (4A) in the same manner furnished a mixture of products (recovery 74%) with RRT 1.00, 1.25, 2.00, 2.62, 3.18 and 8.25 (GLC

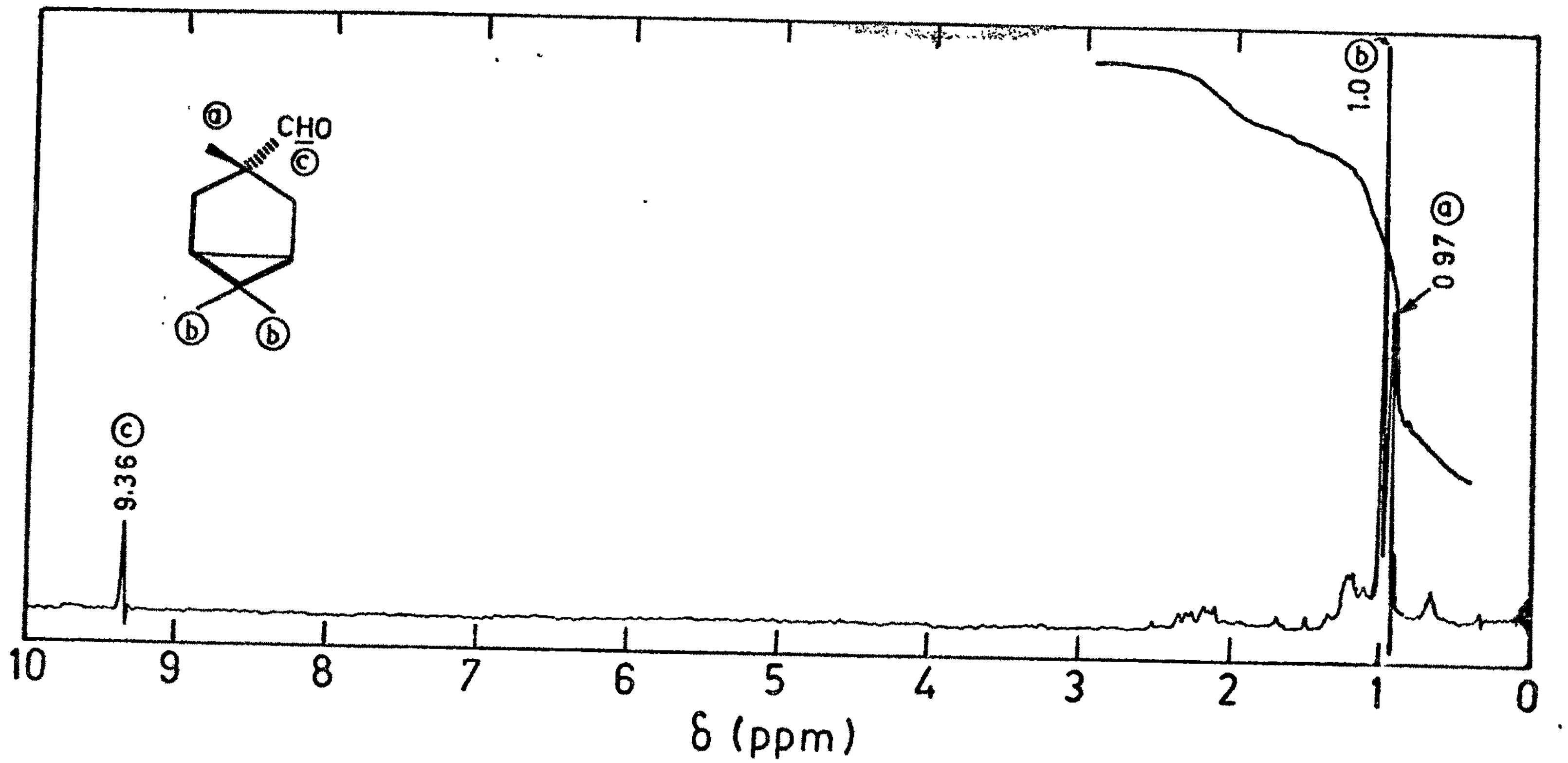


FIG.5-PMR SPECTRUM OF 3,6,6-TRIMETHYL-3-FORMYL-BICYCLO [3·1·0] HEXANE (VI).

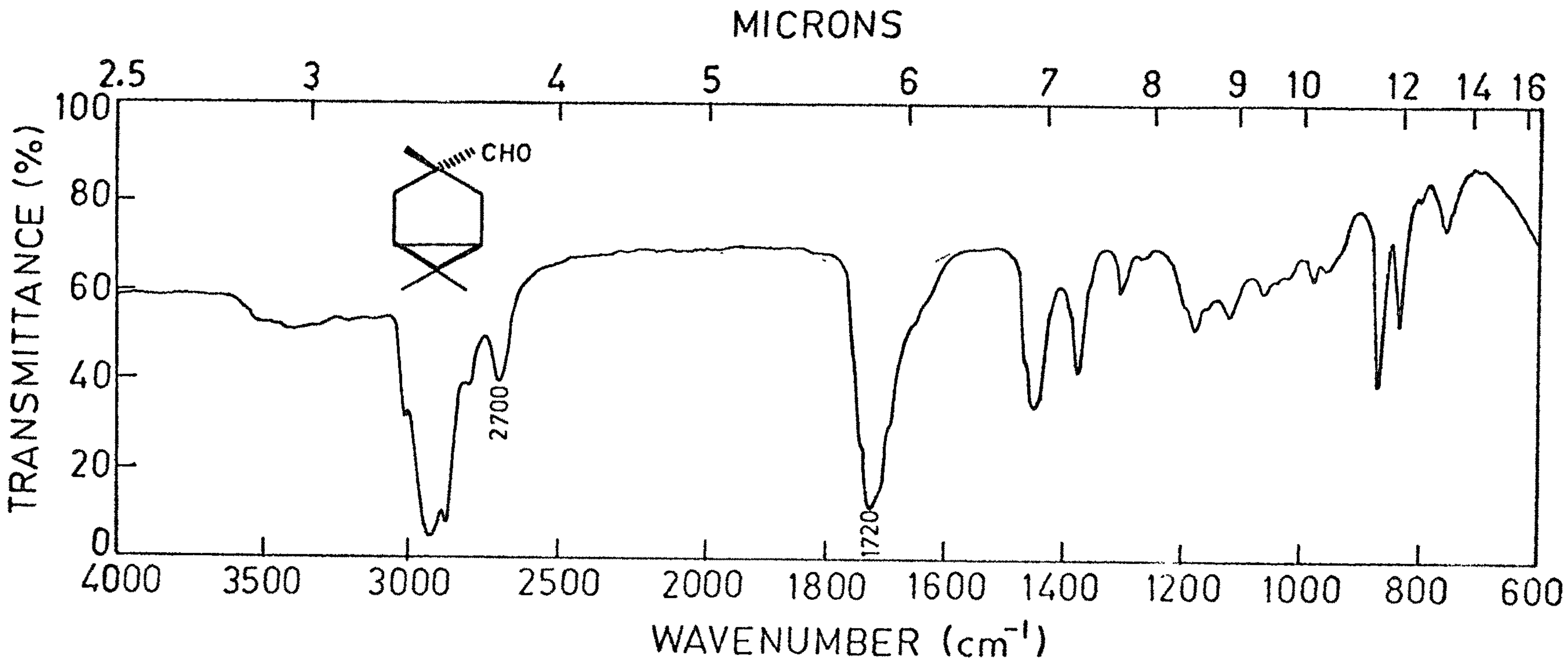


FIG. 6 - IR SPECTRUM OF 3,6,6-TRIMETHYL-3-FORMYL-BICYCLO [3.1.0] HEXANE (VI).

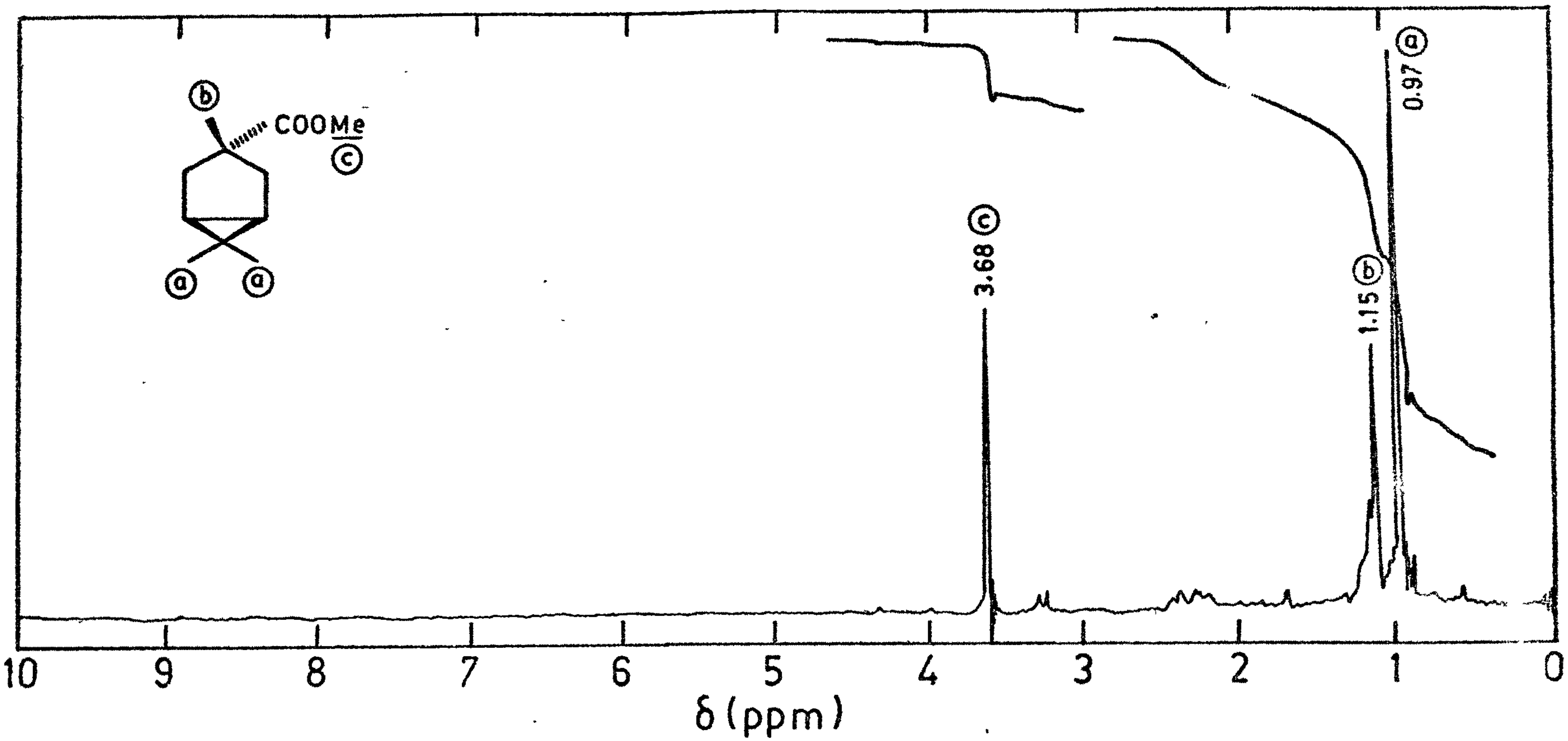


FIG. 7 : PMR SPECTRUM OF 3,6,6-TRIMETHYL-3-CARBOMETHOXY-BICYCLO [3.1.0] HEXANE (XI)

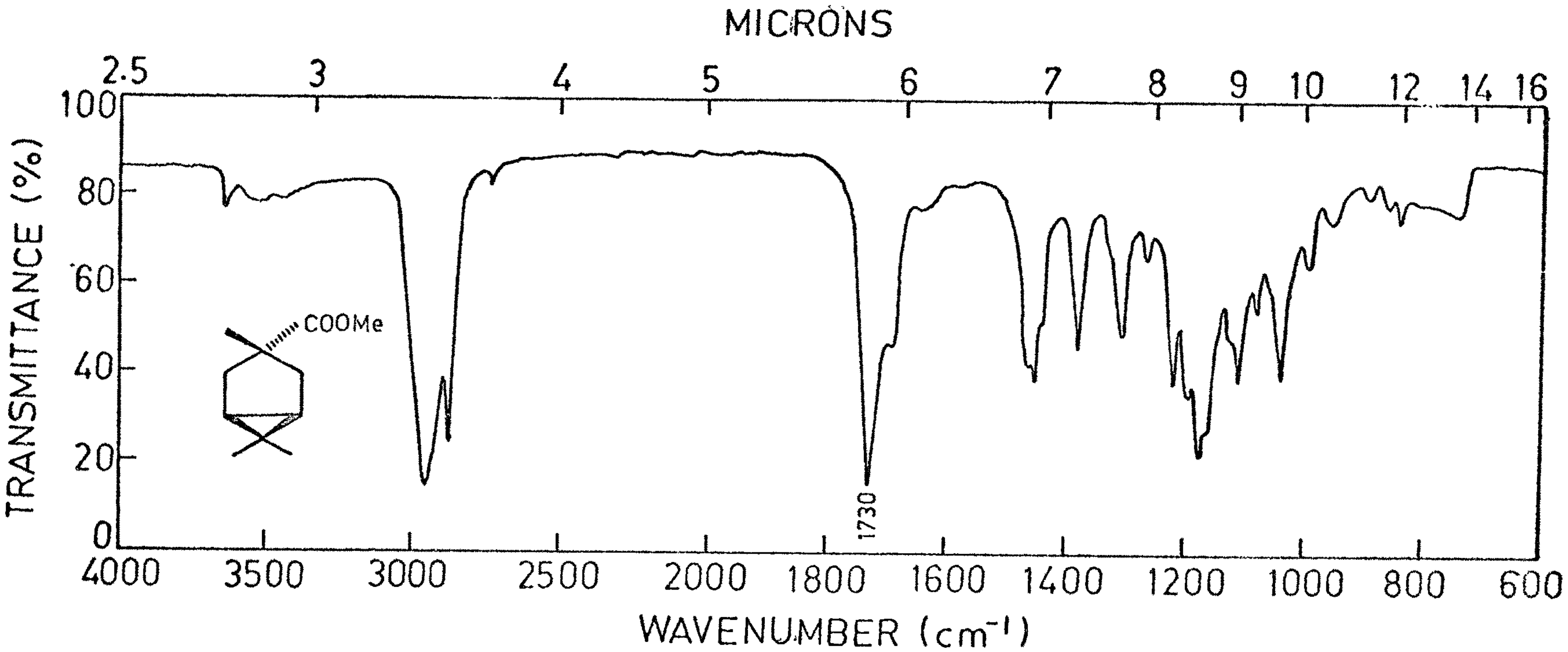


FIG.8 : IR SPECTRUM OF 3,6,6-TRIMETHYL-3-CARBOMETHOXY BICYCLO [3.1.0] HEXANE (XI)

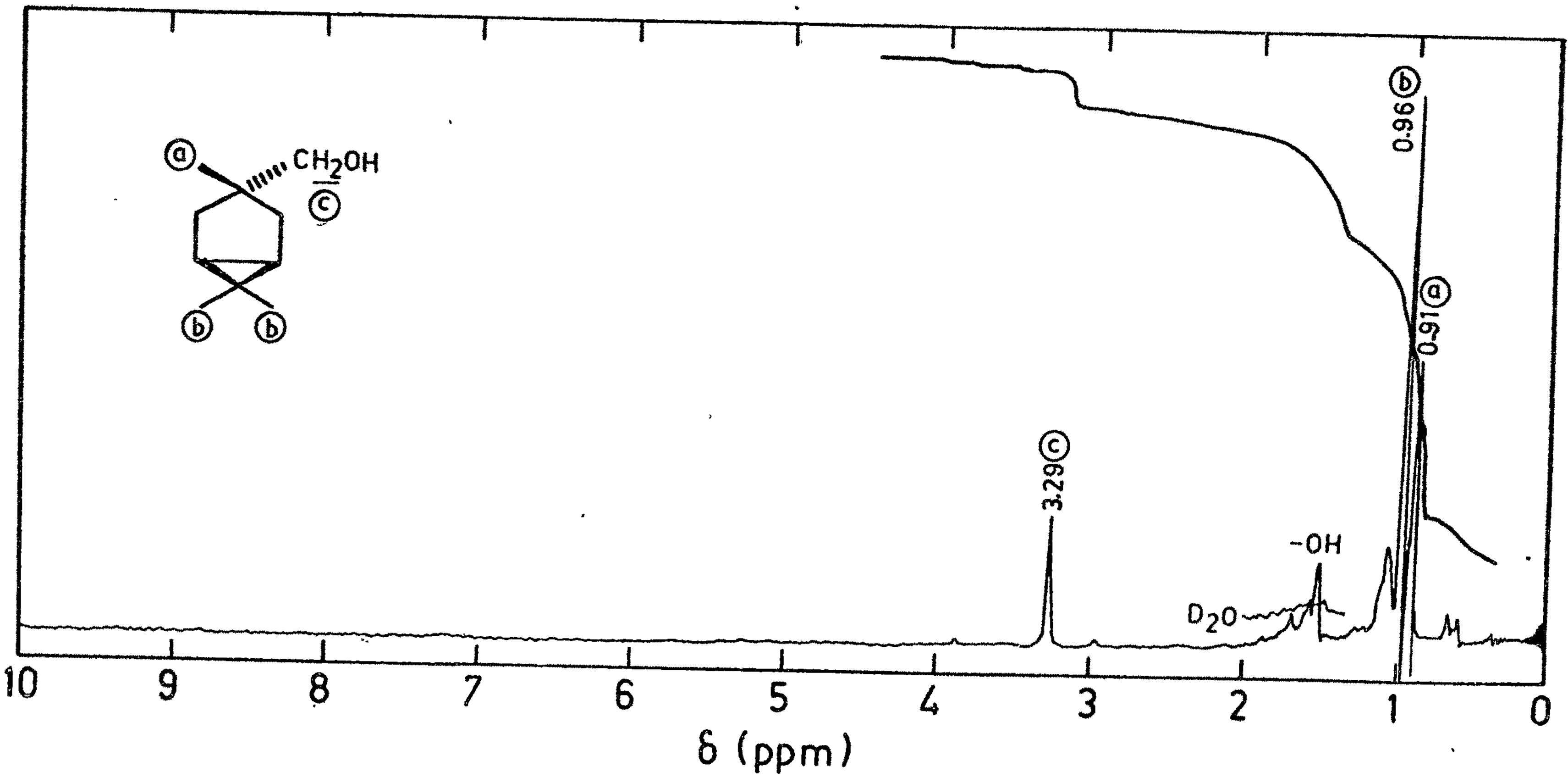


FIG. 9: PMR SPECTRUM OF 3,6,6-TRIMETHYL-3-CARBINOL-BICYCLO [3.1.0] HEXANE (XII)

