CHAPTER-VI

TOWARDS LANCEOL SYNTHESIS

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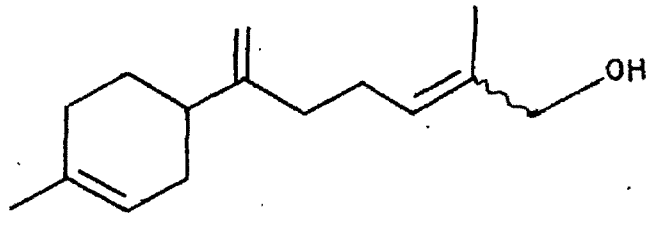
ABSTRACT

In this Chapter is described an attempt directed towards the synthesis of lanceol by oxirane-allylic alcohol rarrangement of the C_{15}-oxide (36). As the targetted compound could not be obtained, the effect of a number of reagents on easily available and closely similar oxide (39) was investigated. The various compounds obtained during this study have been fully characterised.

TOWARDS LANCEOL SYNTHESIS

INTRODUCTION

Lanceol (1) is a sesquiterpenic allylic alcohol occurring in the essential oil of Santalum lanceolatum[1] and Osyris teunofolia[2]. Although, it was isolated as early as 1928,[1] its presently accepted structural formula was determined only in 1951.[3,4] Since then several syntheses of lanceol have been reported.[5-10]



(1)

PREVIOUS SYNTHESES

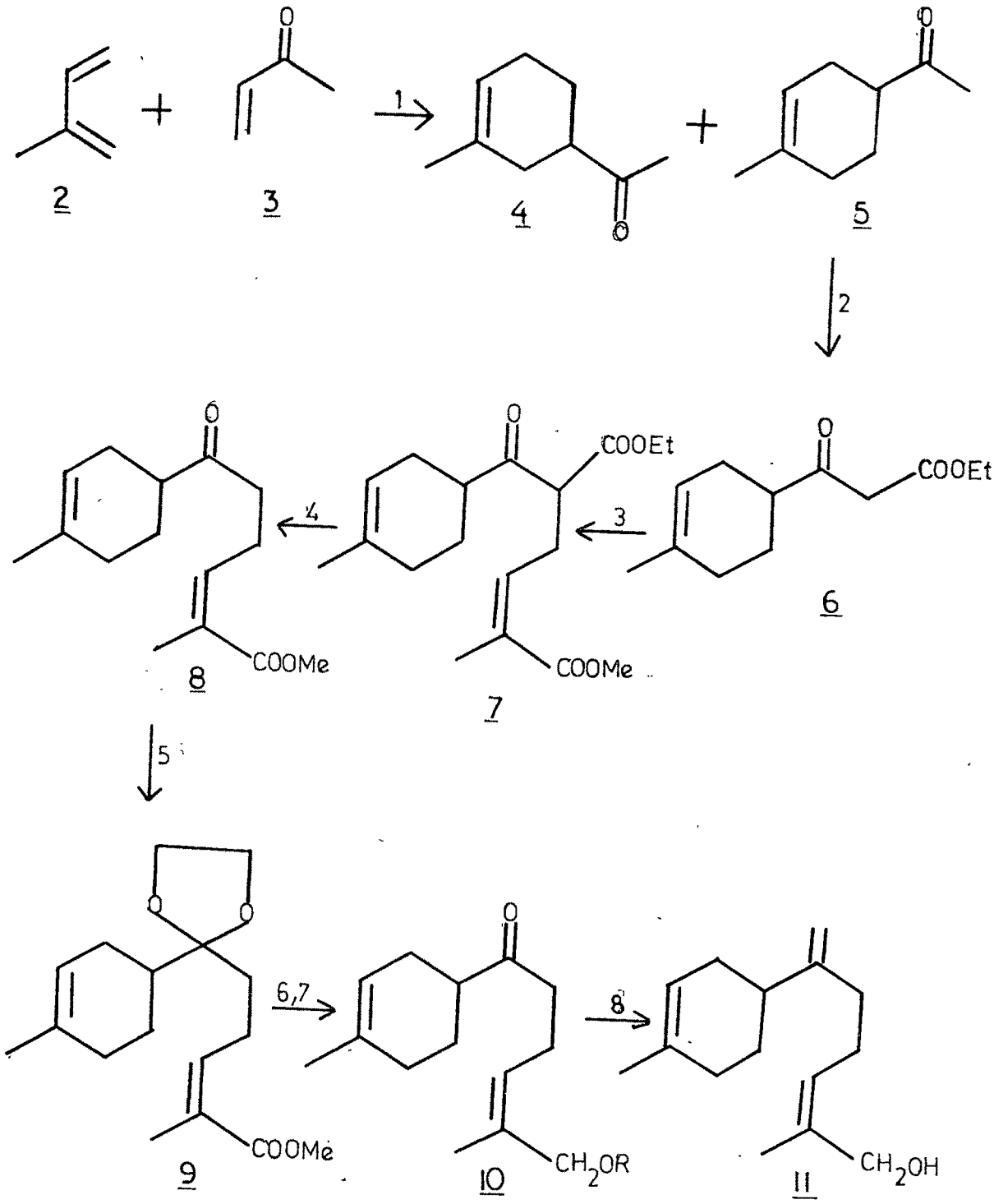
Manjarrez and his co-workers[5] were first to report a successful synthesis of Z-lanceol (11). The synthesis is based on the Diels-Alder addition reaction between isoprene (2) and methyl vinyl ketone (3) to give the

ketonic precusor (5) which was further converted to racemic Z-lanceol (11) by a series of conventional reactions (Fig. 1).

The route developed by Vig's group[7] involves Wittig reaction of ethyl-α-diethylphosphonopropionate (22) on γ-methylene-γ-(4-methyl-Δ^3-cyclohexyl)-butanal (19) as a key step for the synthesis (Fig. 2).

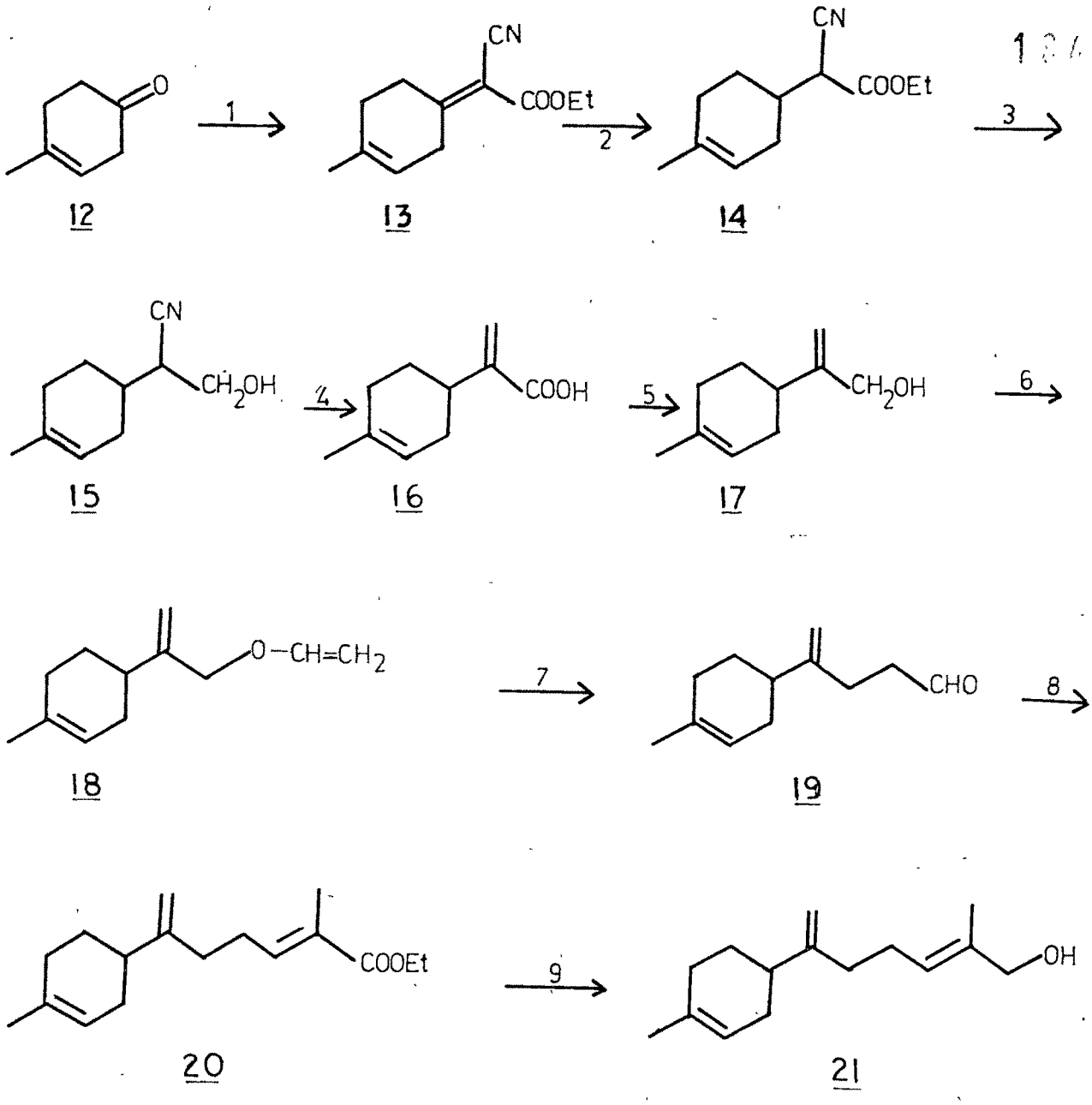
The route conceived by Akutagawa and Otsuka[8] embodies elegant regioselective isoprene insertion into an allyl-magnesium bond. Thus, a THF solution of 2-(4'-methyl-3'-cyclohexyl)-allyl magnesium chloride (23) prepared from 10-chloro-1,8-p-menthadiene when treated with isoprene (2) in the presence of Cp_2TiCl_2 (Fig. 3) followed by oxidation gave the mixture of Z and E-lanceols (11:21) in the ratio of 1:4.

The synthesis by Katzenellenbogen and Crumrine[9] is based on the selective γ-alkylations of the dienolate anions derived from α,β-unsaturated acids. Thus, γ-alkylation of tiglic acid copper dienolate (28) provides a convenient synthesis of dl-E-lanceol (21) (Fig. 4).