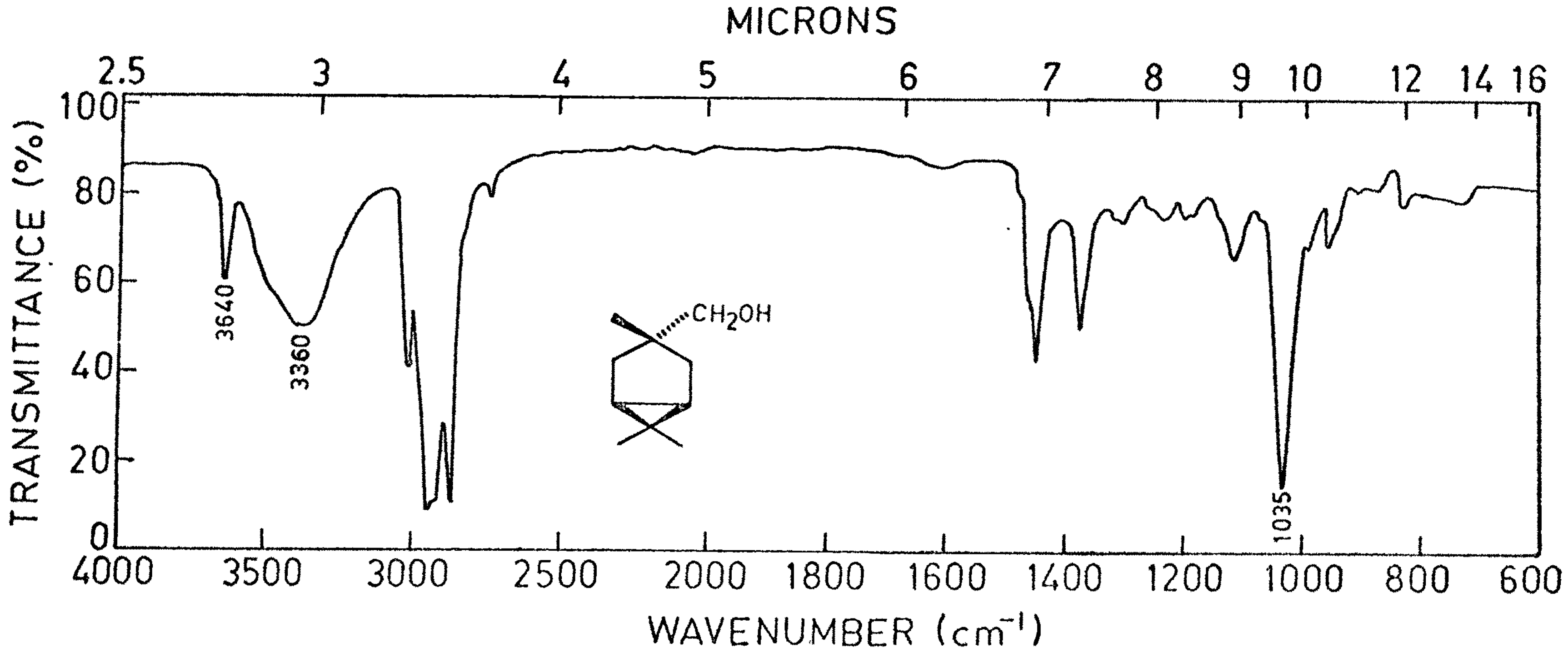


FIG. 10 : IR SPECTRUM OF 3,6,6-TRIMETHYL-3-CARBINOL-BICYCLO [3·1·0] HEXANE (XII)

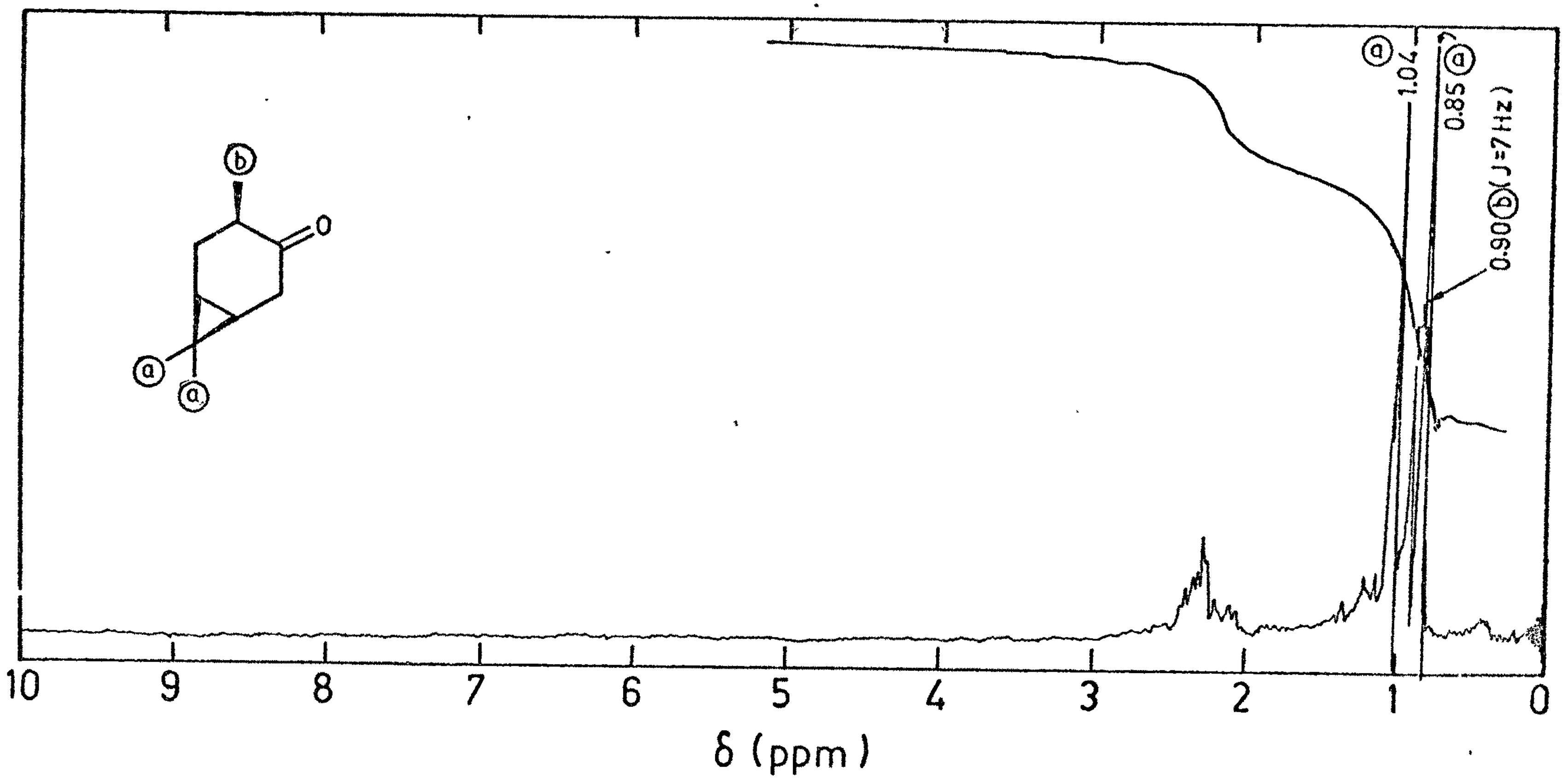


FIG. 11 : PMR SPECTRUM OF ISOCARANONE (VII)

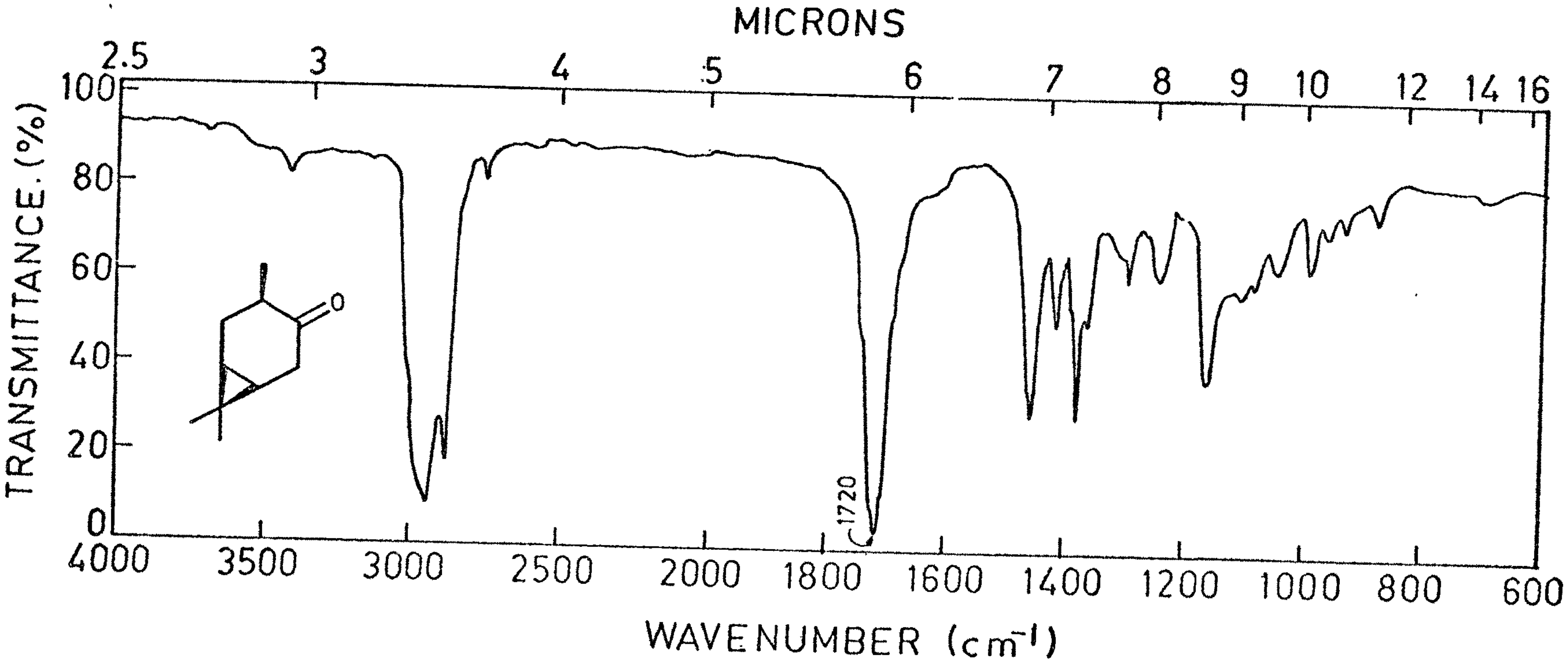


FIG. 12: IR SPECTRUM OF ISOCARANONE (VII)

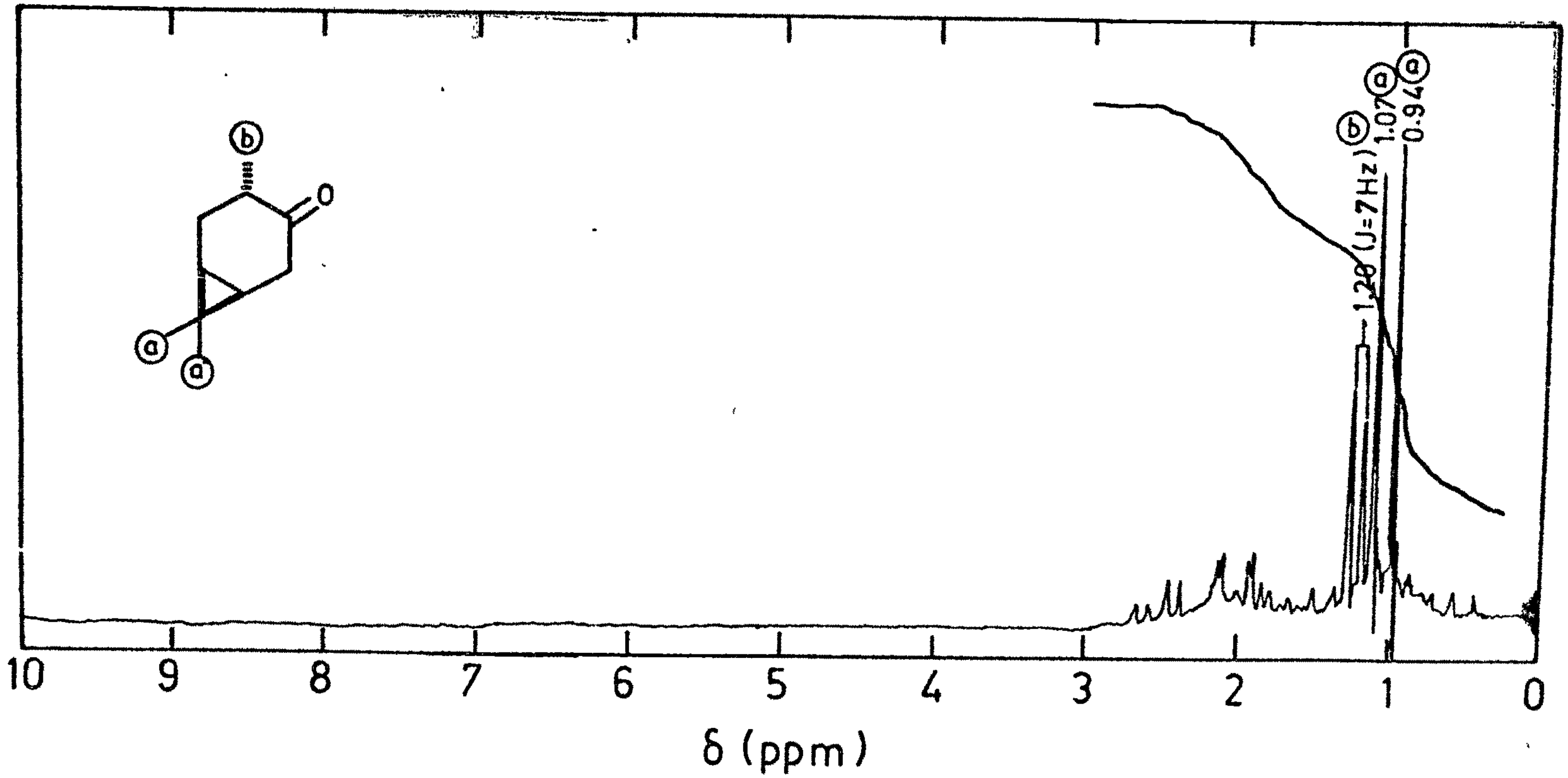


FIG. 13 : PMR SPECTRUM OF CARANONE (VIII)

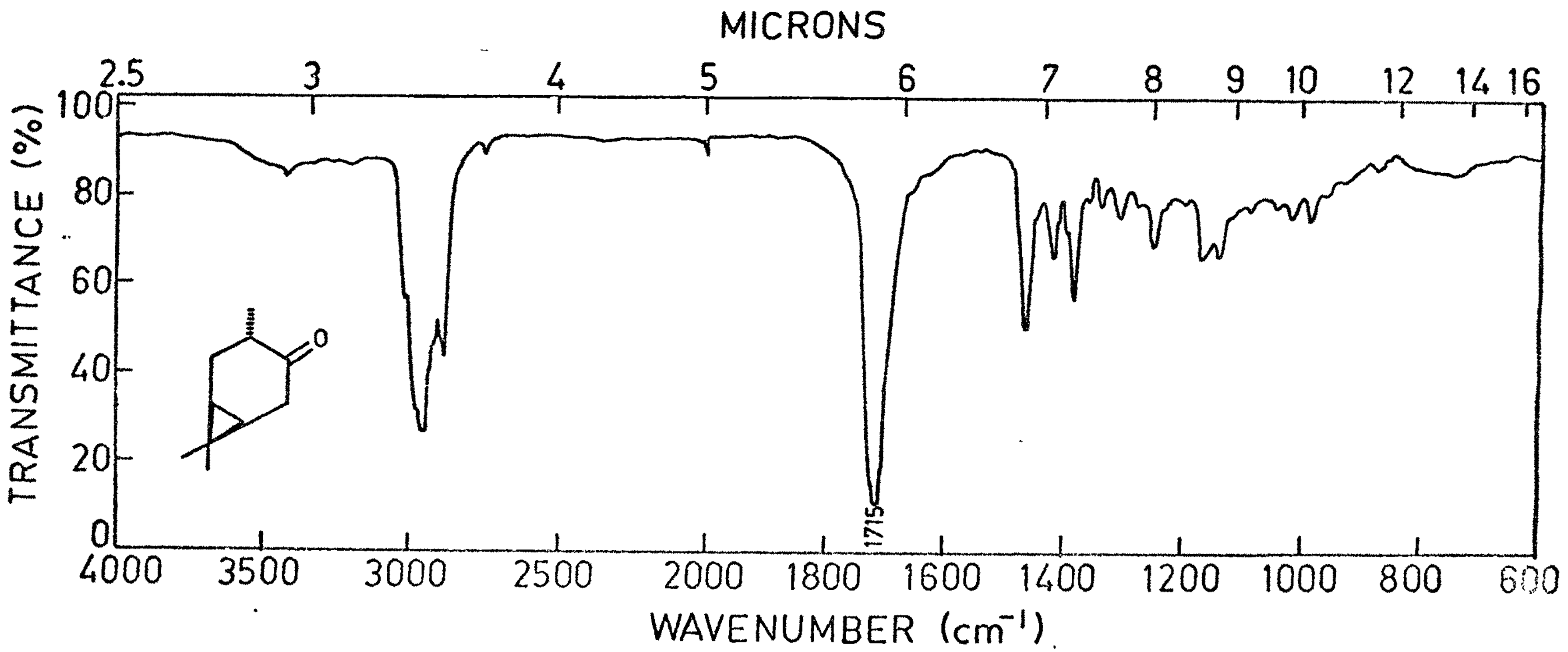


FIG. 14: IR SPECTRUM OF CARANONE (VIII).

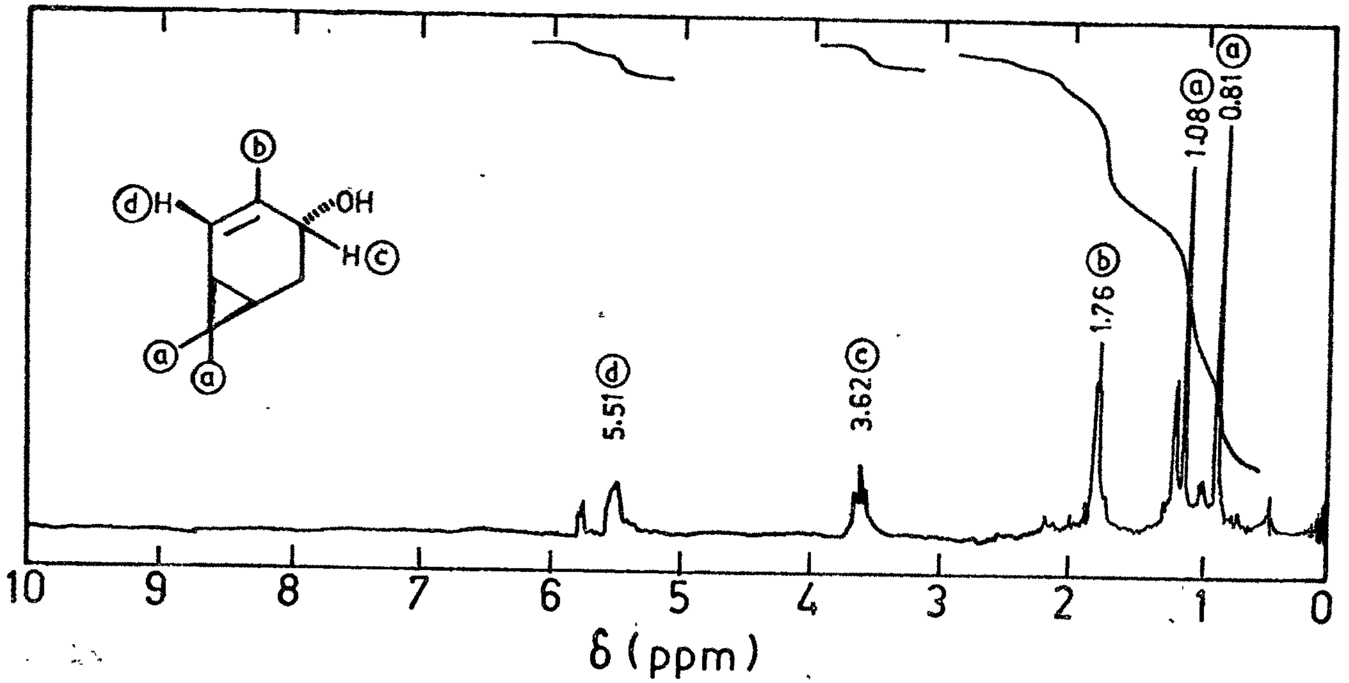


FIG. 15-PMR SPECTRUM OF Δ^4-CARENE-3α-OL (IX)

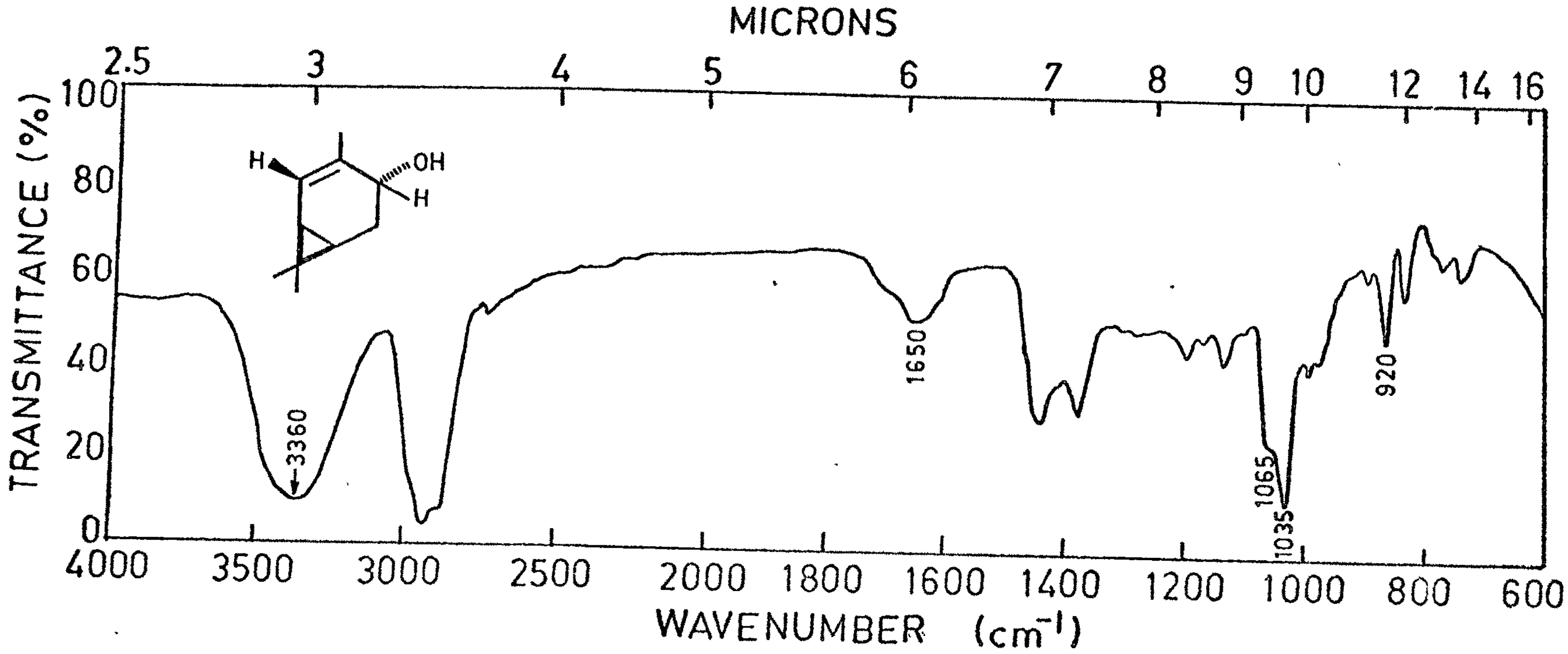


FIG. 16 - IR SPECTRUM OF Δ^4-CARENE-3α-OL (IX).

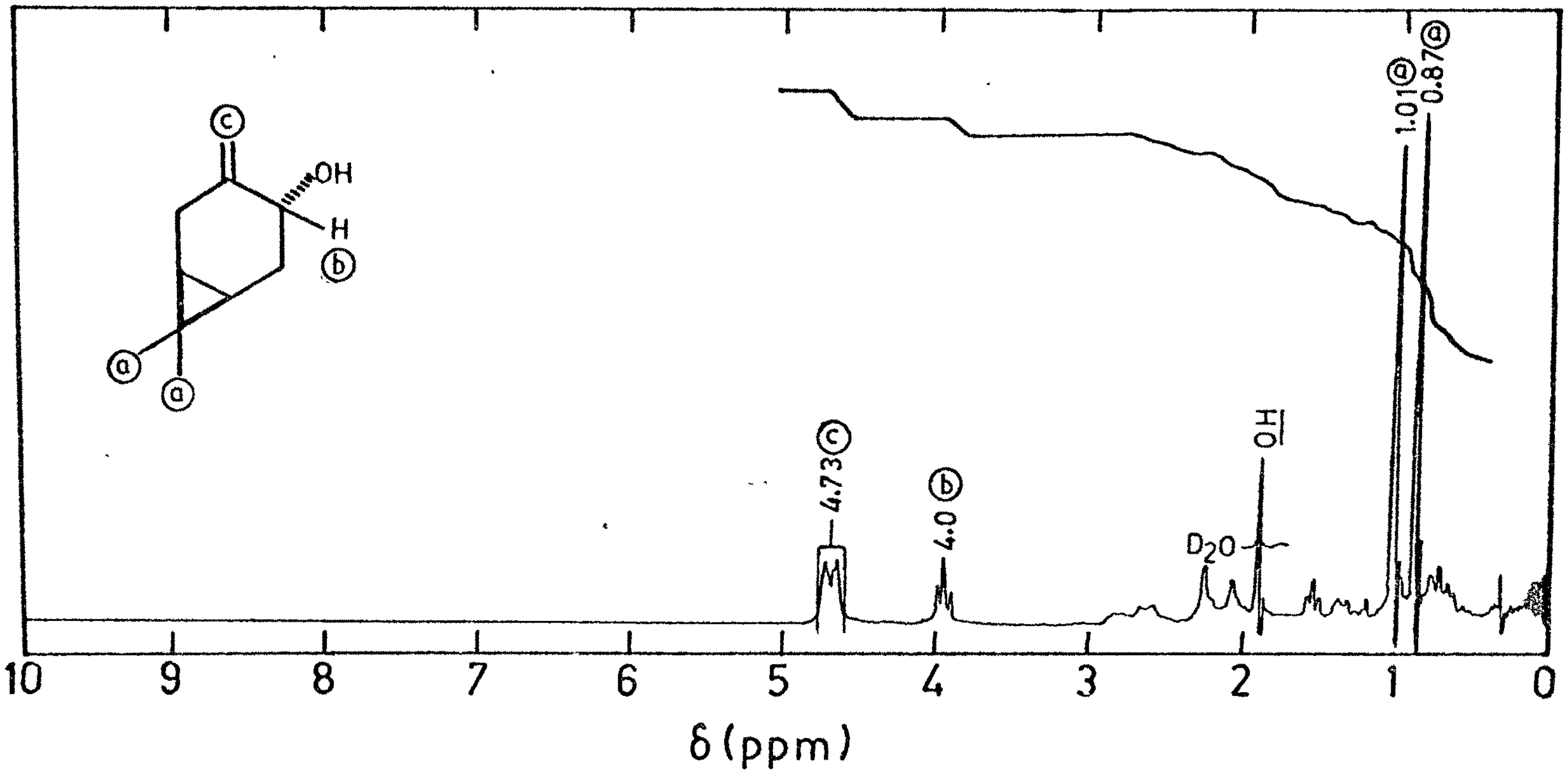


FIG.17 - PMR SPECTRUM OF $\Delta^{4(10)}$-CARENE-3α-OL (X).

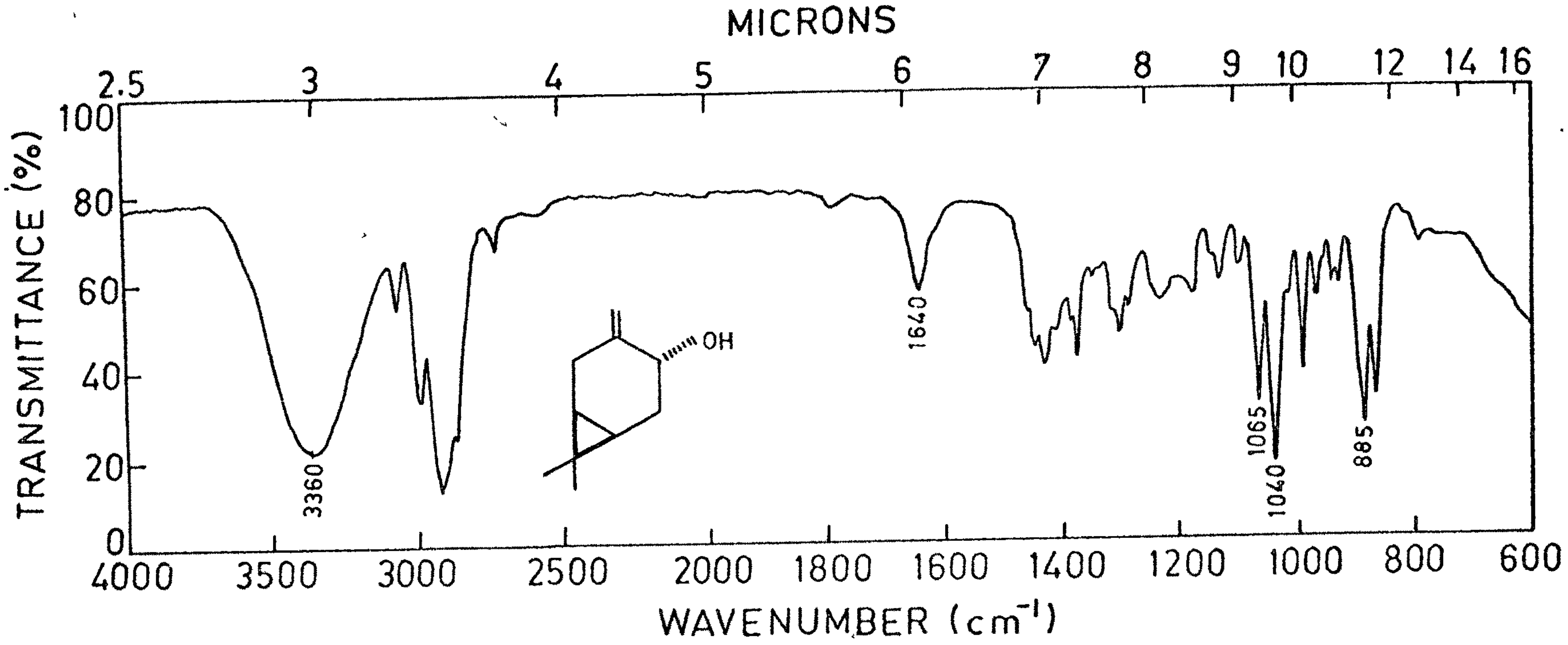
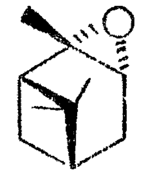


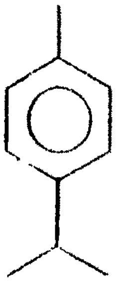
FIG. 18 - IR SPECTRUM OF $\Delta^{4(10)}$-CARENE-3α-OL (X).

Fig. 19). Of the above six components five were isolated by preparative GLC and identified. The minor component (RRT = 3.18, 2%) could not be isolated. Results are given in Table 8.