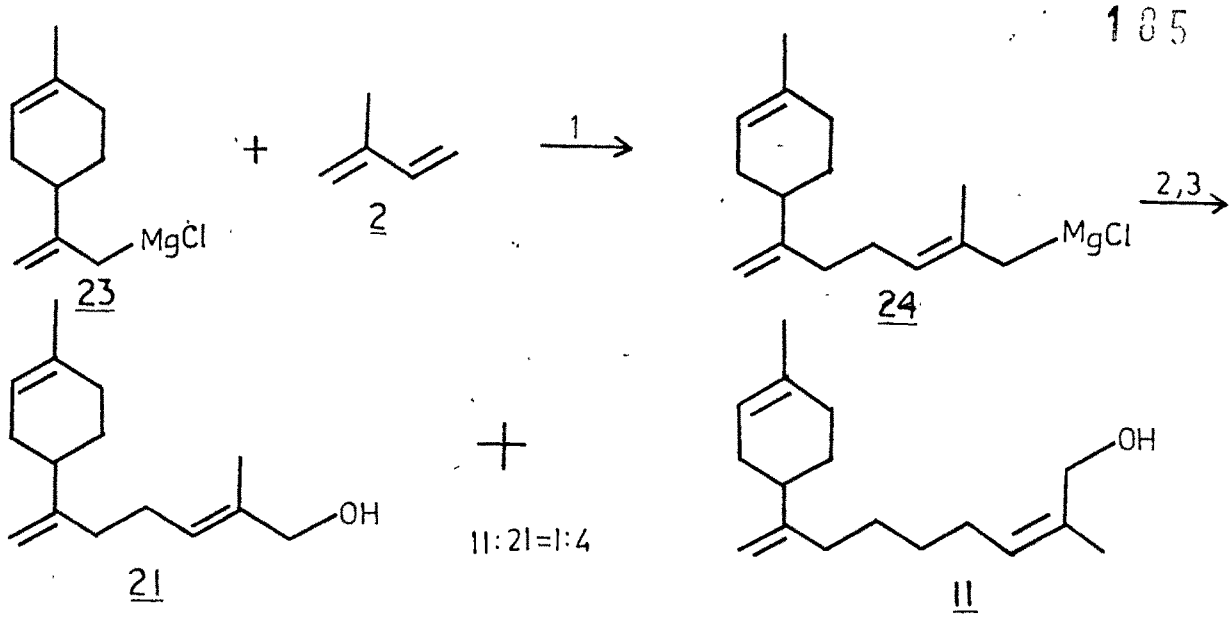
REAGENTS · 1. DIELS-ALDER REACTION, 150°; 2. $NaH/(EtO)_2CO$;
3. $MeOOC(Me)C=C(H)CH_2Br$ NaH; 4. KOH, Δ;
5. $\left[\begin{matrix}OH\\OH\end{matrix}\right]$;
6. LAH; 7. CH_2OH-CH_2OAc; 8. $Ph_3=CH_2$

FIG: 1



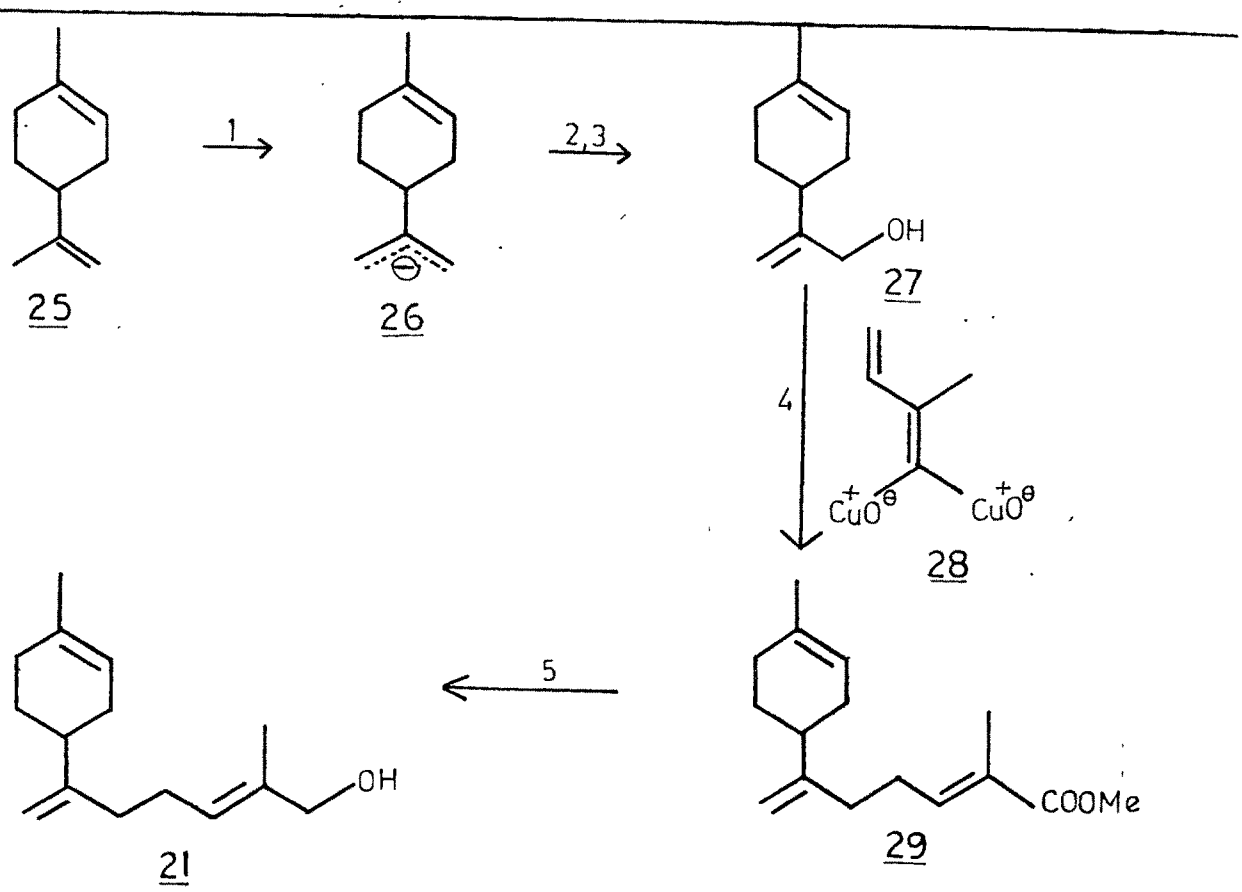
REAGENTS: 1. $EtOOC-CH_2CN/KF$; 2. H_2/Pd-c; 3. $NaBH_4$;
4: $NaOH/EtOH/\begin{bmatrix}OH\\OH\end{bmatrix}$; 5. $HOOC-COOEt$, LAH;
6. $EtOCH=CH_2/(MeCOO)Hg$; 7. Δ;
8. $NaH/(EtO)_2P(O)CH(Me)COOEt$ (22); 9. LAH.

FIG: 2



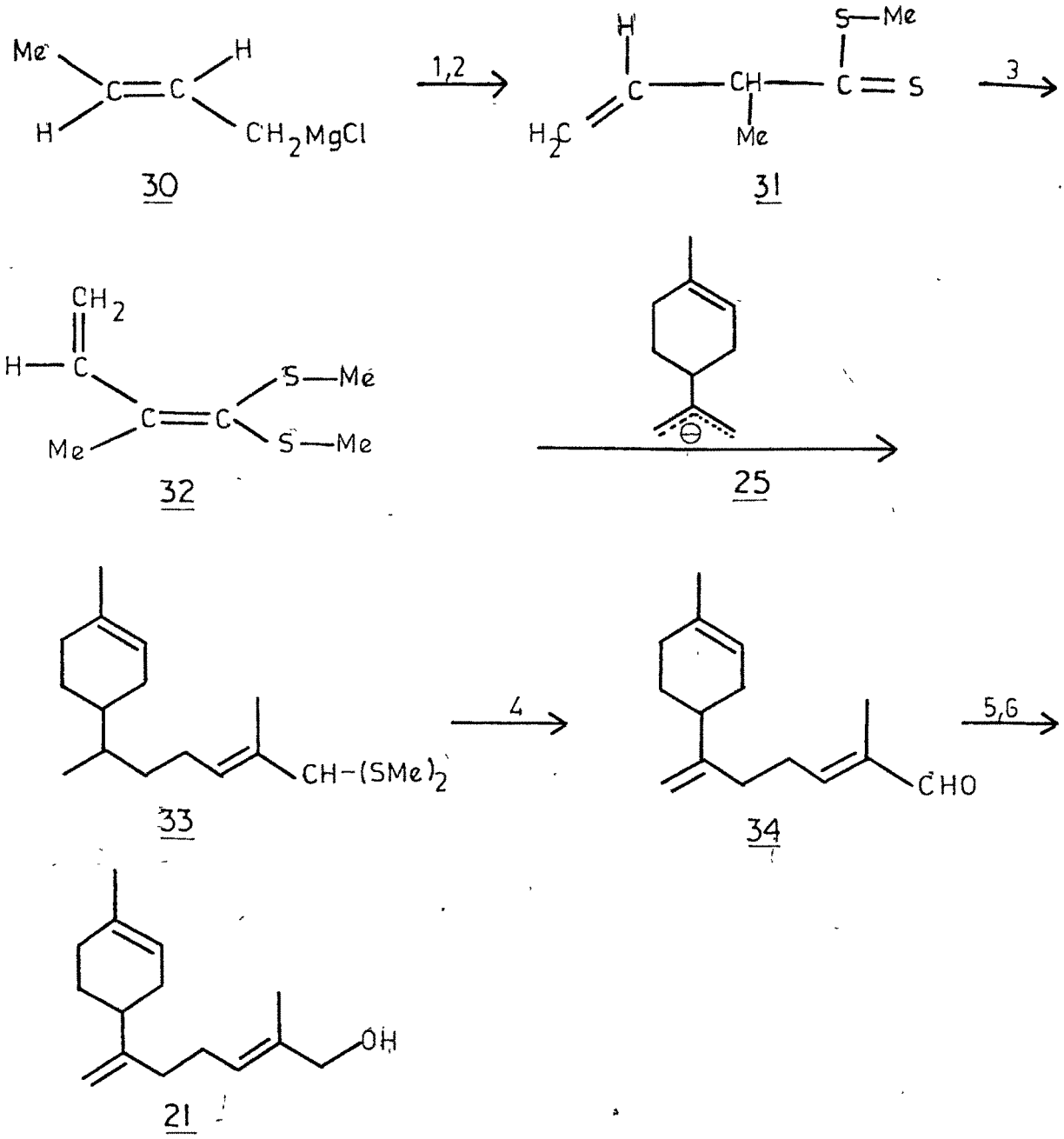
REAGENTS: 1. Cp_2TiCl_2/60 70°; 2. BF_3OEt_2; 3. H_2O_2 aq. KOH

FIG: 3



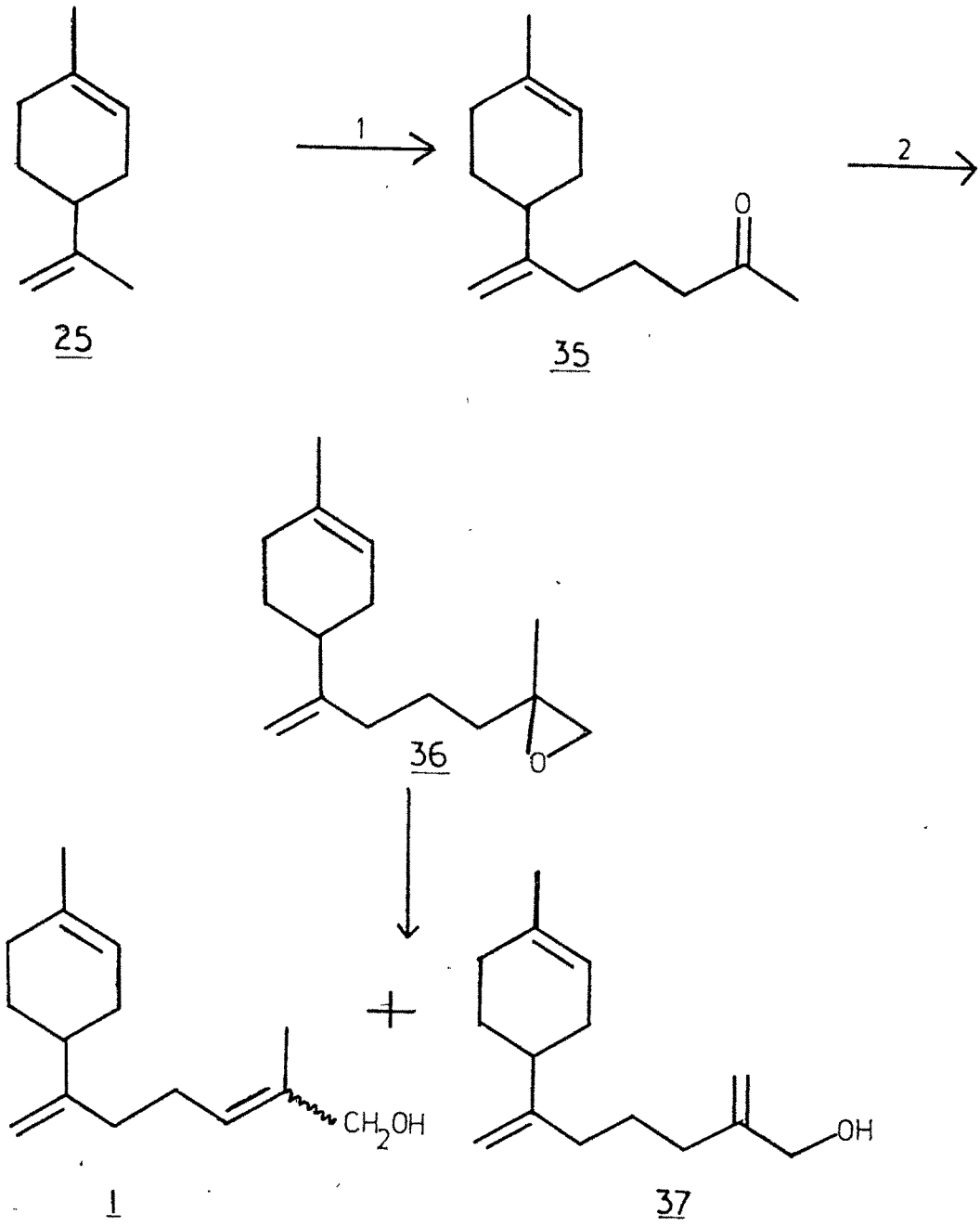
REAGENTS. 1. BuLi/TMEDA; 2. O_2 3. Na_2SO_3; 4. CH_2N_2; 5. LAH

FIG: 4



REAGENTS : 1 CS_2; 2. MeI; 3. LDA / MeI; 4. H^+; 5. $CuCl_2/CuO$; 6. LAH.

FIG : 5



REAGENTS : 1. $CH_2=CH-COMe, \Delta$; 2. $Me_2S(O)=CH_2$

FIG: 6 SCHEME FOR THE SYNTHESIS OF LANCEOL

Julia and Cazes[10] synthesised E-lanceol (21) by a novel conjugate addition of organo-lithium reagent to the isoprene dithioacetals (Fig. 5).

PRESENT WORK

As can be seen from above, the first two schemes involved total synthesis starting from simple molecules while the remaining cases involved addition of C_5 unit to limonene. Our approach is based on 10 + 4 + 1 sequence.

The synthesis of C_{14}-ketone (35) (described in Chapter IV) prompted us to use it as a key intermediate for the synthesis of lanceol.

The strategy adopted consists in converting this ketone (35) to the corresponding C_{15} oxirane (36) with the use of Corey's selective methylene transfer reagent[11] — dimethyloxosulfonium methylide as shown in Fig. 6. Cleavage of the C-O bond of the epoxide ring could be expected to occur under acid-catalysis at the most substituted carbon. β -Proton elimination then should lead hopefully to thermodynamically controlled mixture of E- and Z-lanceol.

The C_{14}-ketone (35) could be easily converted to the epoxy compound, i.e., 1,2-epoxy-6-(4'-methyl-cyclohex-3'-enyl)-2-methyl-hept-6-ene (36) in over 74% yield by Corey's procedure[11] using dimethyloxosulfonium methylide. The spectral data of this compound was in conformity with structural requirements of (36).

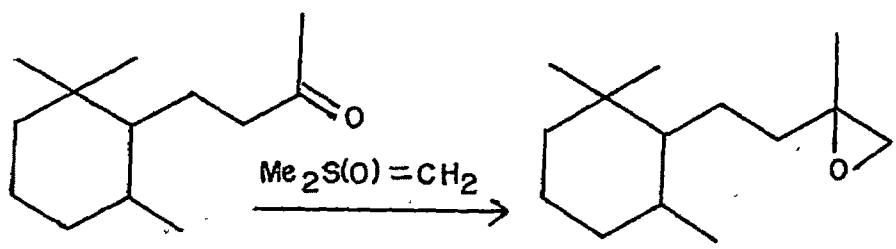
This compound $C_{15}H_{24}O$ (M^+, m/e 220) shows in its IR spectrum (Fig:VI-1) absorptions at 1260, 1110 cm^{-1} (C—C—O); 895 cm^{-1} ($=CH_2$). Its PMR spectrum (Fig: IV-2) shows signals at 2.42 ppm (2H, s, $\underline{CH_2}$-O); 1.25 ppm (3H, s, $\underline{CH_3}$-C-O). 4.72 ppm (2H, bs, $\underline{CH_2}$=C-); 5.34 ppm (1H, bs, CH_3-C=C$\underline{H}$); 1.64 ppm (3H, s, $\underline{CH_3}$-C=C).

This epoxide (36) on shaking with a slurry of silica-gel (grade IIa) in hexane for 6 hrs. under N_2 gave a complex mixture of products. The PMR spectrum of the product, however, did not contain any detectable signals attributable to protons on lanceol molecule.

At this time it was felt advantageous to carry out the epoxide cleavage reactions on an easily available and closely similar model system to arrive at a suitable reagent and reaction conditions which may lead to the

desired allylic alcohol. These conditions then can be duplicated to effect the cleavage of the epoxide ring in (36) to give lanceols.

1,2-Epoxy-4-(2′,2′,6′-trimethyl-cyclohexyl)-2-methyl-butane (39) derived from tetrahydroionone (38) appeared as an ideal model system for such studies. β-Ionone on hydrogenation gave tetrahydroionol which on chromic acid oxidation gave tetrahydroionone (38), latter gave (39) in 75% yield by Corey's procedure.[11]

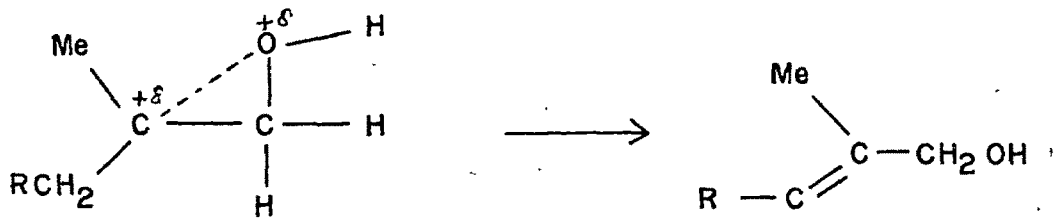


(38) (39)

The IR spectrum (Fig. IV-3) of (39) shows absorptions at 2920, 1270, 1220, 1110, 1070 and 905 cm^{-1}. Its PMR spectrum (Fig. VI-4) shows signals at 2.40 ppm (2H, d, J = 2 Hz, $-\overset{O}{\overset{/\backslash}{C}}-CH_2$); 1.25 ppm (3H, s, CH_3-C-O); 0.94 ppm, 0.87 ppm (6H, s, methyls).

It is established that base-catalised rearrangement of epoxides to allylic alcohols is highly regioselective, involving proton abstraction by the base from the least substituted carbon atom[12] to give in general, kinetically controlled allylic alcohols.

From the studies on acid-catalised cleavages[13] it is known that bond breaking is far advanced in the transition state and thus, the stability of the intermediate carbonium ion becomes an important factor. This would therefore lead to a transition state of the type (A) where the developing carbonium ion is stabilized by the



(A) (B)

methyl group. Subsequent elimination should then give the thermodynamically controlled allylic alcohol (B).

Keeping this in view, following reagents were selected for cleavage studies:

Table 1 : Effect of various reagents on 1,2-epoxy-4-(2,2,6-trimethyl-cyclohexyl)-2-methyl-butane (37)

No.	Reagent	Product distribution %*						
		Hydro-carbons	Alde-hyde (40)	Keto-ne (38)	Allylic alcohol (41)	Ally-lic alco-hol (42)	Gly-col (43)	Dimer
1.	$NaOH-Al_2O_3$	-	-	11.5	18.2	-	27.3	24.2
2.	$ZnO-Al_2O_3$	-	-	-	59.1	-	5.4	11.0
3.	1% Aq. methane sulfonic acid	-	-	-	-	5.7	38.3	29.2
4.	Nafion	-	17.6	7.5	-	-	32.8	32.7
5.	1% Aq. perchloric acid	3.7	10.6	11.9	-	-	-	60.9
6.	Boron phosphate	17.7	27.8	5.3	-	-	-	39.8
7.	Titanic acid	15.5	17.8	3.5	-	-	-	
8.	Picric acid	a complex mixture						
9.	MgO-catalyst	No reaction.						