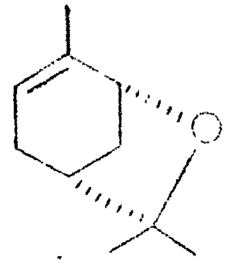
GLC component 1 (RRT = 1.00) was easily recognised as p-cymene. GLC component 2 (RRT = 1.25) was characterised as 2,6,6-trimethyl-7-oxabicyclo [3.2.1] oct-2-ene XV. Its PMR and IR are given in Fig. 20, 21 and are same as reported in literature.[26] Mass spectrum (Fig. 22) of this compound is in complete accord with the structure XV. GLC component 3 (RRT = 2.00) was recognised as 2,2,4-trimethyl-3-cyclopentene-1-acetaldehyde[27] XVI from PMR, IR and Mass (Figs. 23, 24 and 25). The major product (GLC component 4, RRT = 2.62) was easily identified (PMR, IR and Mass; Figs. 26, 27 and 28) as 2,2,3-trimethyl-3-cyclopentene-1-acetaldehyde XVII (or α-campholenic aldehyde)[28a] and also confirmed by the reduction ($LiAlH_4$) to the corresponding alcohol XIX, identical PMR (Fig. 29) with the earlier sample from alumina[1c]. GLC component 6 (RRT = 8.25) was recognised as (+)-trans-sobresol XVIII[29a] from its spectral data (PMR, IR; Figs. 30 and 31) and also comparison with an authentic sample[29b] obtained by the action of aq. H_2SO_4 (1%) on pinene epoxide XIV.



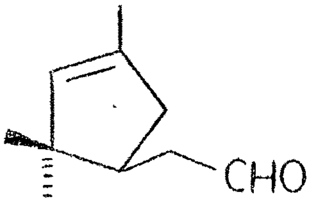
XIV



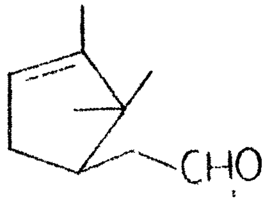
V



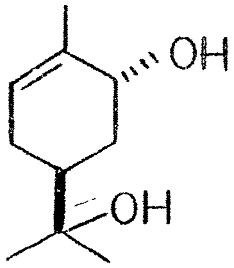
XV



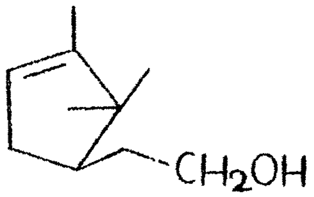
XVI



XVII



XVIII



XIX

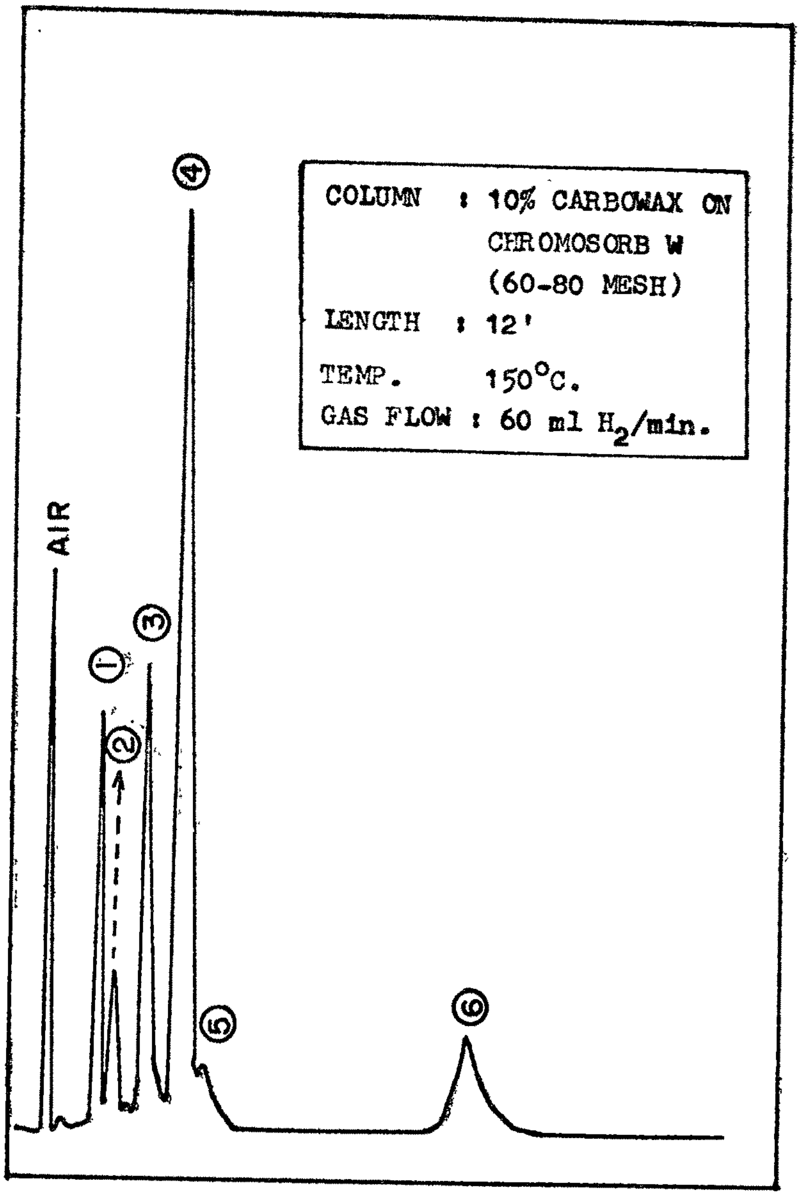
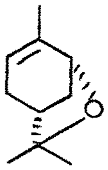
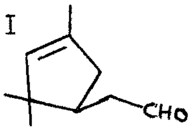
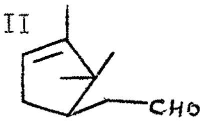
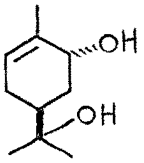


Fig. 19 : GL CHROMATOGRAPH OF REARRANGED PRODUCTS OF 2,3-EPOXYPINANE OVER ZEOLITE (4A)

IDENTIFICATION

① p - CYMENE ② PINOL ③ ALDEHYDE XVI
④ α - CAMPHOLENE ALDEHYDE
⑤ UNIDENTIFIED ⑥ TRANS-SOBREROL

TABLE 8 - Products from rearrangement of α-pinene oxide

GLC Component	Relative retention time (RRT)	Product		Name	PMR Fig. No.	IR Fig. No.	GLC Fig. No.
		Structure No.	Actual structure				
1	1.00	V		p-Cymene			19
2	1.25	XV		2,6,6-Trimethyl-7-oxabicyclo[3.2.1]oct-2-ene	20	21	
3	2.00	XVI		2,2,4-Trimethylcyclopent-3-enylacetaldehyde	23	24	
4	2.62	XVII		2,2,3-Trimethylcyclopent-3-enylacetaldehyde	26	27	
5	3.18	Unidentified					
6	8.25	XVIII		p-Menth-6-ene-*trans*-2,8-diol	30	31	

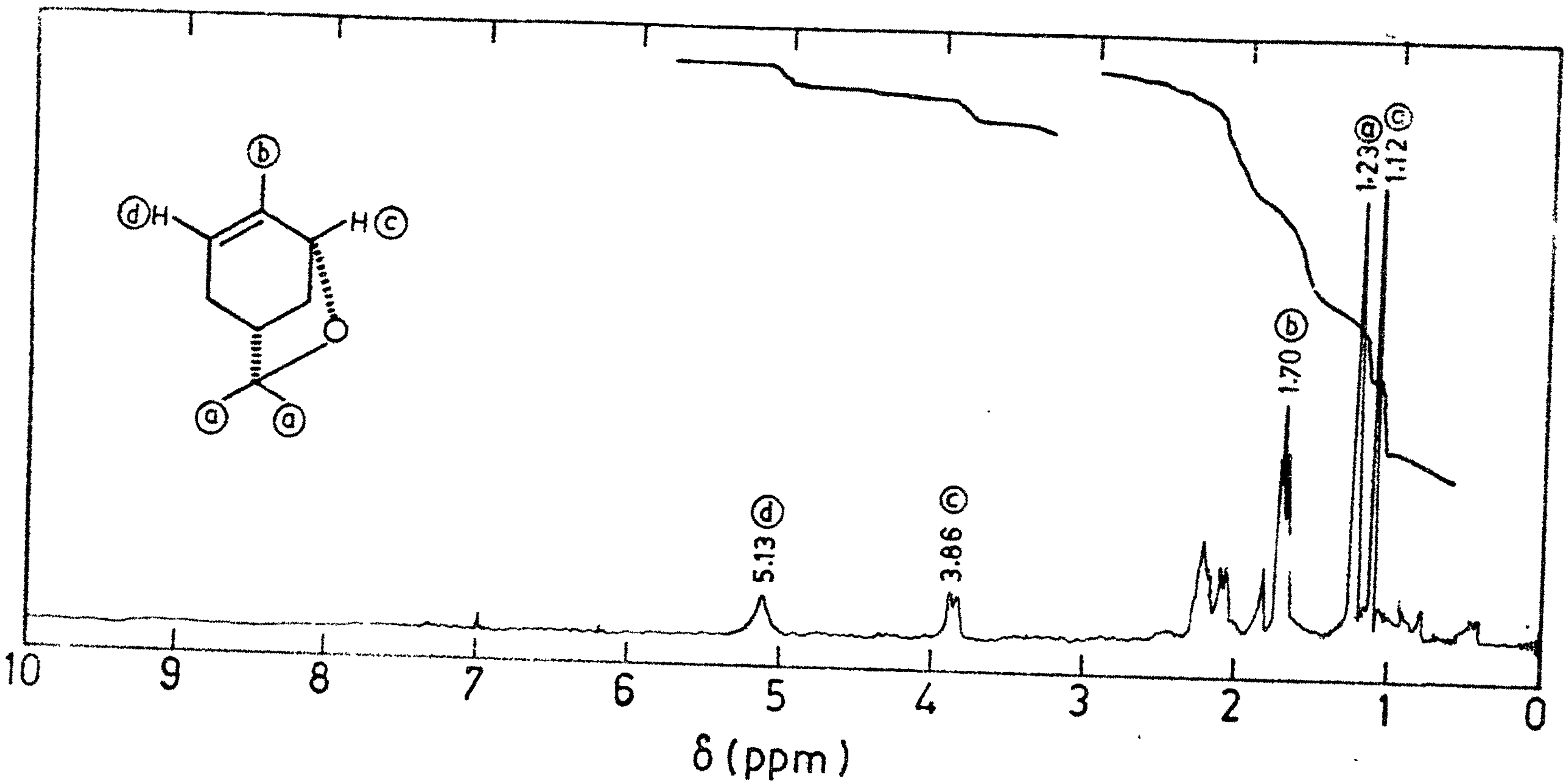


FIG. 20 - PMR SPECTRUM OF 2,6,6-TRIMETHYL-7-OXABICYCLO [3.2.1] OCT-2-ENE (XV).

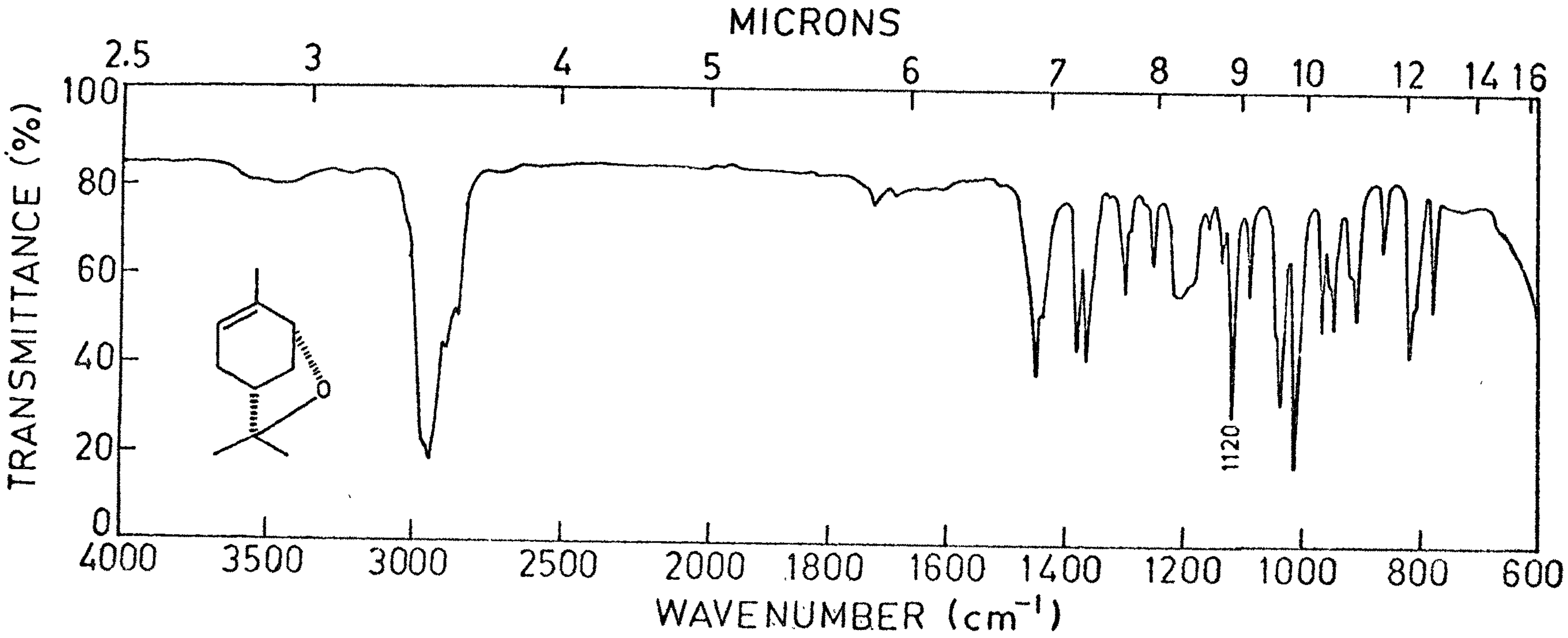


FIG. 21-IR SPECTRUM OF 2,6;6-TRIMETHYL--7-OXABICYCLO [3·2·1] OCT-2--ENE (XV).

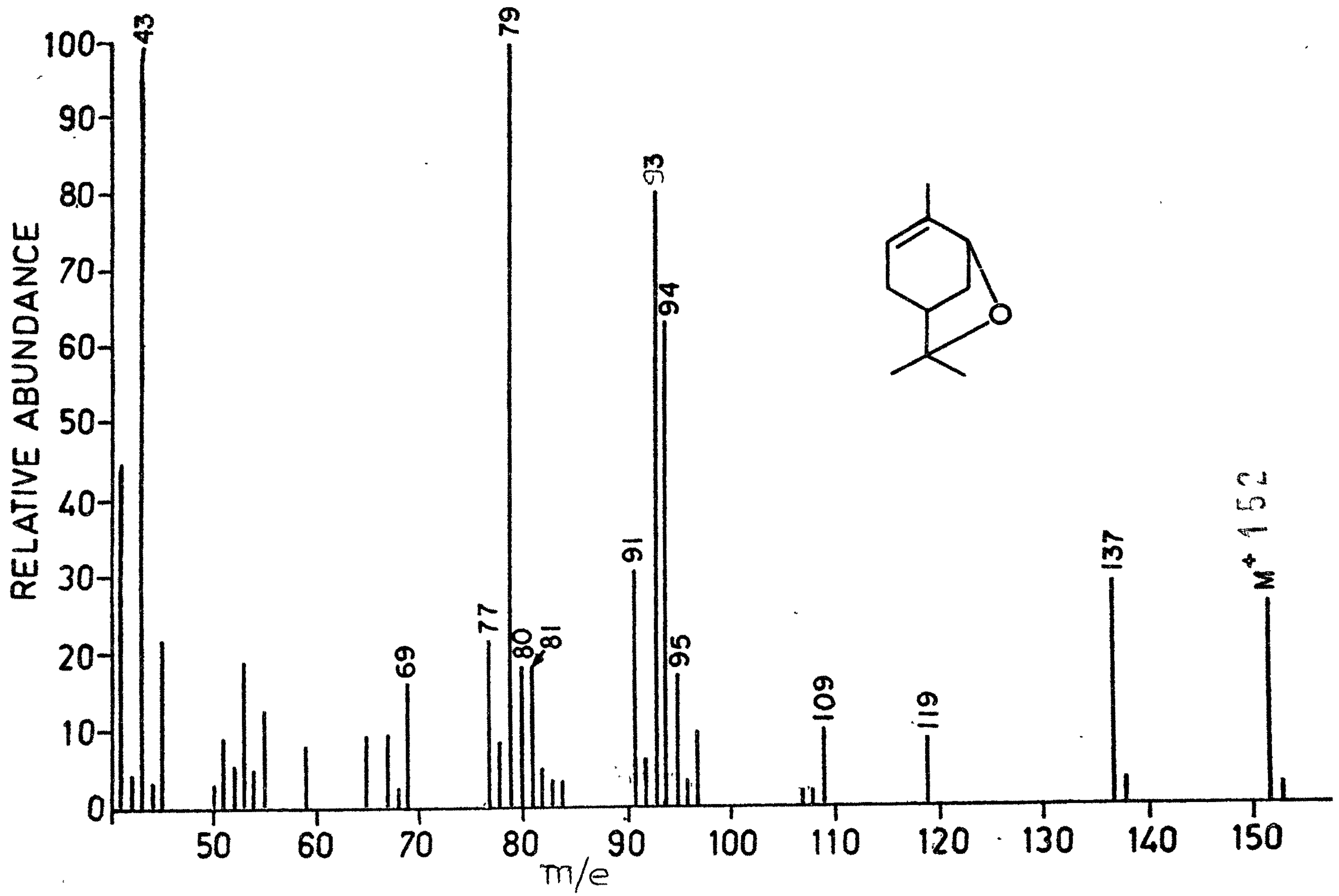


FIG. 22-MASS SPECTRUM OF PINOL (XV).