*Entry 1-4: Product distribution represents percentage of chromatographically isolated products.
Entry 5-7: Product analysis is that of distillate by GLC (10% carbowax, 200°C). The distillate contains glycol 43 (only traces, PMR) which does not show up in GLC and hence is not considered.
Entry 5-6: The whole residue left after distillation is taken as dimer (on the basis of PMR spectra)
Entry 7: Residue constituted 41.3% which appeared as polymeric material.

1) $NaOH-Al_2O_3$[14]

2) Nafion[15]

3) Methanesulfonic acid

4) $Zno-Al_2O_3$[16]

5) Perchloric acid

6) Titanic acid

7) Boron phosphate[17]

8) Picric acid

9) Mgo-catalyst[18]

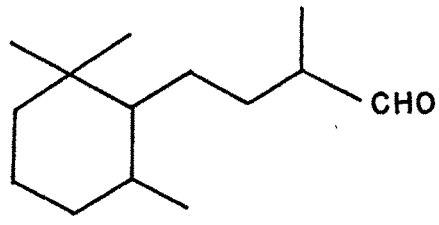
Behaviour of these reagents on the model epoxide viz., 1,2-epoxy-4(2´,2´,6´-trimethyl-cyclohexyl)-2-methyl-butane(39) was investigated and the products obtained are summarised in Table 1.

The structure of the isolated compounds is firmly based on the spectroscopic evidence as given below:

4-(2´,2´,6´-Trimethyl-cyclohexyl)-2-methyl-butraldehyde (40)

RRT 1.0; R_f 0.45

This aldehyde ($C_{14}H_{26}O$, M^+, m/e 210) displays in its IR spectrum (Fig: VI-5) absorptions at 2700, 1730 cm^{-1} (-CHO). Its PMR spectrum (Fig: VI-6) shows signals at



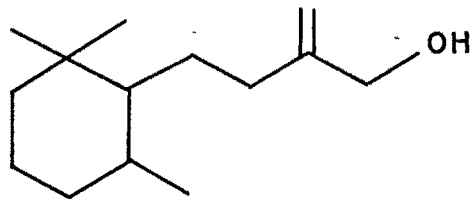
(40)

0.82 ppm, 0.87 ppm and 0.94 ppm (9H, methyls); 9.95 ppm (1H, d, J = 2Hz, -CHO); 1.07 ppm (3H, d, J = 7 Hz, $\underline{CH_3}$-C-CHO).

4-(2́,2́,6́-Trimethyl-cyclohexyl)-2-methylene-butane-1-ol(41)

RRT 1.77; R_f 0.35

This alcohol ($C_{14}H_{26}O$; M^+, m/e 210) displays in its IR spectrum (Fig: VI-7) absorptions at 3325, 1030 cm^{-1} (-OH) and 900 cm^{-1} ($=CH_2$). Its PMR spectrum (Fig: VI-8)

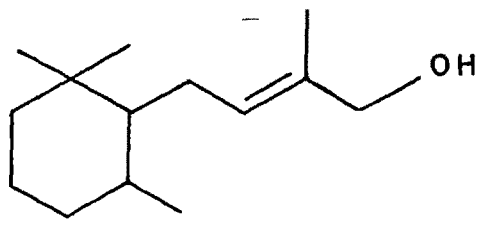


(41)

shows signals at 0.83 ppm, 0.9 ppm and 0.95 ppm (9H, methyls); 3.96 (2H, s, C-$\underline{CH_2}$OH); 4.78 ppm and 4.95 ppm (2H, two singlets, $\underline{CH_2}$=C-CH_2OH).

4-(2́,2́,6́-Trimethyl-cyclohexyl)-2-methyl-but-2-ene-1-ol (42) RRT 1.25 R_f 0.3.

This alcohol ($C_{14}H_{26}O$, M^+, m/e 210) displays in its IR spectrum (Fig: IV-9) absorptions at 3325, 1010 cm^{-1} (-OH).



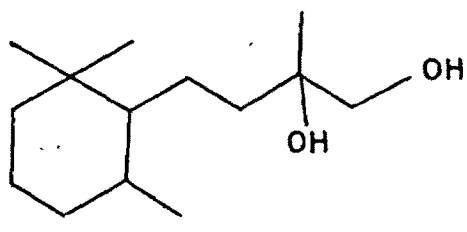
(42)

Its PMR spectrum (Fig: VI-10) reveals signals at 0.84 ppm, 0.90 p and 0.97 ppm (9H, methyls); 1.65 ppm (3H, s, $C\underline{H}_3$-C=C); 5.32 ppm (1H, bm, -C<u>H</u>=C-CH_3); 3.86 ppm (2H, s, C-$C\underline{H}_2$OH).

4-(2́,2́,6́-Trimethyl-cyclohexyl)-2-methyl-butane-1,2-diol(43)

R_f 0.06

This glycol ($C_{14}H_{28}O_2$, M^+, m/e 228) shows IR absorptions (Fig: VI-11) at 3380, 1060 cm^{-1} (-OH). Its PMR spectrum



(43)

(Fig: VI-12) shows following structural features: 0.90 ppm, 0.95 ppm and 0.83 ppm (9H, methyls); 1.12 ppm (3H, s, $C\underline{H}_3$-C-OH); 3.34 ppm (2H, s, C-$C\underline{H}_2$OH).

In practically all cases chromatography or distillation yielded a non-distillable material which could be purified by rechromatography into a single spot material. This apparently is a dimeric compound.

This dimer R_f 0.50 shows in its IR spectrum (Fig: VI-13) absence of hydroxyl, ketonic or olefinic absorptions. Absorptions are shown at 2930, 2870, 1100, 970 cm^{-1}.

Its PMR spectrum (Fig: VI-14) shows methyl signals at 0.82 ppm, 0.89 ppm and 0.93 ppm along with signals at 4.67 ppm and 3.51 ppm.

Although, the products obtained from the above series of reactions can be rationalised on the basis of known oxirane cleavage mechanisms, our approach towards the synthesis of lanceol was rendered unsuccessful due to failure of the 1,1-disubstituted epoxide to transform into the thermodynamically stable allylic alcohol. Only with one reagent viz. methanesulfonic acid, was the required

transformation achieved. However, the rather low yields (5.7%) forced us to abandon this approach for the synthesis of lanceol.

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

For general remarks see Chapter II. GLC analysis were carried out on 10% carbowax column at 200°C. R_f values are given for 20% diethyl ether/petroleum ether solvent system.

1,2-Epoxy-6-(4'-methyl-cyclohex-3'-enyl)-2-methyl-hept-6-ene (36)

A mixture of sodium hydride (0.036g, 50% dispersion in oil, oil freed by repeatedly washing with dry hexane; NaH, 0.0015 mole); trimethyloxosulfonium iodide (0.33g; 0.0015 mole) and dry DMSO (1.0 ml) was stirred under N_2 blanket at room temperature for 20 mins. To this was injected C_{14} ketone (35) (0.206g, 0.001 mole) in dry DMSO (1 ml) and the mixture stirred at 25° for 18 hrs. and at 50°C for one hour. After cooling, water (15 ml) was added and the mixture extracted with ethyl acetate (5 x 15 ml). The organics were washed with water (4 x 25 ml), brine (1 x 25 ml) and dried. Stripping of solvent gave a product (0.2044 gms) which was distilled at 140-145°(bath)/ 3 mm to give the pure epoxide (0.1634 gms, 74.2% yield) n_D^{28}: 1.4862. Mass: m/e 220 (4%); 93(100%); 121(90%); 79(83%); 91(70%); 105(60%); 55(47%); 119(43%); 77(42%); 67(34%); 68(30%). (Found C, 81.30; H, 11.24. $C_{15}H_{24}O$; requires C, 81.81; H, 10.90).

Treatment of (36) with silica gel[19]

Epoxide (36) (0.200 g) was added to a slurry of silica gel (grade IIA) in dry hexane (6 ml) under nitrogen atmosphere, the contents shaken for 6 hrs at 25°C and then allowed to stand further for 18 hrs. at same temperature. Filtration and washing the residue with 5% MeOH-ether (160 ml) gave after careful solvent removal the product (0.1739 g), revealed to be a complex mixture (PMR).

Tetrahydroionone (38)

Freshly distilled β-ionone (38.4g, 0.2 mole) in absolute alcohol (100 ml) was hydrogenated at 160° at 1500 psi pressure for 6 hrs. using Raney nickel (6 g) as catalyst in a rocking type autoclave till three equivalents of hydrogen were consumed. Filtration and solvent removal gave tetrahydroionol (39.94 gms) IR: 3380,1120 cm^{-1} (-OH); PMR: 3.69 ppm (1H, m, J = 6 Hz) C<u>H</u>OH) .

Oxidation of this alcohol (39.9g) using Brown's reagent[20] followed by usual work up and distillation at 108-110°C/4 mm gave tetrahydroionone (38) (35.2 gms, 89.9% overall yield). PMR: 2.02 ppm (3H, s, $C\underline{H}_3$-CO); IR: 1720 cm^{-1} (C=O) RRT 1.18.

Table 2. Cleavage of 1,2-epoxy-4-(2',2',6-trimethyl-cyclohexyl)-2-methyl-butane (39) with various reagents.

No.	Epoxide (39) (g)	Reagent Name	Reagent Wt./ (gm)	Solvent Name	Solvent Vol. (ml)	Reaction condition	Crude product	Chromatographic separation Dimer (g)	Allylic alc. (41) (g)	Allylic alc. (42) (g)	Aldehyde (46) (g)	Ketone (38) (g)	Glycol (43) (g)
1.	2.0	NaOH-Al_2O_3	100	Hexane	120	shake: 6 hrs stand: 6 hrs	1.68	0.4065	0.3063	-	-	0.1926	0.4588
2.	1.3	Zno-Al_2O_3	32	Hexane	40	Shake: 6 hrs Stand: 18 hrs	0.9926	0.1097	0.5872	-	-	-	0.0536
3.	3.5	1% Aq. methane sulfonic acid	25 ml	CH_3NO_2	50	Stir at -8° 2.5 hrs	3.4	0.9247	-	0.1937	-	-	1.3013
4.	1.2	Nafion	0.36	-	-	1% suspension/wt. 24 hrs:-5°	No reaction						
						10% "	"						
						30% "	0.7650 (distilled	0.3892 (residue)	-	-	0.2102	0.0891	0.3912
	0.2	Picric acid	0.02	C_6H_6	10	Stand: 48 hrs Reflux: 3 hrs	A bad mixture						
	0.3	MgO Catalyst	7.5	Toluene	15	Reflux: 24 hrs	No reaction.						