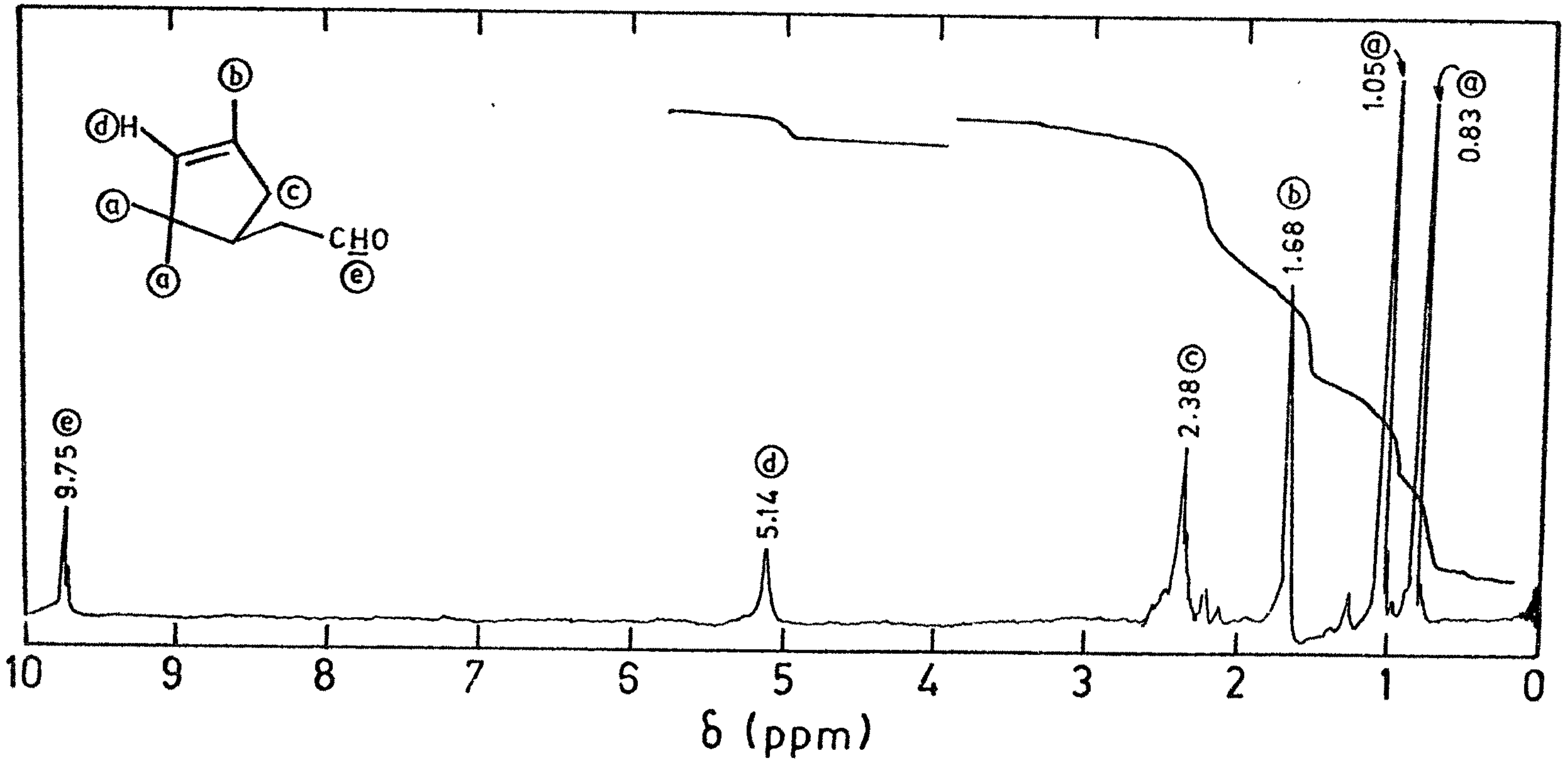


FIG.23-PMR SPECTRUM OF 2,2,4-TRIMETHYL CYCLOPENT-3-ENYLACETALDEHYDE (XVI).

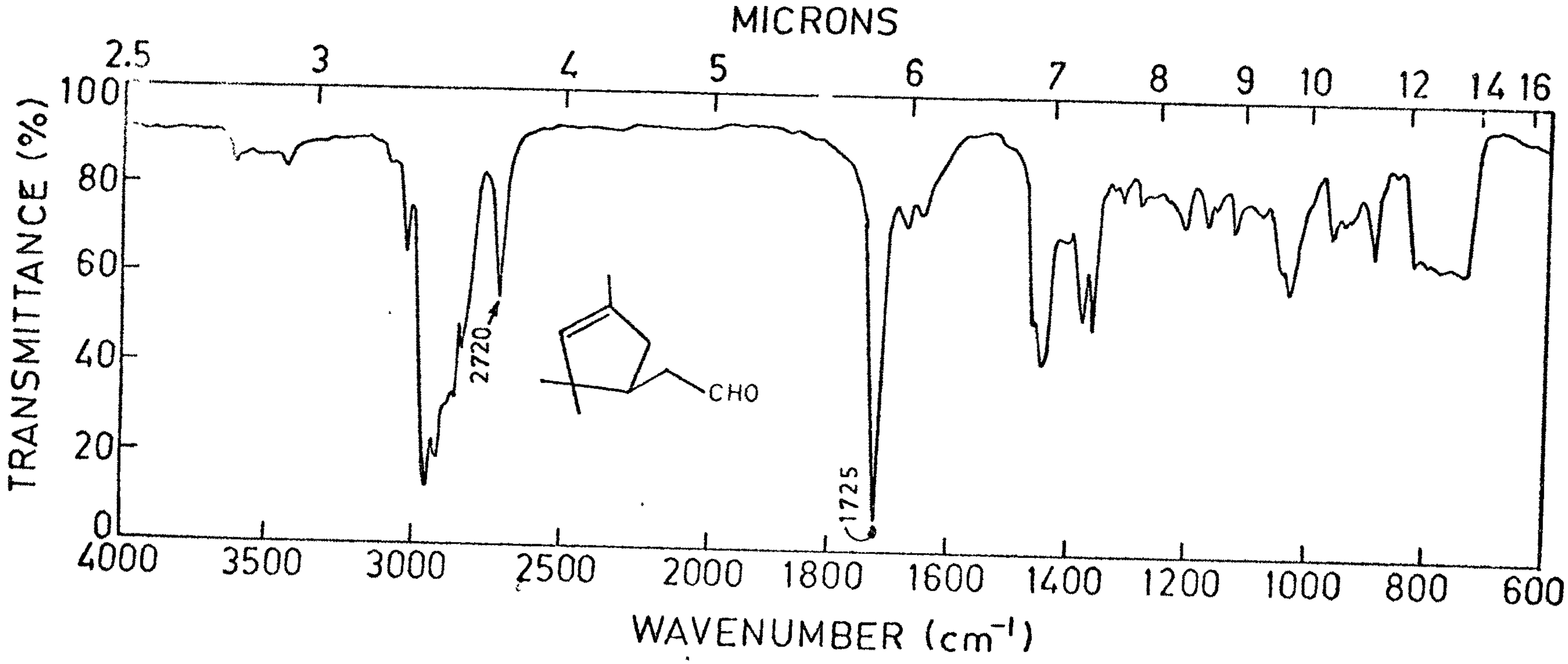


FIG. 24 -IR SPECTRUM OF 2,2,4-TRIMETHYL CYCLOPENT-3-ENYLACETALDEHYDE (XVI).

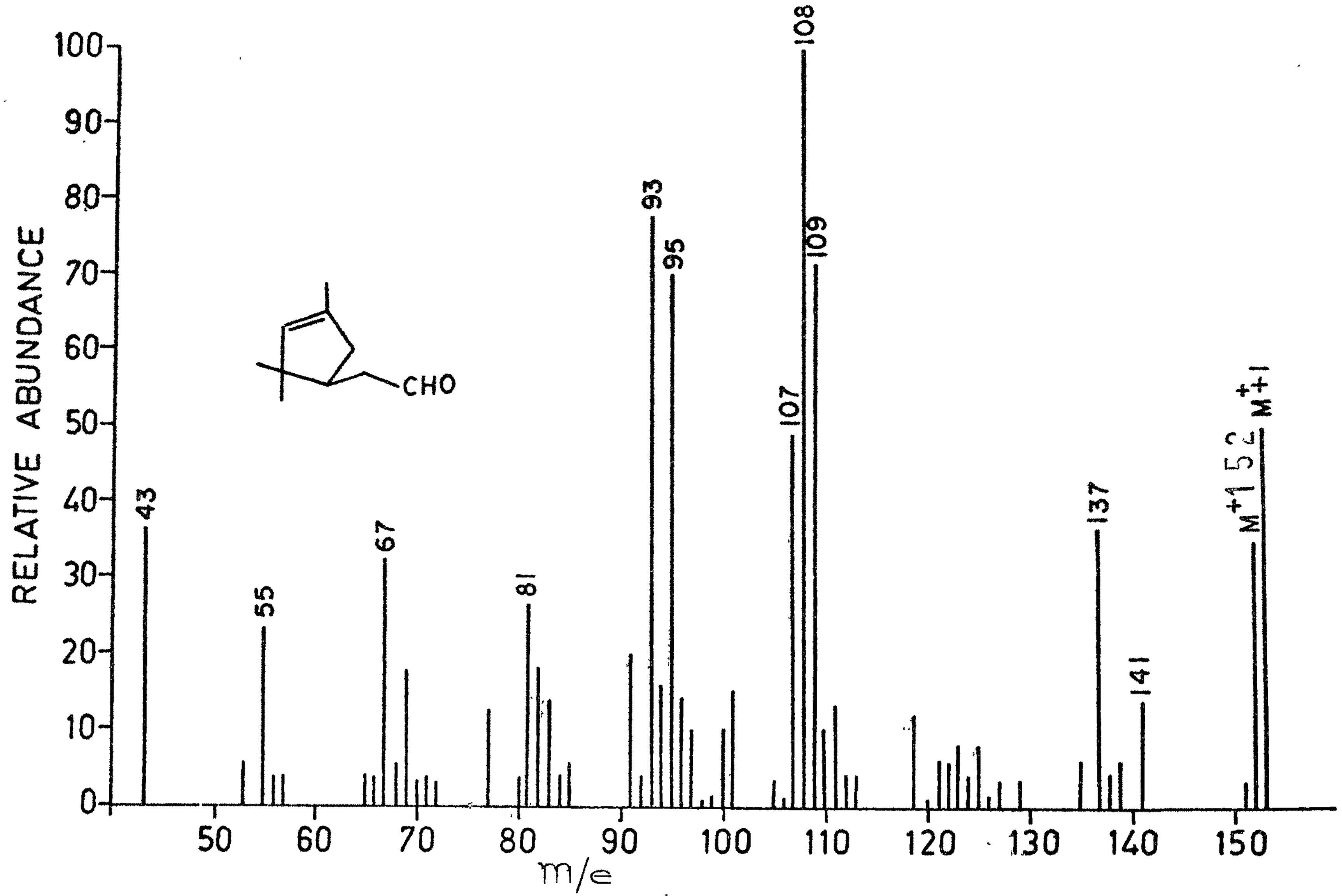


FIG. 25-MASS SPECTRUM OF ALDEHYDE (XVI).

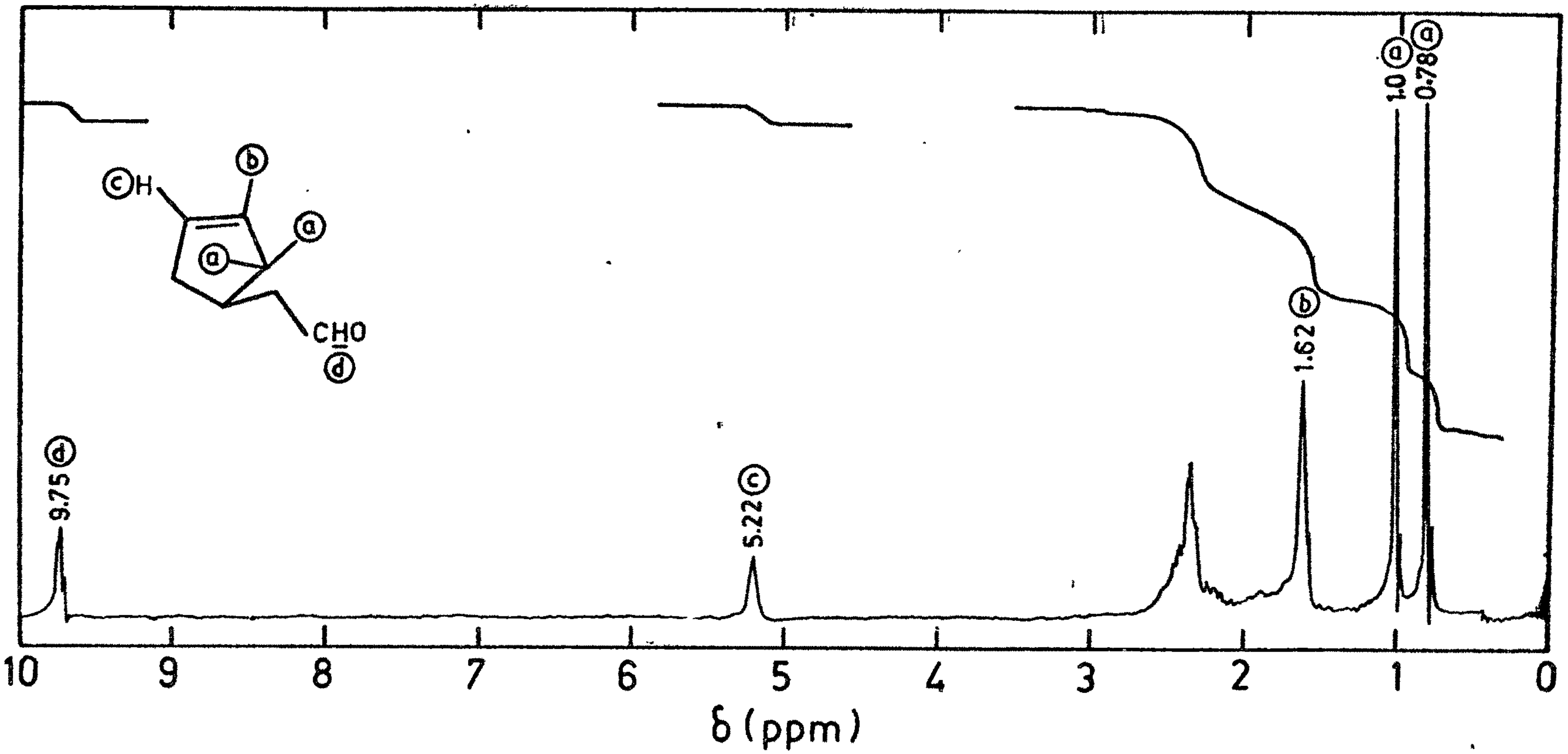


FIG.26-PMR SPECTRUM OF 2,2,3-TRIMETHYLCYCLOPENT-3-ENYLACETALDEHYDE (XVII).