Table 3. Cleavage of 1,2-epoxy-4-(2',2',6-trimethyl-cyclohexyl)-2-methyl-butane (39) with various reagents

No.	Epoxide (39) (g)	Reagent Name	Reagent Wt/ (g)	Solvent Name	Solvent vol. (ml)	Reaction condition	Crude product (g)	Distilled at 140-200°(bath)/ 4mm Residue*	Distilled at 140-200°(bath)/ 4mm Distillate	Distillate composition** Hydrocarbons	Ketone (38)	Aldehyde (40)	Allylic alc. (41)
1.	0.64	1% perchloric acid	10 ml	THF	20	Stir at -10°: 2.5 hrs,	0.5827	0.3550	0.1550	14	45	40	-
2.	0.30	Titanic acid	0.300	Hexane	10	Shake: 6 hrs stand: 12 hrs	0.2086	0.0863 (polymer)	0.1015	31.9	73	36.6	24.4
3.	0.30	Boron phosphate	0.300	Hexane	5	Stand-5°; 12 hrs.	0.2348	0.0935	0.1194	34.9	10.4	54.7	-

* Residue was essentially the dimer

** Analysis of GLC: Column 10% carbowax, 200°C

1,2-Epoxy-4-(2́,2́,6́-trimethyl-cyclohexyl)-2-methyl-butane (39)

This was prepared from tetrahydroionone (19.2g; 0.1 mole) by reacting with sodium hydride (3.6 g, 0.15 mole); trimethyloxosulfonium iodide (33g, 0.15 mole) and DMSO by procedure given earlier to give the pure epoxide (16.2 gms, 79% yield) b.p. 105-108°/ 5 mm, n_D^{25} 1.4660.

Cleavage of the epoxide (39) with various reagents.

This has been summarised in Table 2, 3.

NaOH-doped Alumina

NaOH-Al_2O_3 was prepared by the method of Dev et al.[14]

Oxirane (39) (2 gms) was added to a slurry of NaOH-Al_2O_3 (100 gms) in dry hexane (120 ml). The vessel was flushed with nitrogen and shaken at room temperature (30°C) for 6 hrs and allowed to stand at 30° for additional 18 hrs. Filtration and washing the residue with 5% MeOH-ether (1750 ml) followed by careful solvent removal furnished a product (1.68 gms) shown to be a mixture (TLC). It was next chromatographed over silica gel.

Chromatogram - 1

Material charged: 1.68 gms; Silica gel (IVA): 90 gms
Column (28 x 3 cms).

Fr. No.	Eluent	Vol. of eluent/ml	Weight/gms.
1.	Pet. ether	100 x 5	0.0926
2.	2% ether/pet. ether	100 x 5	0.4065
3.	-do-	100 x 2	0.1926
4.	4% ether/pet. ether	100 x 4	0.3063
5.	5% ether/pet. ether	100 x 6	0.4588
6.	50% ether/pet. ether	100 x 5	0.1324
7.	Ether	100 x 2	
		Total	1.5902

Fraction 3 was identified as(38).

Fraction 2 was found as the dimer n_D^{25}: 1.4807.

Fr. 4 was found homogenous on TLC; R_f 0.35 (20% ether/pet. ether). It was distilled at 100° (bath)/0.3 mm to furnish the pure allylic alcohol (41) n_D^{25}; 1.4770.

Mass: m/e$^+$ 210(9.5%); 123(100%); 69(80.9%); 95, 138 (64.3%); 109(60-7%); 82(60%); 124(54.7%), 125(45.2%); 83(44%); 137 (40.4%); 81, 96(33.7%); 177(16.6%); 192(9.5%). (Found C, 79.62; H, 12.23. $C_{14}H_{16}O$; requires C, 80.8; H, 12.38).

Fraction 5 found homogenous on TLC (20% ether/ pet. ether) and distilled at 140°C(bath)/0.3 mm to furnish the glycol (43); n_D^{25}: 1.4833.

Mass: m/e^+ 226(2.6%), 197(100%); 179(50.8%); 123(47.3%); 75(46.4%); 69(35.7%); 109(34%); 95(28.5%); 97(25%); 83(21.4%); 137; 177(16%); 81(14.2%); 210(13.4%).

(Found: C, 73.18; H, 11.91; $C_{14}H_{28}O_2$; requires C, 73.63; H, 12.28).

ii) Nafion-H (DuPont product)

Nafion-H was washed with 40% nitric acid[15], filtered and dried at 120°C for 6 hrs. before use.

Oxirane (39), (1.2 gms) in dry hexane (25 ml) was kept at -5°C with Nafion (0.3600 gms) for 24 hrs with occasional shaking. Filtration and washing the residue with ether (20 ml) followed by solvent removal gave the crude product (1.19 gms) which was distilled at 140-200°C (bath)/ 4 mm to give a distillate (0.7650 gms). The residue (0.3892) was found to be comprising essentially of the dimer.

The distillate was chromatographed over silica gel (60 gms; 16 x 3 cm column).

Chromatogram-II

Fr.No.	Solvent	Volume/ml	Weight/gm
1.	Pet. ether	5 x 50	0.0246
2.	1% ether/pet. ether	4 x 50	0.2102
3.	-do-	2 x 50	0.0891
4.	5% -do-	6 x 50	0.3912
5.	10% -do-	5 x 50	0.0122
6.	Ether	4 x 50	
	Total		0.7273

Fraction 2, was found homogenous on TLC. R_f 0.45 (20% ether/ pet. ether) and identified as the aldehyde (40). n_D^{25}: 1.4666. Mass: m/e^+ 210(30.2%); 69(100%); 82(55.2%); 109(52.6%); 55(50%); 123 (44.7%); 83 (43.4%); 97,152(36.8%); 81,95 (34.2%); 96(29%); 195 (26.3%).

Fraction 3, was identified as (38).

Fraction 4, found homogenous on TLC was identified as the glycol (43) on the basis of spectral features.

iii) Methane sulfonic acid

Epoxide (39) (3.5 gms) in nitromethane (50 ml) was stirred with 1% aq. methane sulfonic acid (25 ml) for 2.5 hrs

at -8°C. The product was allowed to come to room temperature, the aqueous layer separated and extracted with ether (4 x 25 ml). The combined organics were washed with 5% Na_2CO_3 (3 x 25 ml), water (4 x 25 ml) and brine (2 x 25 ml). Drying over anhydrous Na_2SO_4 and removal of solvent furnished the product (3.4 gms) which was chromatographed over silica gel.

Chromatogram-III

Silica gel: 140 gms, (IIIA); Column: 4 x 30 cms.

Material charged: 3.4 gms.

Fr.No.	Solvent	Volume/ml	Weight/gms
1.	Pet. ether	6 x 200	0.0246
2.	2% ether/pet. ether	5 x 200	0.9247
3.	5% Ether/pet.ether	2 x 200	0.5019
4.	-do-	5 x 200	0.0829
5.	10% ether/pet.ether	6 x 200	0.0875
6.	20% ether/pet.ether	5 x 200	0.1937
7.	50% ether/pet. ether	5 x 200	0.0572
8.	Ether	2 x 200	1.3013
		Total	3.2738

Fr. 2 was identified as the dimer.

Fr. 8 was distilled at 140°(bath)/0.3 mm to furnish pure (TLC) product identified as the glycol (43).

Fr. 6 was found homogenous on TLC, R_f 0.3 (20% ether/pet. ether) was distilled at 100°C(bath)/0.3 mm and identified as the allylic alcohol (42) n_D^{25}; 1.4835.

Mass: m/e^+ 210(2.5%); 69(100%); 50(50.2%); 95(22.4%); 57(21.5%); 12.5(20%); 81(18.1%); 67(16.33%); 124(15.5%); 109(13.8%); 68(13.7%); 79, 123 (11.2%).

(Found C, 79.50, H, 12.17 $C_{14}H_{26}O$; requires C, 80.8, H, 12.38).

iv) ZnO-Al_2O_3 (1:1)

ZnO-Al_2O_3 was prepared by the method of Tanabe *et al.*[16] Epoxide (39) (1.3 gms) in dry hexane (40 ml) was shaken with ZnO-Al_2O_3 (32 gms) at 30°C for 6 hrs. followed by standing for 18 hrs. at the same temperature. Filtration and washing the residue with 5% MeOH-ether (1500 ml) followed by solvent removal gave the crude product (0.9926 gms) which was chromatographed over silica gel (30 gms, 1.5 x 50 cm).

Chromatogram-IV

Fr. No.	Solvent	Volume/ml	Weight/gms
1.	Pet. ether	6 x 100	0.1097
2.	5% ether/pet. ether	5 x 100	0.1499
3.	10% ether/pet. ether	6 x 100	0.5872
4.	20% ether/pet. ether	2 x 100	0.0520
5.	Ether	4 x 100	0.0536
		Total	0.9524

Fr. 3 was identified as the allylic alcohol (41).

Fr. 5 was identified as the glycol (43).

v) Perchloric acid

Oxirane (39) (0.640 gms) in THF (20 ml) was stirred at -10°C with 1% aqueous perchloric acid (10 ml) for 2.5 hrs. The reaction product was extracted with ether (5 x 20 ml) and the ether layer washed with 1% Na_2CO_3, (2 x 30 ml), water (4 x 30 ml) and brine (2 x 50 ml). Drying over anhydrous sodium sulfate and removal of solvent gave the product (0.5827 gms) which was distilled 140-200°C (bath/4 mm)to give the distillate (0.1550 gms) and the

residue (0.4550 gms). The latter comprised essentially of the dimeric compound. Distillate was found (by GLC) to be comprising of hydrocarbons (14%) aldehyde (40) (40%) and the ketone (38) (45%).

vi) Titanic acid

The oxirane (39) (0.300 gms) in dry hexane (10 ml) was shaken with titanic acid (0.300 gms) at room temperature (30°C) for 12 hrs. Filtration and washing the residue with 5% methanolic-ether (250 ml) followed by careful solvent removal gave the product (0.2086 gms) which was distilled at 140-200°C (bath)/4 mm to give the distillate (0.1015) found comprising of hydrocarbons (31.9%), ketone (38) (7.3%); aldehyde (40) (24.4%) and the allylic alcohol (41) (24.4%). The residue (0.0863 gms) left behind after distillation was found comprising essentially of polymeric material.

vii) Boron phosphate

Boron phosphate was prepared by the method of Moffat and Riggs[17]. The oxide (39) (0.300 gm) in dry hexane (5 ml) was kept with Boron phosphate (0.300 gms) at -5°C for 12 hrs with occasional shaking. Filtration and washing the residue with 5% methanolic-ether (100 ml) followed by careful

ether removal gave the product (0.2348 gms) which was distilled at 140-200°C(bath)/4 mm to furnish the residue (0.0935 gms) comprising of the dimer. The distillate (0.1194 gms) comprised of hydrocarbons (34.9%); aldehyde (40) (54.7%) and ketone (38) (10.4%).

viii) Picric acid

The epoxide (39) (0.200 gms) was taken in dry benzene (10 ml) and picric acid (0.020 gms) added to it. The contents were allowed to stand at room temperature for 48 hrs. followed by three hours at reflux. The product was found to be a complex mixture. Chromatography over silica gel did not result in the isolation of any pure compound.

ix) Magnesium oxide catalyst[18]

Epoxide (39) (0.300 gms) was taken in dry toluene (15 ml) and MgO catalyst (7.5 gms) added. Refluxing for 24 hrs. gave no oxirane cleaved product after the work-up Essentially, the starting material was recovered.

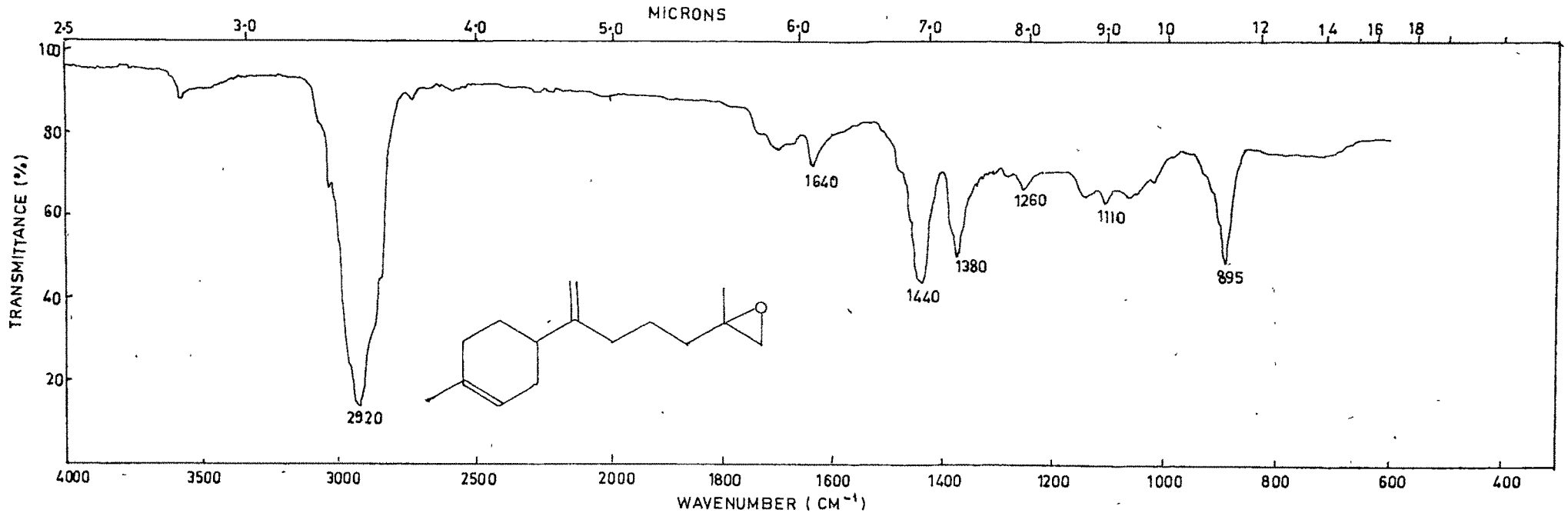


FIG VI-1: IR SPECTRUM OF 1,2-EPOXY-6-(4'-METHYL-CYCLOHEX-3-ENYL)-2-METHYL-HEPT-6-ENE (36)

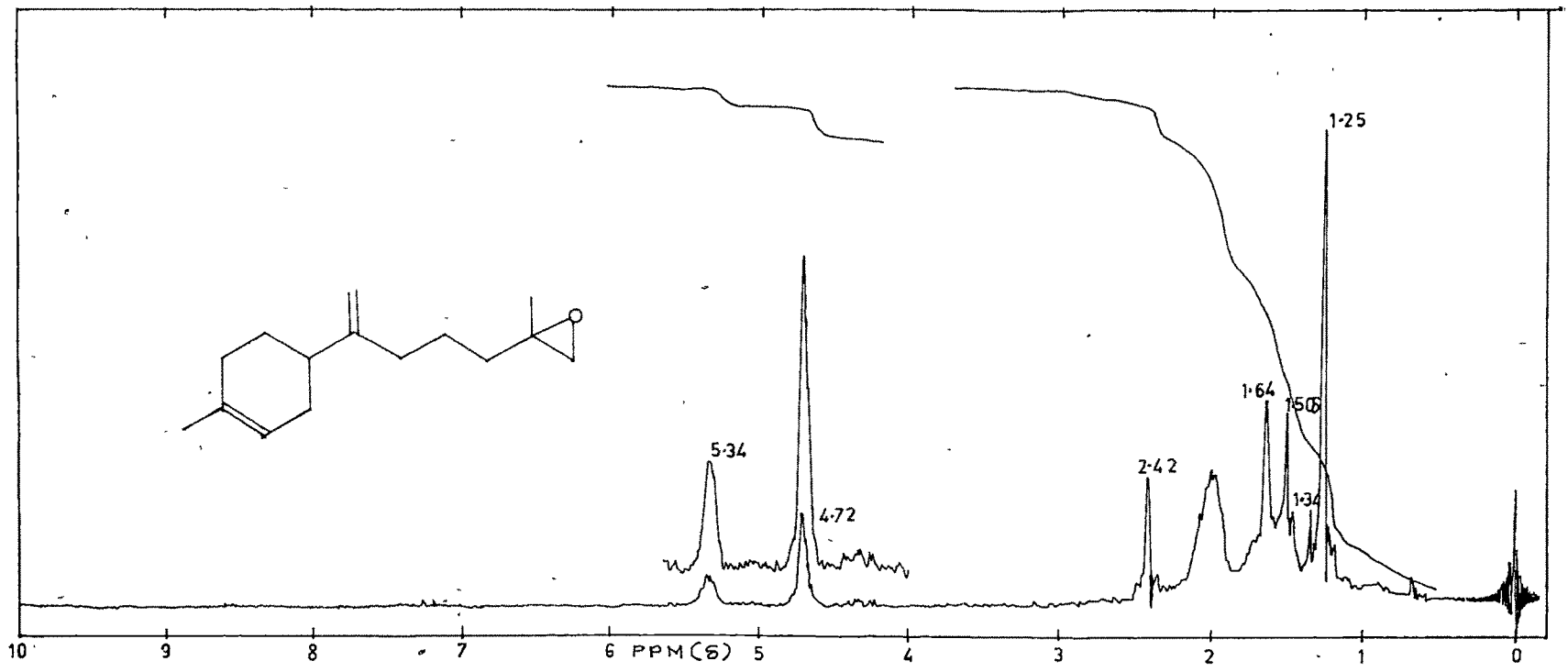


FIG VI-2: PMR SPECTRUM OF 1,2-EPOXY-6-(4'-METHYL-CYCLOHEX-3-ENYL)-2-METHYL-HEPT-6-ENE (36)

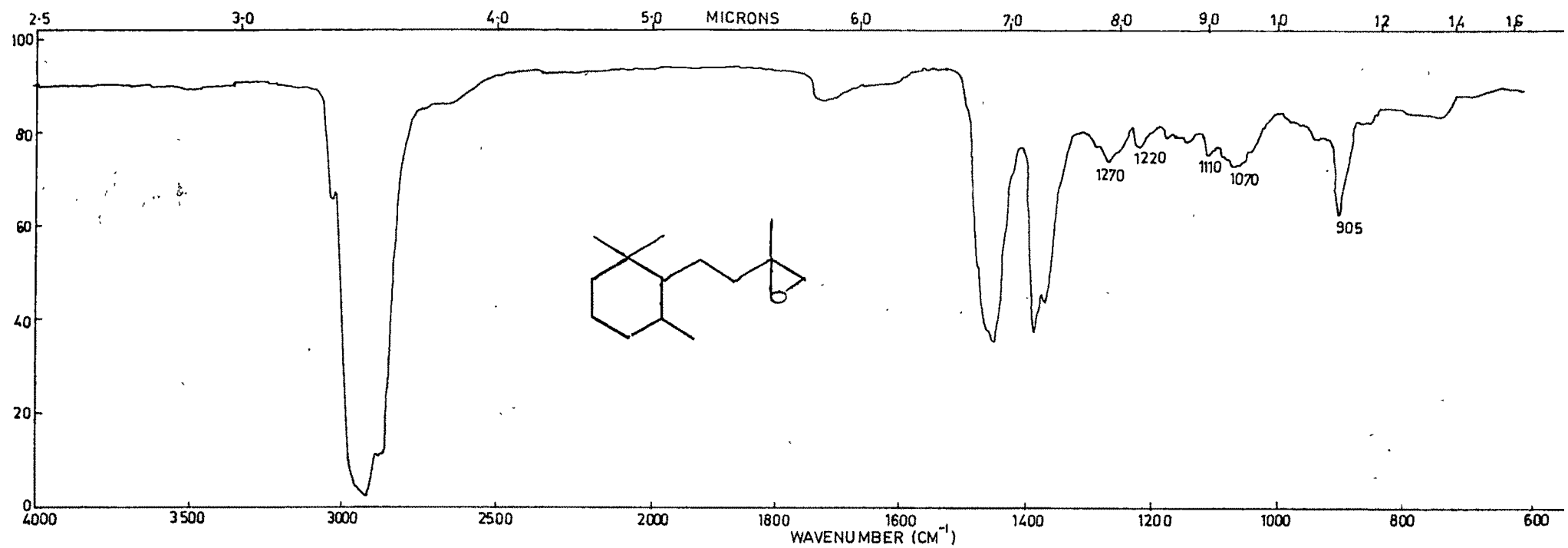


FIG VI-3 : IR SPECTRUM OF 1,2-EPOXY-4-(2',2',6',-TRIMETHYL-CYCLOHEXYL)-2-METHYL-BUTANE (39)