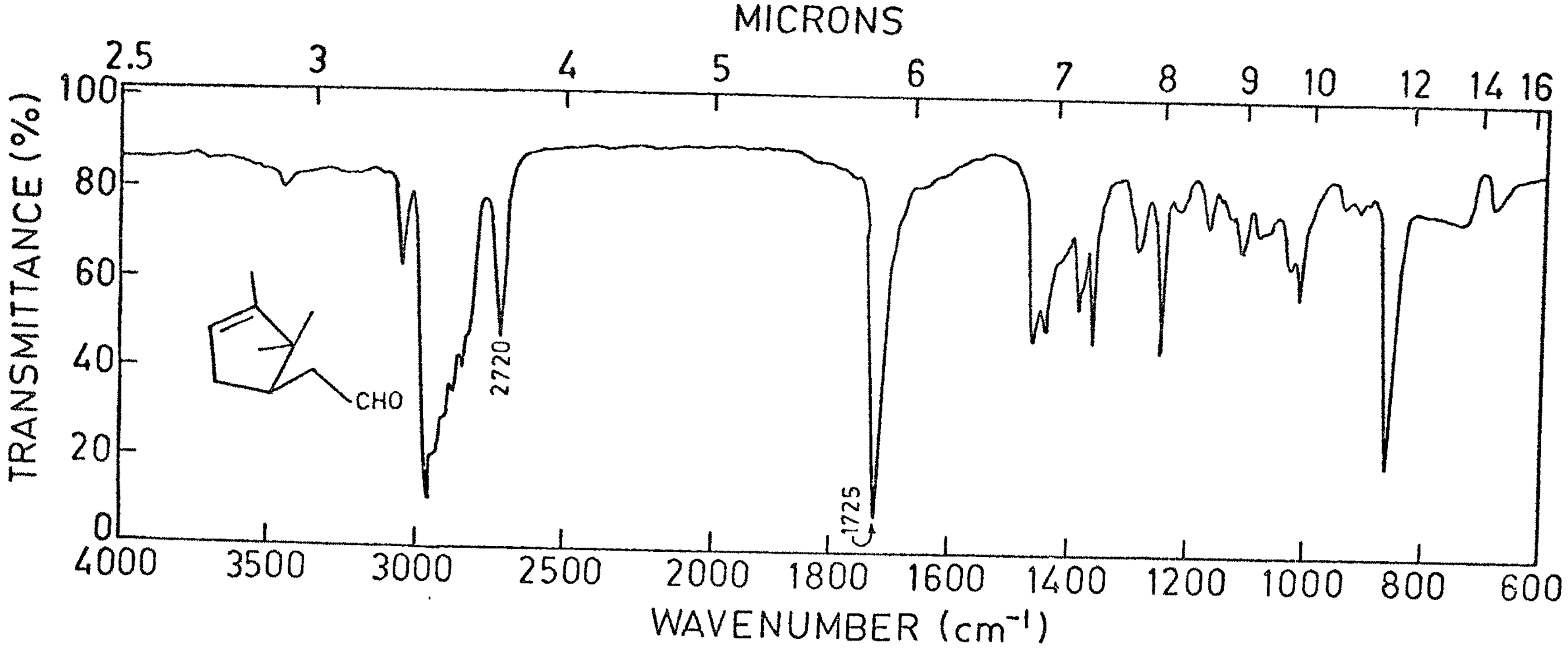


FIG.27-IR SPECTRUM OF 2,2,3-TRIMETHYLCYCLOPENT-3-ENYLACETALDEHYDE (XVII)

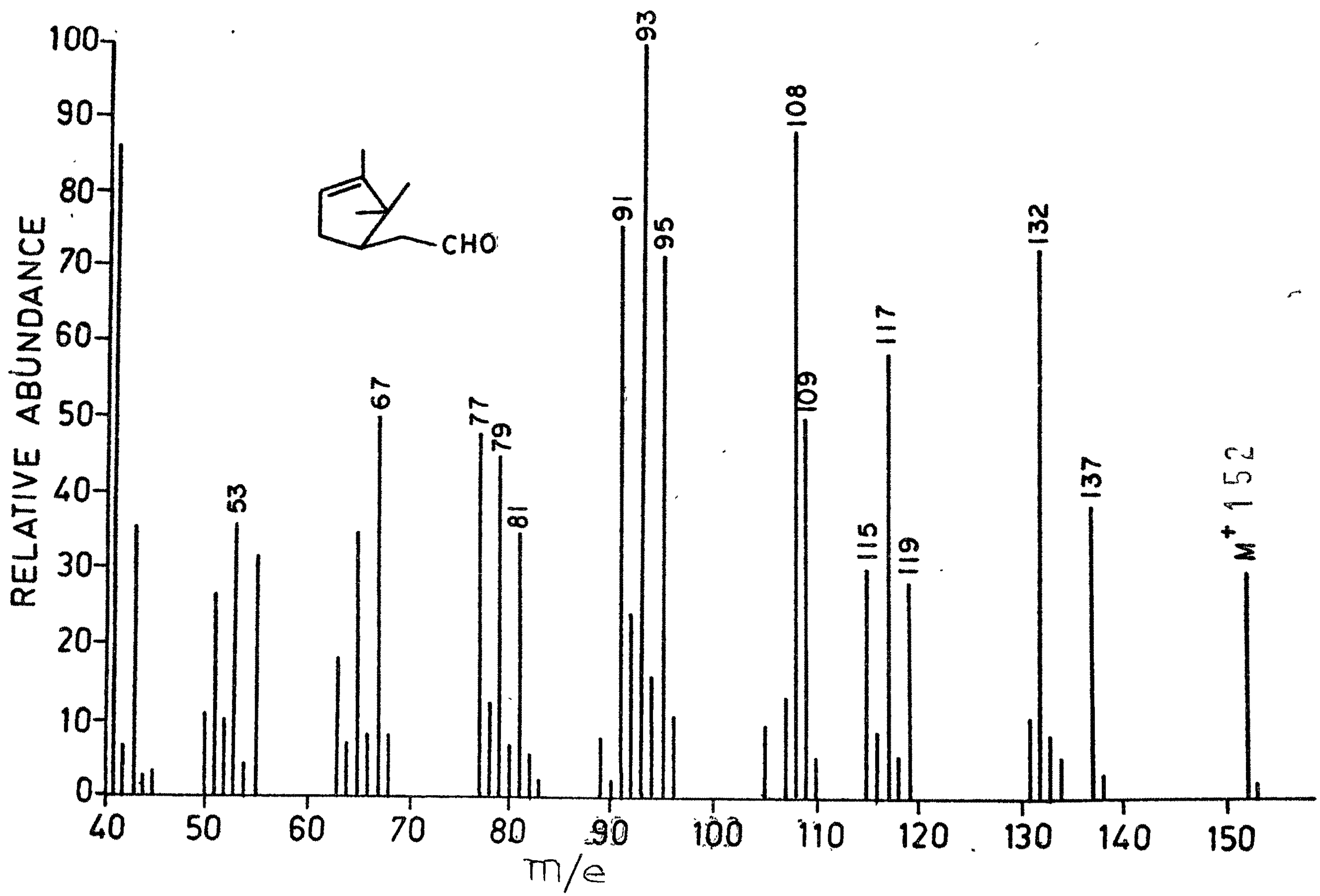


FIG. 28-MASS SPECTRUM OF α-CAMPHOLENE ALDEHYDE (XVII).

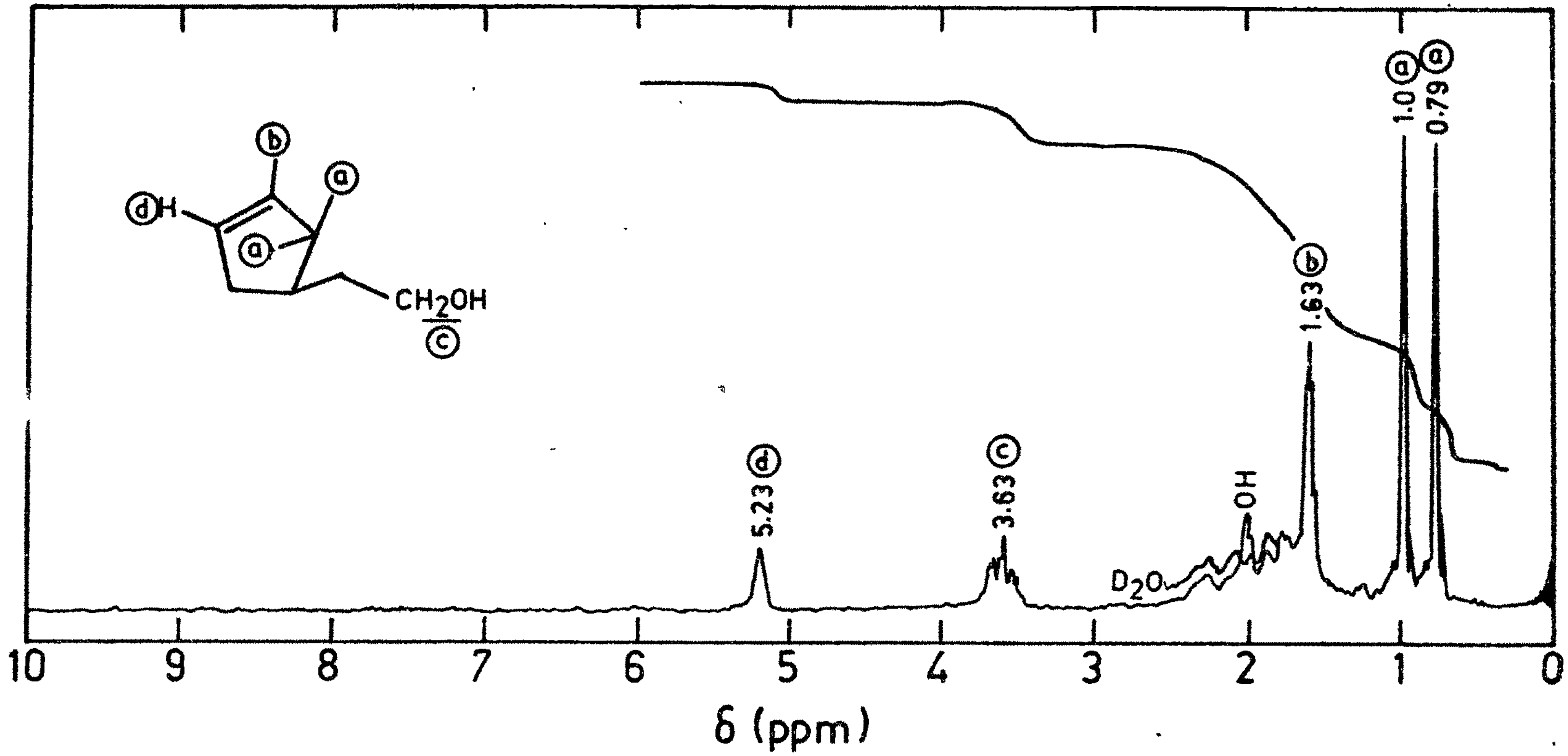


FIG.29-PMR SPECTRUM OF 2,2,3-TRIMETHYL-3-CYCLOPENTENE -1-ETHANOL (XIX)

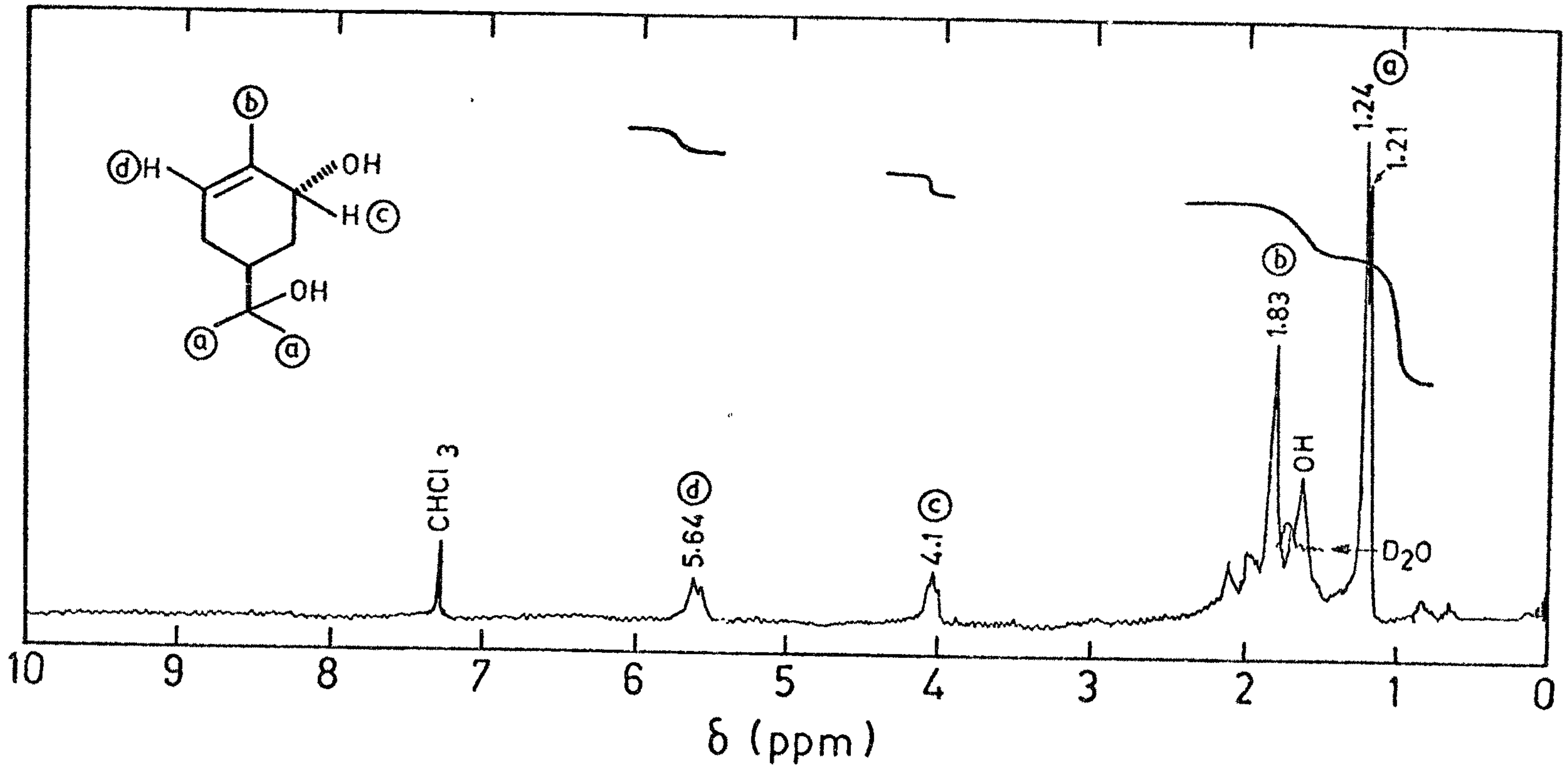


FIG. 30: PMR SPECTRUM OF TRANS-SOBREROL (XVIII)

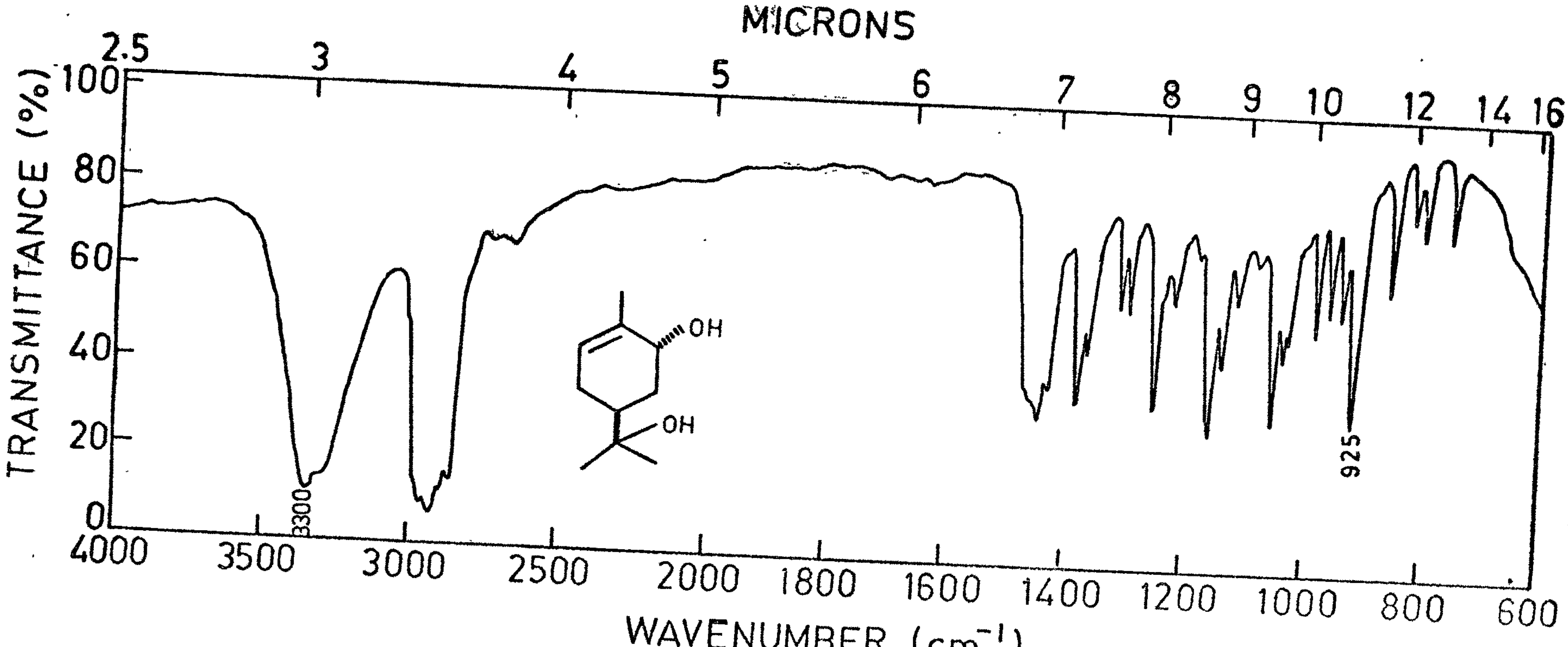


FIG.31:IR SPECTRUM OF TRANS-SOBREROL (XVIII)

4. DISCUSSION

In earlier work on reactions in a solid matrix, alumina and silica gel have been used individually for epoxide rearrangements.[1] In order to examine the effect of change in acidity and catalytic activity (of aluminosilicates)*, we have carried out the isomerisation of 3-carene oxide and α-pinene oxide.

First, let us assume that the chemical transformations in zeolite catalyst system occur within the high surface area intracrystalline volumes. Thus, for a reaction within a zeolite particle it is apparent that both the entry pores and the channel-cavity system must be open enough to allow transport of reactant molecules from the bulk phase to the active sites (and vice-versa). Thus, any crystalline sieve that could absorb simple organic molecules might conceivably have catalytic potential. However, some role must be allocated to the external surface.

Aluminosilicates (molecular sieve zeolites) composed of silica and alumina are highly acidic.[30] Zeolites are now used as acidic catalysts for hydrocarbon reactions which include disproportionation, cracking, isomerization, alkylation of paraffins and aromatics with olefins and polymerization of

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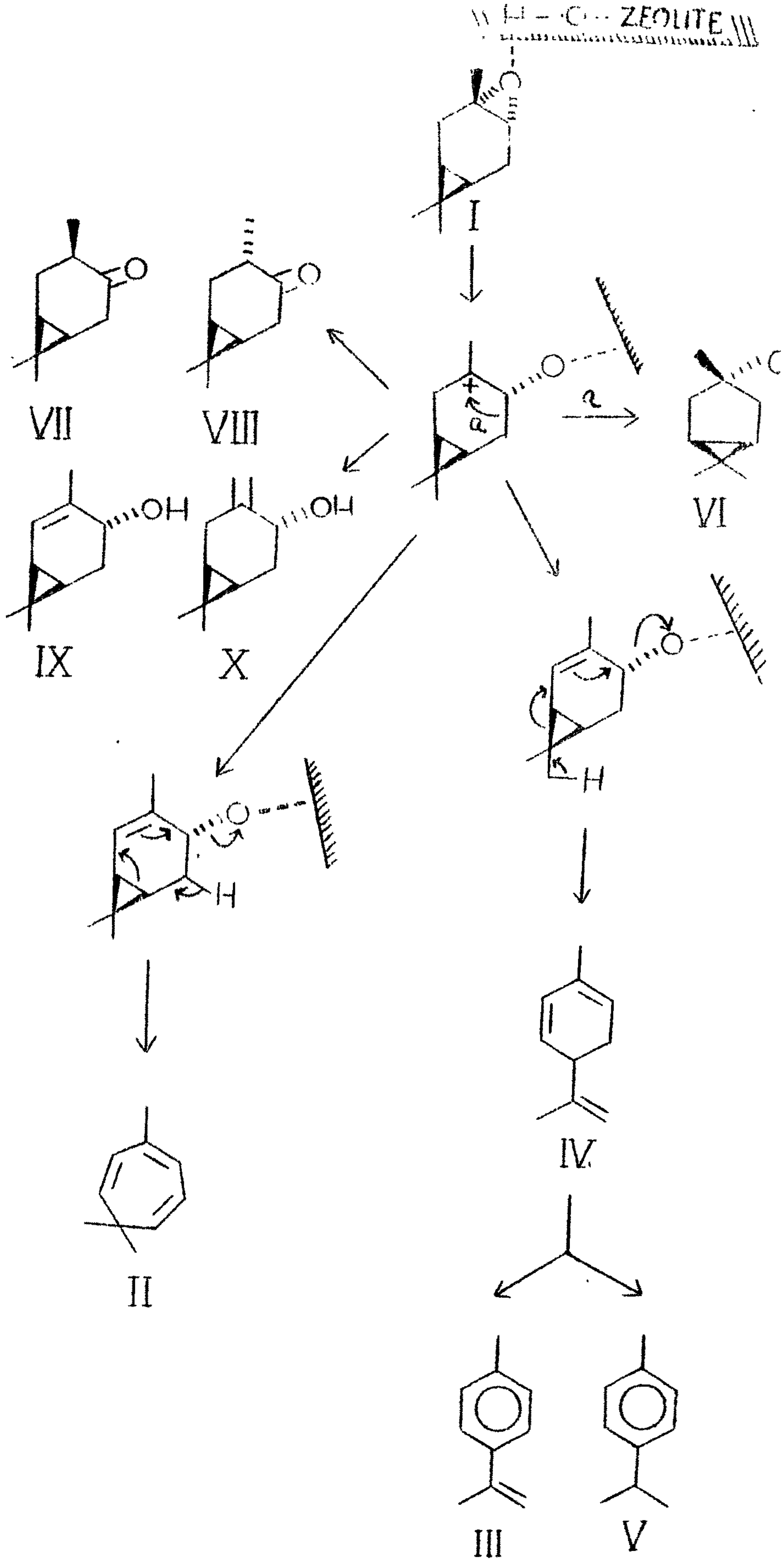
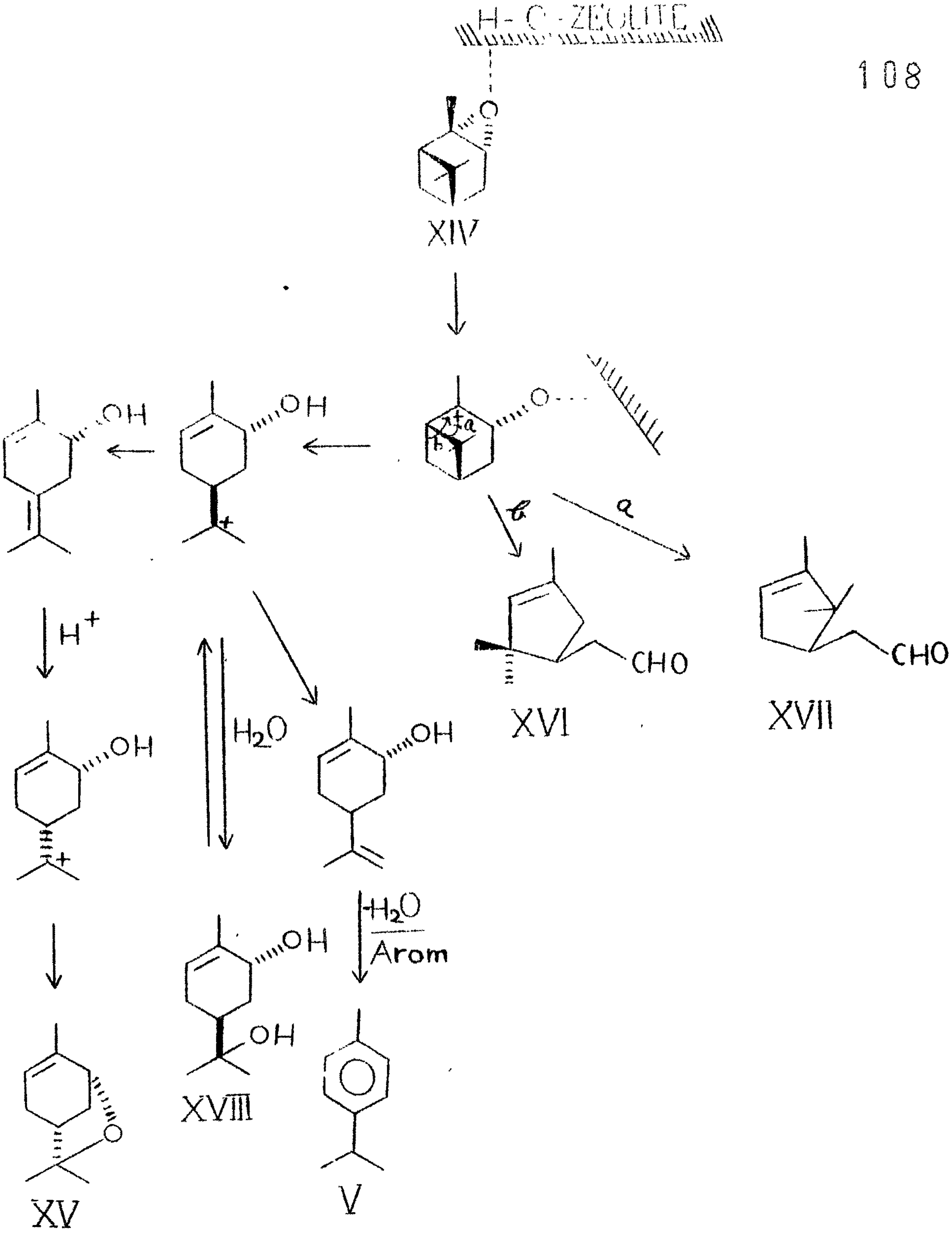
* Since aluminosilicates are composed of silica and alumina but differ from pure silica-alumina in crystal structure, acidity and catalytic activity and also have sieving properties.[30c]

olefins.[30a] It is generally accepted that these reactions occur by means of carbonium ion (vide supra) which can be formed by interaction between the reacting substance (hydrocarbon and acid centre). It was concluded that the Bronsted sites rather than Lewis sites were primary source of catalytic activity. On the mechanistic grounds the formation of the products described above when 3-carene oxide and ⍺-pinene oxide come in contact witn Lowry-Bronsted acid should be expected. Thus, in these reactions zeolite behaves as a matrix with proton donar sites, this concept suffice to rationalise the products observed. Schemes 1 and 2 rationalise the formation of products from 3-carene oxide and ⍺-pinene oxide.

Zeolite 13X is ascribed to be highly acidic.[30] The high acidity is due to silica/alumina ratio ($SiO_2/Al_2O_3 \sim 1.23$), more the silica more acidic the zeolite. The more active, more acidic zeolites are less selective to aldehyde[30a] and the major products (II and V) with zeolite 13X resulted from opening of cyclopropane ring. It appears likely that 13X having channels of about 10 Angstroms in diameter must be allowing epoxide as well as cyclopropane rings incoming in contact with active sites of zeolite which might not be possible in case of zeolite 4A (having channels of about 4.0 A^0).

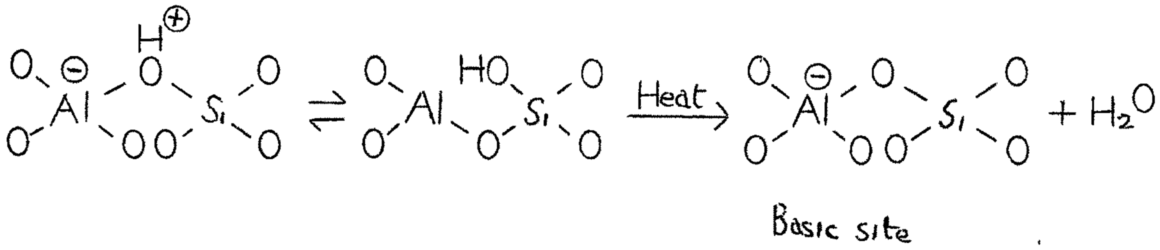


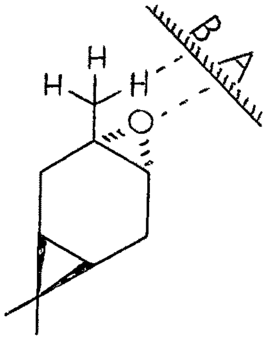
SCHEME-1



SCHEME-2

The formation of allylic alcohols (IX and X) could be best explained from the basic site of zeolite. The fact that these alcohols are not the creation of dehydration of corresponding glycols. In a separate experiment it was demonstrated that the allylic alcohols do not arise by dehydration of the corresponding glycol, because when glycol XIII was treated with zeolite under the same conditions, it was recovered unchanged quantitatively.





A = Acidic site

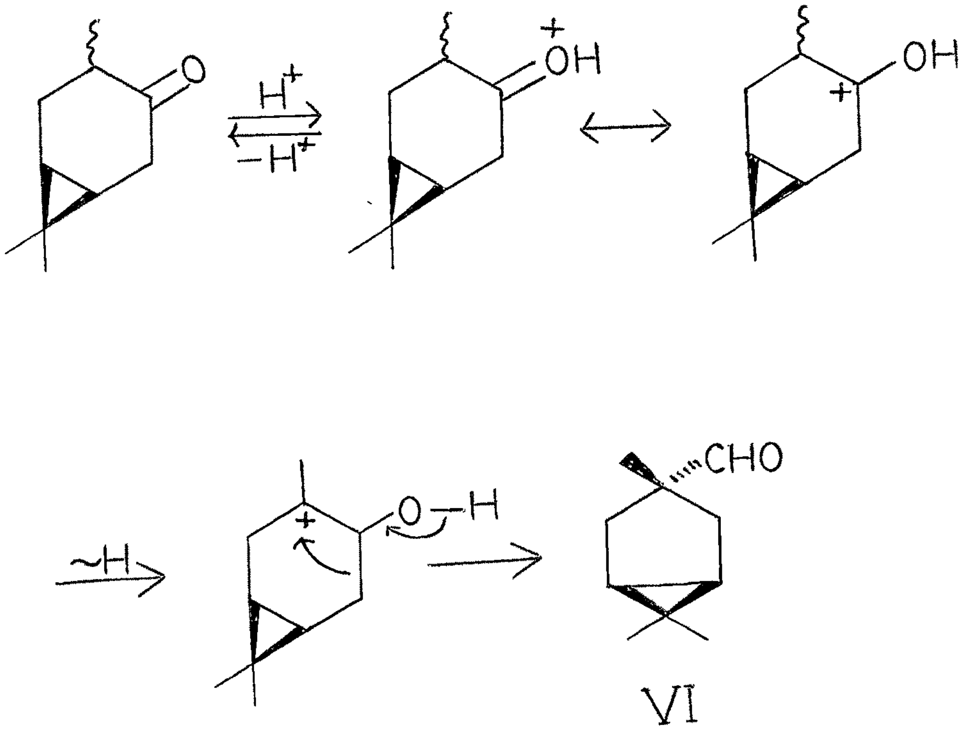
B = Basic site

In the case of α-pinene oxide, there appears to be no significant change in product composition by changing from A to X series of zeolite (see Table 6). In all cases major products were aldehydes (XVI and XVII). With the X series of zeolites an increase in the formation of sobrerol (XVIII) at the cost of aldehyde could be explained by an increase in the amount of sinanol groups because of more silica (see above). It is also remarkable that when α-pinene oxide was treated with SrA, pinol percentage had increased at the expense of sobrerol and is evident from the above reaction that sobrerol is the potential precursor of pinol.

Effect of cations

The ability to undergo reversible cation-exchange is one of the most important properties of zeolites. It enables one to modify the electric fields inside zeolite crystals,[31] which in turn modifies the sorptive and catalytic properties. The most striking modification that can be made is to change the molecular sieve properties. The number, size, valency and location in the lattice of zeolite cation have important effects on the size and the shape of the entry pores. This is most dramatically demonstrated in zeolite A, where replacement of sodium ions (60%) by potassium ions result in decrease in effective pore diameter from about $4.0A^{0}$ to about $3.0A^{0}$ and less reactive towards epoxide (see Table 4, item 4).

The main product of the rearrangement of 3-carene oxide with 4A was aldehyde (VI). Though the Cannizzaro reaction on zeolite is known,[30a] but no Cannizzaro product was isolated in any case. With SrA, epoxycarene gives a product rich in ketones (VII and VIII), but surprisingly when it was switched on to X series the bicyclic aldehyde (VI) was the major constituents as in the case in 4A and HA. This may probably be an indication that like SrA, the main product with SrX may be caronones, which act as precursor of VI, hence the enrichment of VI is the product.



VI

5. EXPERIMENTAL

5.1. General practice adopted

All m.ps and b.ps are uncorrected. Petroleum-ether refers to the fraction, b.p. 60-80°. All other solvents were reagent grade. All solvent extracts were finally washed with saturated brine solution before drying over anhydrous Na_2SO_4. All reaction products were monitored by GLC or TLC.* All yields reported for epoxide-aluminosilicates reaction, are on w/w basis. Optical rotations were measured in $CHCl_3$ at 25° on a Schmidt + Haensch electronic Polarimeter model Polatronic 1.

IR spectra were recorded as smears (liquids) or Nujol mulls (solids) or in CCl_4 on Perkin-Elmer Infracord model 267. UV spectra were taken on a Perkin-Elmer model 402 in rectified spirit (95% ethanol) solution. PMR spectra were taken with 10-20% solution in CCl_4 with TMS as the internal standard on Perkin-Elmer model R32 (90 MHz); signals are recorded in ppm (δ) relative to TMS as zero.

---

* TLC was carried out on SiO_2 (200-300 mesh) layer (0.25 mm) containing 10% gypsum, solvent: 10% EtOAc in benzene, visualisation of spots were carried out with 20% H_2SO_4 in methanol mix spray followed by heating at 120°/10 min.

While citing PMR data, following abbreviations have been used; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad etc. Mass spectra were recorded on a Varian Mat CH7 mass spectrometer using an ionising potential of 70 eV and a direct inlet system. While summarising mass spectral data, besides the molecular ion, ten most abundant ions (m/e) are reported with their relative intensities.