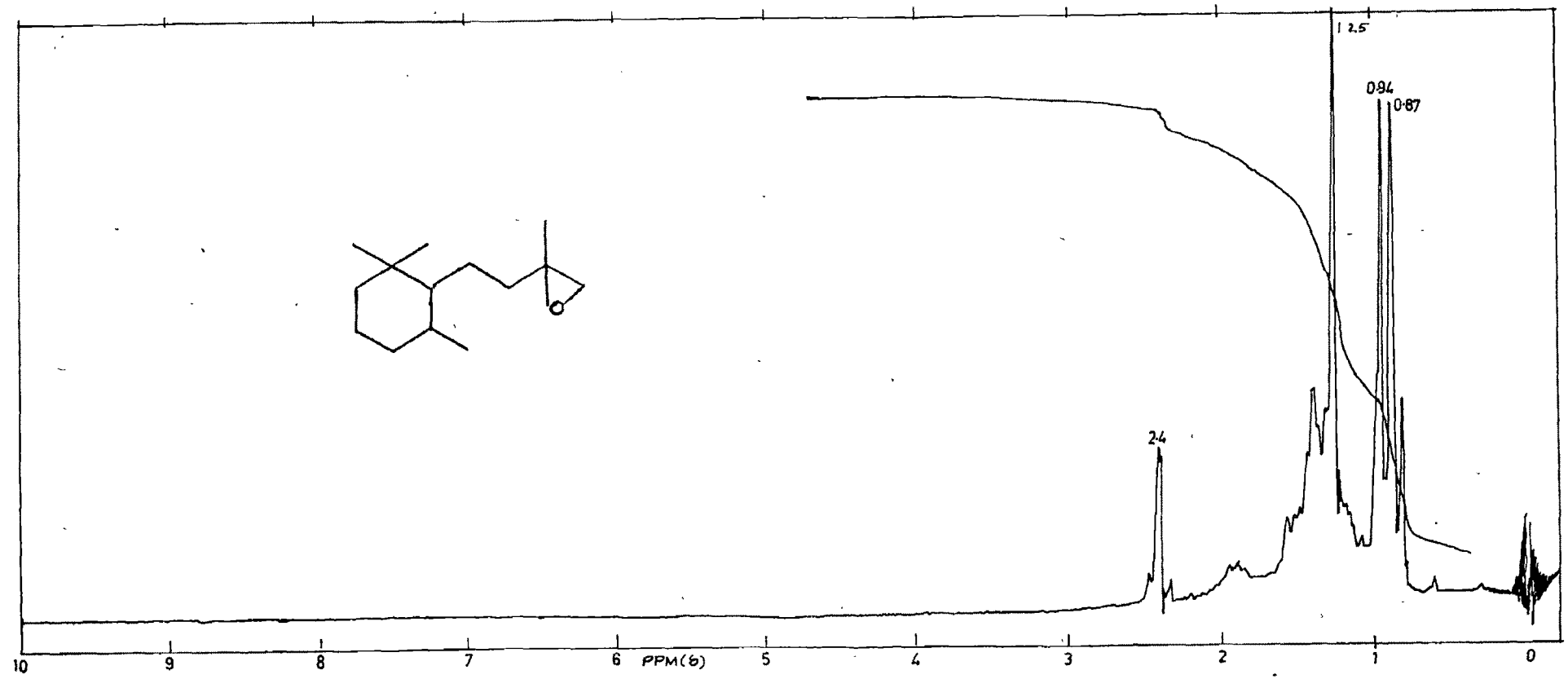


FIG VI-4: PMR SPECTRUM OF 1,2-EPOXY-4-(2',2',6'-TRIMETHYL-CYCLOHEXYL)-2-METHYL-BUTANE (39)

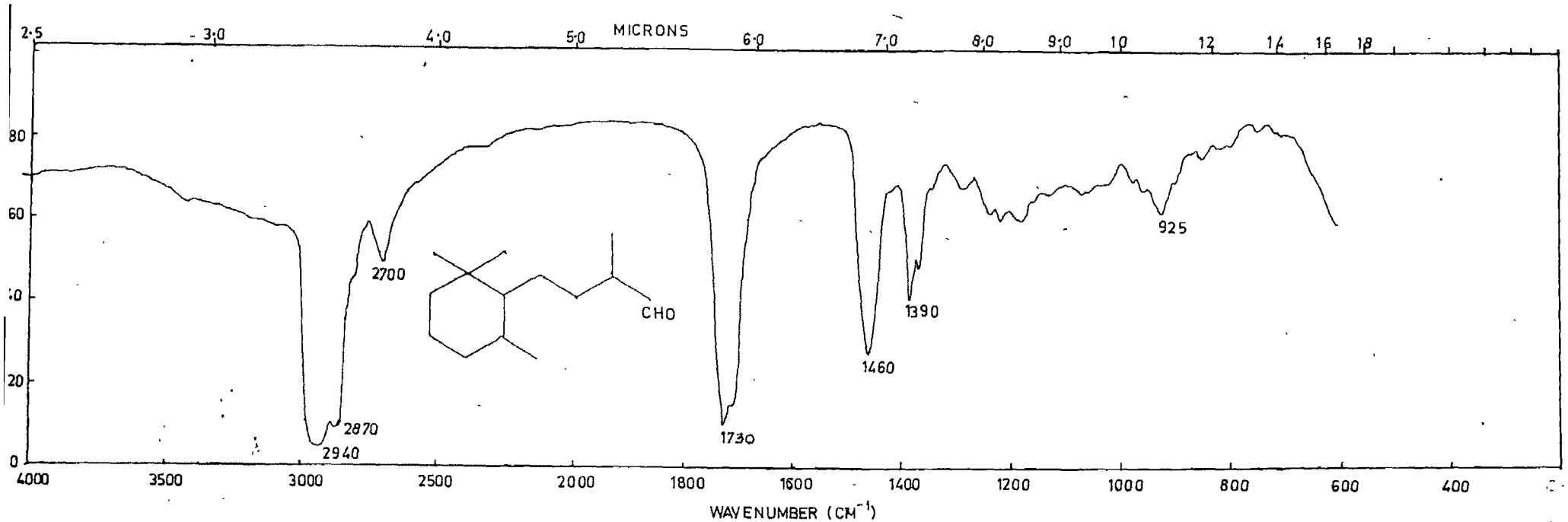


FIG VI-5; IR SPECTRUM OF 4-(2',2',6'-TRIMETHYL-CYCLOHEXYL)-2-METHYL-BUTRALDEHYDE (40)

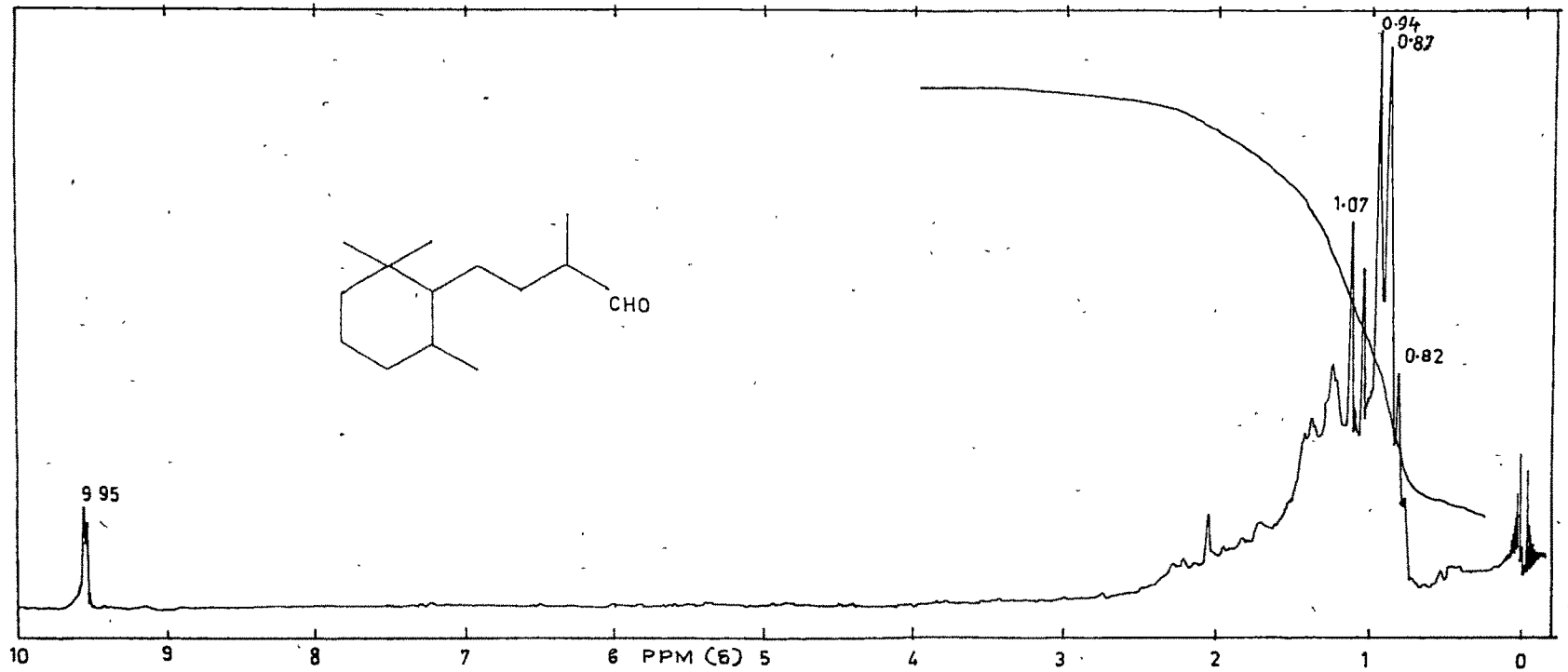


FIG VI-6 : PMR SPECTRUM OF 4-(2',2',6',-TRIMETHYL-CYCLOHEXYL)-2-METHYL-BUTRALDEHYDE (40)

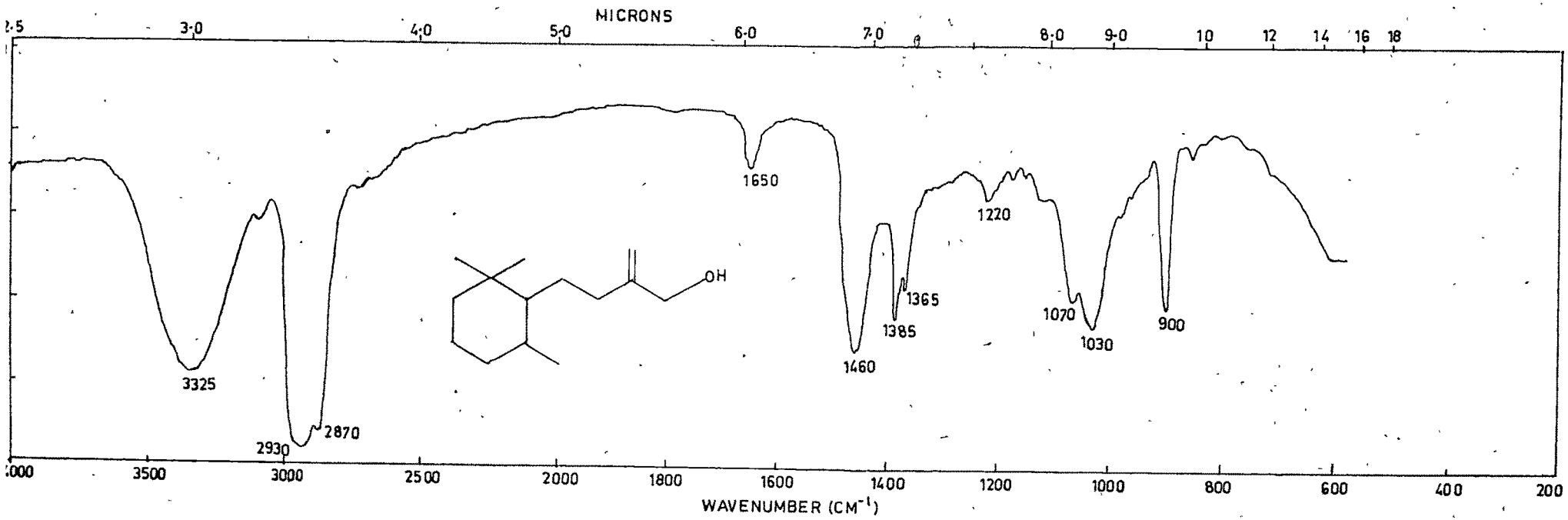


FIG VI-7: IR SPECTRUM OF 4-(2',2',6'-TRIMETHYL-CYCLOHEXYL)-2-METHYLENE-BUTANE-1-OI (41)