GLC were run on Hewlett-Packard model 5712A, using a 360 x 0.6 cm column packed with 10% carbowax 20M on 60-80 mesh Chromosorb W for analytical purposes and model 7624A, using a 360 x 0.9 cm column packed with 20% carbowax 20M on 45-60 mesh Chromosorb W for preparative use, unless otherwise stated; H_2 was used as carrier gas.

5.2. Materials

5.2.1. Molecular sieve zeolites: The original zeolite samples were Linde 4A and 13X (extrudated) in the sodium forms, manufactured by ACC, Thana, Bombay and were activated at 120°-130° for 6 hr and cooled over P_2O_5 in desiccator until use.

5.2.2. Solvents: Solvents used for reactions were purified as under: n-Hexane by stirring with conc. H_2SO_4-HNO_3 (1:1), washing, drying and passing through Al_2O_3-I^{33}. Acetone by refluxing and distilling over $KMnO_4$^{34}.

5.2.3. Epoxides

5.2.3.1. (+)-2α,3α-Epoxypinane (XIV): (+)-α-Pinene ($[\alpha]_D$ + 16.8 neat, 38.0g; 0.279 mole) in ether (25 ml) was cooled to ($\sim$0°) and with stirring treated with an ethereal solution of monoperphthalic acid (400 ml, containing 51.0 g peracid; 0.28 mole during 0.5 hr). After another 6 hr at 0-2° and 14 hr at 10°, the precipitated phthalic acid was filtered off, the filtrate washed successively with aqueous sodium sulfite (5%, 50 ml x 2), water (50 ml x 2), 10% Na_2CO_3 (50 ml x 2), water (50 ml x 3), brine (50 ml) and dried over anhydrous sodium sulfate. The solvent was flashed off carefully and the residue (34.3g; 78% epoxide, 62% yield, b.p. 76-86°/20 mm) containing 16.5% unchanged hydrocarbon was purified by fractionation gave (+)-α-pinene oxide (24.1 g), b.p. 83-84°/20 mm; n_D^{25} 1.4702; $[\alpha]_D$ + 32.06 (neat) (Lit.[1c] b.p. 91-93°/27 mm; n_D^{25} 1.4690; $[\alpha]_D^{34}$ + 53.8).

5.2.3.2 (+)-3α,4α-Epoxycarane (I): The above epoxide (I) b.p. 80-81°/10 mm; n_D^{25} 1.4632; $[\alpha]_D$ + 7.2 (neat) was prepared in 80% yield from (+)-Δ^3-carene ($[\alpha]_D$ + 7.1 (neat), by the above method (Lit.[1c] b.p. 102-103°/48 mm; n_D^{20} 1.4650; $[\alpha]_D^{30}$ + 12.5,neat).

5.3. Cation-exchange on zeolites

5.3.1. Decationised or proton form: Molecular sieve zeolite type 4A or 13X (30g, equilibrated with water vapour over saturated NH_4Cl aqueous solution at room temperature) was covered with aqueous solution of ammonia (5%, 75 ml for every 30g of zeolites). After this was kept at room temperature for 4 hr, the aqueous layer was decanted out and put fresh ammonia solution (5%, 75 ml), kept for 1 hr, the process was repeated (total 6 hr, and total volume of ammonia solution, 5%, 225 ml for 30g of zeolite) and finally washed with distilled water (30 ml x 10) till neutral (pH~7) and dried in air at 120^0-30^0 for 6 hr. Ammonia was knocked off from ammonia form of zeolite made as above by calcination at $350^0 \pm 10^0$ in an electrically heated furnace in a fixed-bed type reactor in presence of inert atmosphere (N_2-gas) and kept in a desiccator over P_2O_5 until use.

5.3.2. Cation-exchange with Sr^{+2} ion: Molar solution of strontium chloride ($SrCl_2 \cdot 6H_2O$) was used for preparing the cation-exchanged form. Zeolite (4A or 13X, 30g, saturated with NH_4Cl aqueous vapour at room temperature) was covered with aqueous strontium chloride solution (750 ml containing

200g of strontium chloride) for 6 hr at room temperature with intermitent shaking, the excess solution was decanted off, zeolite washed with water (30 ml x 10) until free of chloride ($AgNO_3$-test) and dried in air at 120°-30° for 6 hr and cooled over P_2O_5 in a desiccator until use.

The degree of cation-exchange was determined by direct analysis of the aqueous portion by flame photometer.

5.4. Standard procedure for reaction with aluminosilicates

The epoxide was added to the zeolite (25 times of the weight of epoxide) suspended in hexane (30 ml for every 25g pf zeolite) in a suitable stoppered flask, flushed with N_2, and kept aside for 6 hr at room temp. Hexane was filtered and zeolite washed with hexane (25 ml x 3 for 25 g of zeolite) and finally soxhleted with 10% acetone in hexane (80 ml for 25g of zeolite) for 4-6 hr. The combined solvent (filtrate and extract) was carefully fractionated and the residue distilled in vacuo.

5.5. Action of zeolite on (+)-3α,4α-epoxycarane (I).

Epoxide (2.0g) on treatment with zeolite-type 4A (50g; hexane 60 ml) according to the standard procedure furnished a neutral product (1.56g, 78%), b.p. 80-130°/(bath)/30-5 mm showing eight components on GLC (Fig. 2) and preparative GLC afforded these components.

5.5.1. 3,7,7-Trimethyltropilidene (II): G.L.C. component 1 (RRT=1, Table 7) was distilled to give 3,7,7-trimethyltropilidene, b.p. 100°(bath)/80 mm; (Lit.[21] b.p. 65°/70 mm); n_D^{25} 1.5023 (Lit.[21] n_D^{20} 1.4960).

UV: λ_{max} 268 m , ε=3722

IR: no OH or C=O; conj. C=C 1630, 1615, 1575 cm^{-1}; gemdimethyl 1360 and 1380 cm^{-1}.

PMR: two quaternary methyls (6H, s, 0.97 ppm), one vinylic methyl (3H, somewhat broad singlet at 2.03 ppm), vinylic protons (2H, m, located between 4.92-5.15 ppm; 2H, m, located between 5.75-6.05 ppm and 1H, located between 6.1-6.3 ppm.

Mass: M^+, m/e = 134; $M-15^+$, m/e = 119 (base peak)[22,35].

5.5.2. α,p-Dimethyl styrene (III) and 1,5,8(9)-p-Menthatriene (IV): GLC component 2 (RRT=1.13) had b.p. 110°(bath)/80 mm was revealed from its PMR spectrum to be a mixture, but the mixture could be readily analysed by close scrutiny of its PMR. The minor component (~20%) of the mixture was identified as α,p-dimethyl styrene (III).

PMR: Vinylic methyl (3H, d, centered at 2.11 ppm, J=1Hz); methyl on aromatic ring (3H,s,2.33 ppm); $-\overset{|}{C}=CH_2$ (2H, singlets at 4.96 ppm and 5.25 ppm);

aromatic protons (4H, q, AB type, p-substituted benzene at 7.17 ppm) are fully consistent with the PMR spectrum of III described in literature.[36] The major component,

PMR: two vinylic methyls (6H, bs at 1.72 ppm), $-\underset{|}{C}=C\underline{H}_2$ (2H, bs at 4.75 ppm), three more vinylic protons (3H, m, located between 4.35-5.95 ppm) is considered to be IV, in view of mechanistic considerations and a comparison of the PMR data with that reported in the literature.[36]

5.5.3. <u>p-Cymene (V)</u>: GLC component 3 (RRT=1.39) distilled at 110°(bath)/80 mm was easily recognised as p-cymene; n_D^{25} 1.4910.

IR: 1375, 1355, 1100, 1050, 1015 and 810 cm^{-1}.

PMR: gem-dimethyl (3H, s, 1.17 and 1.25 ppm); methyl on aromatic ring (3H, s, 2.28 ppm); vicinal gem-dimethyl proton (1H, m, centered at 2.83 ppm) and aromatic protons (4H,s, 7.0 ppm).

5.5.4. <u>3,6,6-Trimethyl-3-formyl-bicyclo[3.1.0] hexane(VI)</u>: The major product (GLC component 4, RRT=2.34) was distilled to give bicyclic aldehyde (VI), b.p. 110°(bath)/40 mm, n_D^{25} 1.4651 (Lit.[23] b.p. 70-72°/9 mm, n_D^{20} 1.4644); semicarbazone, m.p. 187-188° (Lit.[23] 189-190°).

IR: HC=O 2700, 1720 cm^{-1}.

PMR: three quaternary methyls (3H, s at 0.97 and 6H, s at 1.00 ppm); $\underline{H}C=O$ (1H, s, 9.36 ppm).

5.5.5. Isocaranone (VII): GLC component 5 (RRT= 4.34) had b.p. 120°(bath)/ 30mm; n_D^{25} 1.4686 (Lit.[24] b.p. 80-81°/5.3 mm; n_D^{20} 1.4703).

IR: C=O 1720 cm^{-1}

PMR: two quaternary methyls (3H, singlets at 0.85 and 1.04 ppm); $C\underline{H}_3$-CH (3H, d, centered at 0.90 ppm, J= 7 Hz).

5.5.6. Caranone (VIII): GLC component 6 (RRT = 4.78), b.p. 120°(bath)/30 mm; n_D^{25} 1.4691 (Lit.[24] n_D^{20} 1.4706).

IR: C=O 1715 cm^{-1}

PMR: two quaternary methyls (3H, singlets at 0.94 and 1.07 ppm); $C\underline{H}_3$-CH (3H,d, centered at 1.20 ppm, J = 7Hz).

5.5.7. Δ^{4}-Carene-3α-ol (IX): GLC component 7 (RRT = 6.60), b.p. 130°(bath)/10mm.

IR: OH 3360, 1065, 1035 cm^{-1}

PMR: two quaternary methyls (3H, singlets at 0.81 and 1.08 ppm); $C\underline{H}_3\overset{|}{C}$=(3H, s, partly split, 1.76 ppm); $C\underline{H}$-OH (1H, t, 3.62 ppm; J = 5Hz); -C=$C\underline{H}$ (1H,b, 5.51 ppm) (Lit.[1c] PMR)

5.5.8. $\Delta^{4(10)}$-Carene-3α-ol (X): GLC component 8 (RRT = 7.73) distilled at 130°(bath)/10 mm to give pure (X).

IR: OH 3360, 1065, 1040 cm^{-1}; $-\overset{|}{C}=CH_2$ 1640 cm^{-1}

PMR: quaternary methyls (3H, singlets at 0.87 and 1.01 ppm); $C\underline{H}OH$ (1H, t, 4.0 ppm, J = 4Hz); $CH=C\underline{H}_2$ (2H, b, 4.73 ppm).

5.6. Action of zeolite on (+)-2α,3α-epoxypinane[1e] (XIV)

(+)-2α,3α-Epoxypinane (2.0 g) on exposure to zeolite 4A (50g, in hexane, 60 ml, 6 hr), furnished a product (1.4821g, 74%), b.p. 65-80°/20-5 mm, consisting essentially of five major components (GLC: Fig.19)with RRT 1.0, 1.25, 2.00, 2.62 and 8.25. These components were separated by preparative glc and identified as follows:

5.6.1. p-Cymene (V): GLC component 1 (RRT=1.00) was easily distinguishable as p-cymene from its physical and spectral data.

5.6.2. 2,6,6-Trimethyl-7-oxabicyclo[3.2.1]oct-2-ene (XV): GLC component 2 (RRT = 1.25) was distilled to give compound XV b.p. 90°(bath)/30 mm, n_D^{25} 1.4699 (Lit.[26] b.p. 61-65°/2 mm, n_D^{20} 1.4716).

IR: CH-O- 1120 cm^{-1}

PMR: quaternary Me's (3H, singlets, 1.12 and 1.23 ppm); $C\underline{H}_3\overset{|}{C}{=}CH-$ (3H, t, 1.70 ppm, J = 2Hz); $C\underline{H}-O-$(1H, broad doublet, 3.86 ppm) and $-C\underline{H}{=}\overset{|}{C}-$ (1H, b, 5.13 ppm).

5.6.3. 2,2,4-Trimethylcyclopent-3-enylacetaldehyde (XVI): GLC component 3 (RRT=2.00) had b.p. 90°(bath)/20 mm, n_D^{25} 1.4558 (Lit.[37], b.p. 35-36° at 0.5 mm, n_D^{19} 1.4592).

IR: HC=O 2720 and 1725 cm^{-1}

PMR: quaternary Me's (3H, singlets, 0.83 and 1.05 ppm); one vinylic Me (3H, bs, 1.68 ppm); $-C\underline{H}_2-\overset{|}{C}{=}$ (2H, m, 2.38 ppm); one olefinic proton (1H, bs, 5.14 ppm); $\underline{H}C{=}O$ (1H, broad signal at 9.75 ppm) (Lit.[37]: PMR).

5.6.4. 2,2,3-Trimethylcyclopent-3-enylacetaldehyde (XVII): GLC component 4 (RRT = 2.62.), b.p. 90° (bath)/20 mm, n_D^{25} 1.4632 (Lit.[37] b.p. 32-33°/0.15 mm, n_D^{19} 1.4702).

IR: HC=O 2720 and 1725 cm^{-1} (Lit.[37]: IR).

PMR: quaternary methyls (3H, singlets at 0.78 and 1.0 ppm); one vinylic methyl (3H, b, 1.62 ppm); one olefenic proton (1H, b, 5.22 ppm) and $\underline{H}C=O$ (1H, b, 9.75 ppm) (Lit.[37,1e]: PMR).

5.6.5. (+)-trans-Sobrerol (XVIII): GLC component 6 (RRT= 8.25) was recrystallised from acetone to give white plates of (+)-*trans*-sobrerol (XVIII), m.p. 142-144°, $[\alpha]_D$+ 86.3 (EtOH, *c*, 2.3%)(Lit.[1e]: m.p. 150°, $[\alpha]_D$ + 147.1°).

IR: 3300, 925 cm^{-1}, (Lit.[1e]: IR).

PMR: $(C\underline{H}_3)_2\text{-}\overset{|}{C}\text{-}OH$ (3H, s, 1.21 and 1.24 ppm); vinylic methyl (3H, bs, 1.83 ppm); $C\underline{H}OH$ (1H, ill-resolved triplet at 4.1 ppm) and $-\underset{|}{C}=C\underline{H}$ (1H, ill-resolved triplet at 5.64 ppm) (Lit.[1e]: PMR).

2,2,3-Trimethyl-3-cyclopentene-1-ethanol (XIX)

α-Campholene aldehyde (XVII, 76 mg, 0.5 mmole) in dry ether (5 ml) was stirred with a slurry of LAH (40 mg, 1 mmole) in dry ether (5 ml) at 0^{0} for 1 hr and then at 20^{0} for 5 hr. The usual work up gave pure XIX (69 mg; b.p. 125^{0}(bath)/20 mm; n_D^{25} 1.4686) (Lit.[28b]: b.p. 105^{0}/8 mm, n_D^{20} 1.4710).

IR: OH 3620, 3360, 1050, 1035 cm^{-1}

PMR: quaternary methyls (3H, singlets at 0.79 and 1.0 ppm); vinylic methyl (3H, bs, 1.63 ppm); $-\underset{|}{C}{=}C\underline{H}$ (1H, b, 5.23 ppm); $C\underline{H}_2OH$ (2H, overlaping triplets centered at 3.63 ppm, J = 6Hz),(Lit.[1c]: PMR).

3,6,6-Trimethyl-3-carbomethoxy-bicyclo 3.1.0 hexane (XI)

The aldehyde VI (228 mg, 1.5 mmole in 3 ml ethanol) was oxidised with Ag_2O slurry, obtained by mixing 0.2g $AgNO_3$ (in 1 ml water) with aqueous NaOH (100 mg in 1 ml water), then worked up in the usual manner to furnish an acid (226 mg, 90%) which was esterified (CH_2N_2) to give methyl ester XI (207 mg, 84.5% overall yield), b.p. 120^{0}

(bath)/20 mm, n_D^{25} 1.4508 (Lit.[1e] b.p. 165°(bath)/25 mm, n_D^{20} 1.4549).

IR: COOMe 1730 cm^{-1}

PMR: quaternary methyls (0.97, 0.97 and 1.15 ppm); O$\underline{Me}$ (3H, s, 3.68 ppm) (Lit.[1e]: PMR).

3,6,6-Trimethyl-3-carbinol-bicyclo[3.1.0]hexane (XII)

A solution of aldehyde VI (152 mg, 1 mmole in 2 ml ether) was reduced with LAH (40 mg, 1 mmole in 5 ml ether) by stirring at 0°/1 hr and 4 hr at room temperature. The usual work up (saturated Rochelle salt solution, 5 ml, for decomposing the Al-complex) furnished a crude (XII) which was distilled to give colourless liquid (131 mg), b.p. 95°(bath)/5 mm, n_D^{25} 1.4706 (Lit.[23]: b.p. 65-66°/0.3 mm, n_D^{20} 1.4740).

IR: 3640, 1035 cm^{-1} (Lit.[1c]: IR)

PMR: quaternary methyls (0.91, 0.96 and 0.96 ppm); C$\underline{H}_2$OH (2H, s, 3.29 ppm) (Lit.[1c]: PMR).

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