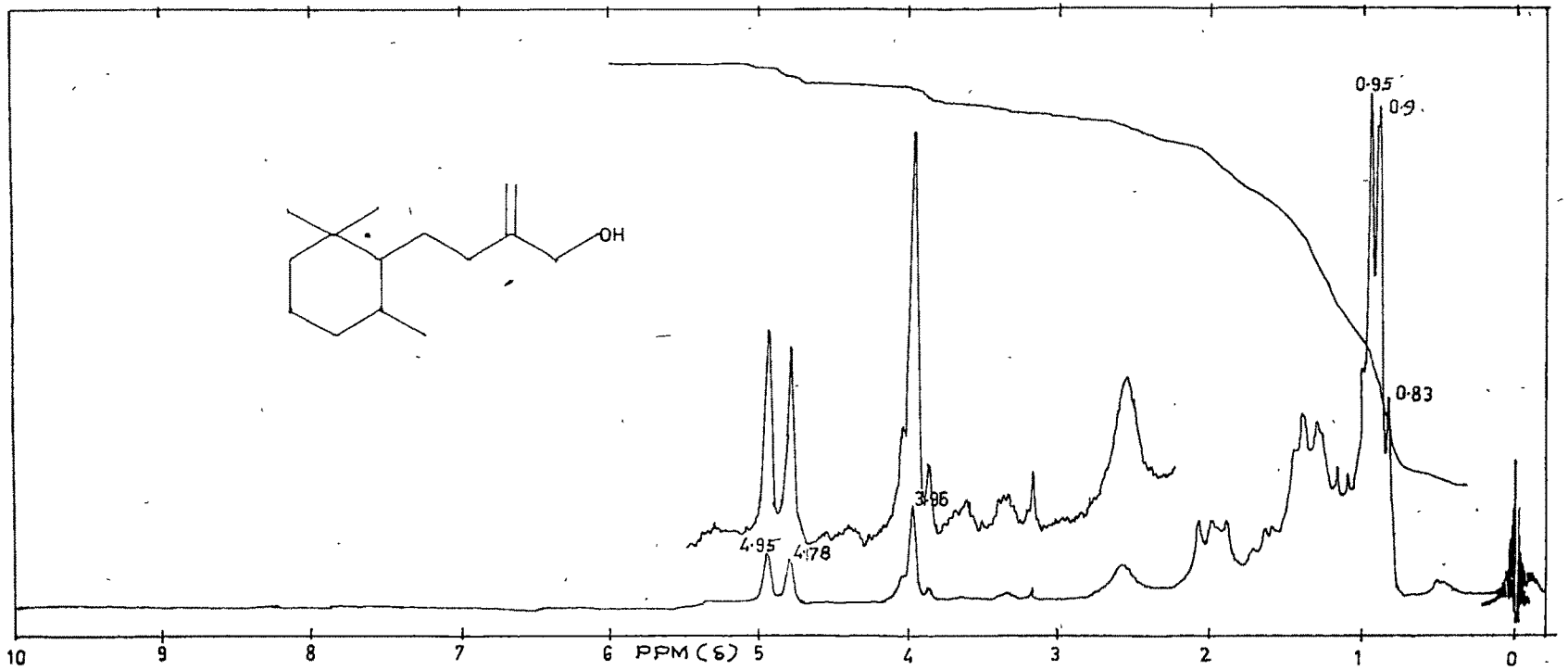


FIG VI-8 : PMR SPECTRUM OF 4-(2',2',6'-TRIMETHYL-CYCLOHEXYL)-2-METHYLENE-BUTANE-1-OL (41)

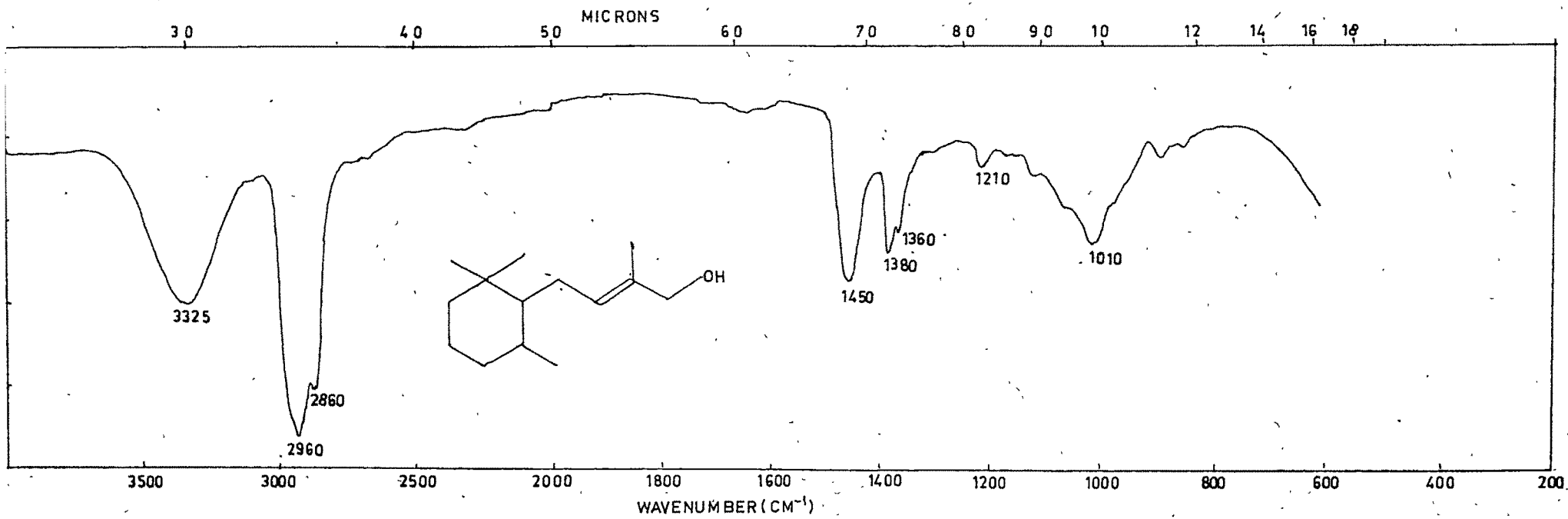


FIG VI-9: IR SPECTRUM OF 4-(2',2',6'-TRIMETHYL-CYCLOHEXYL)-2-METHYL-BUT-2-ENE-1-OL (42)

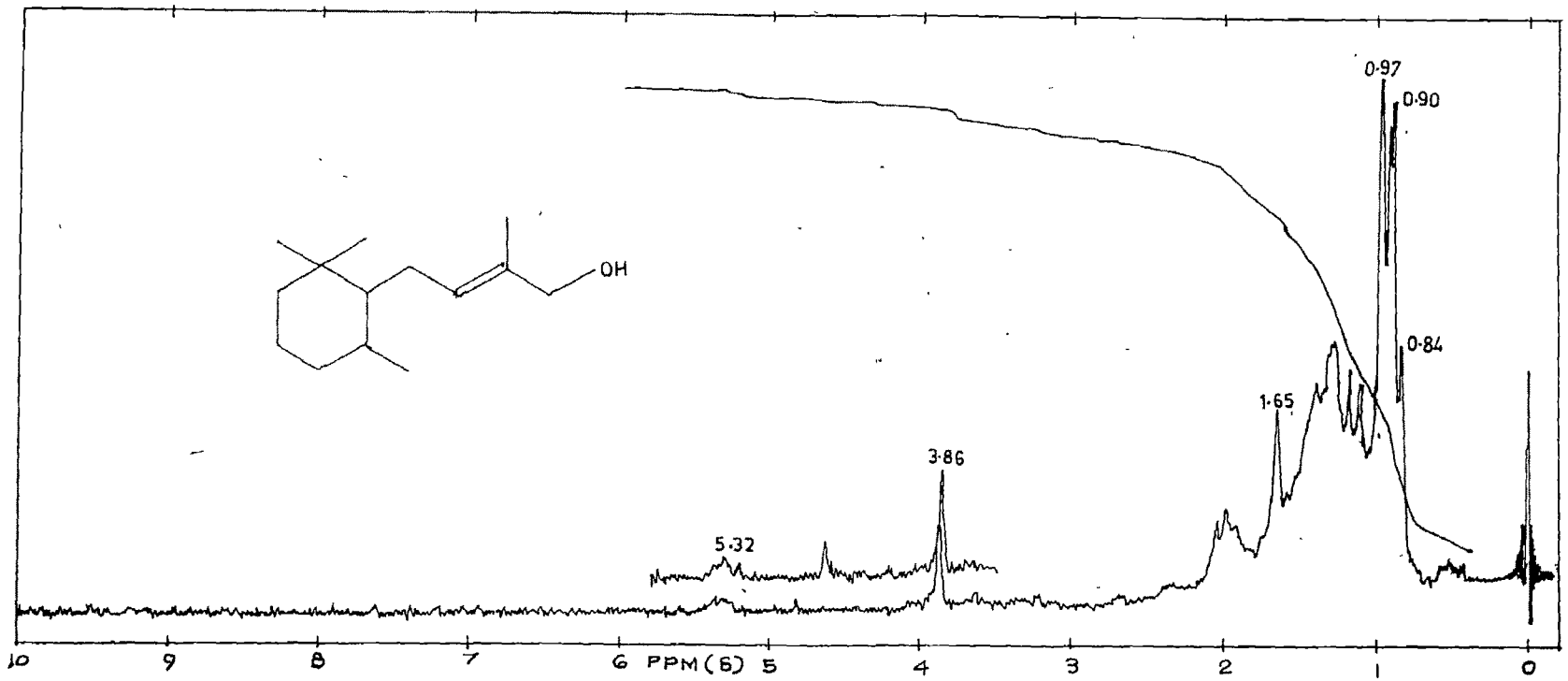


FIG VI-10: PMR SPECTRUM OF 4-(2',2',6'-TRIMETHYL-CYCLOHEXYL)-2-METHYL-BUT-2-ENE-1-OL (42)

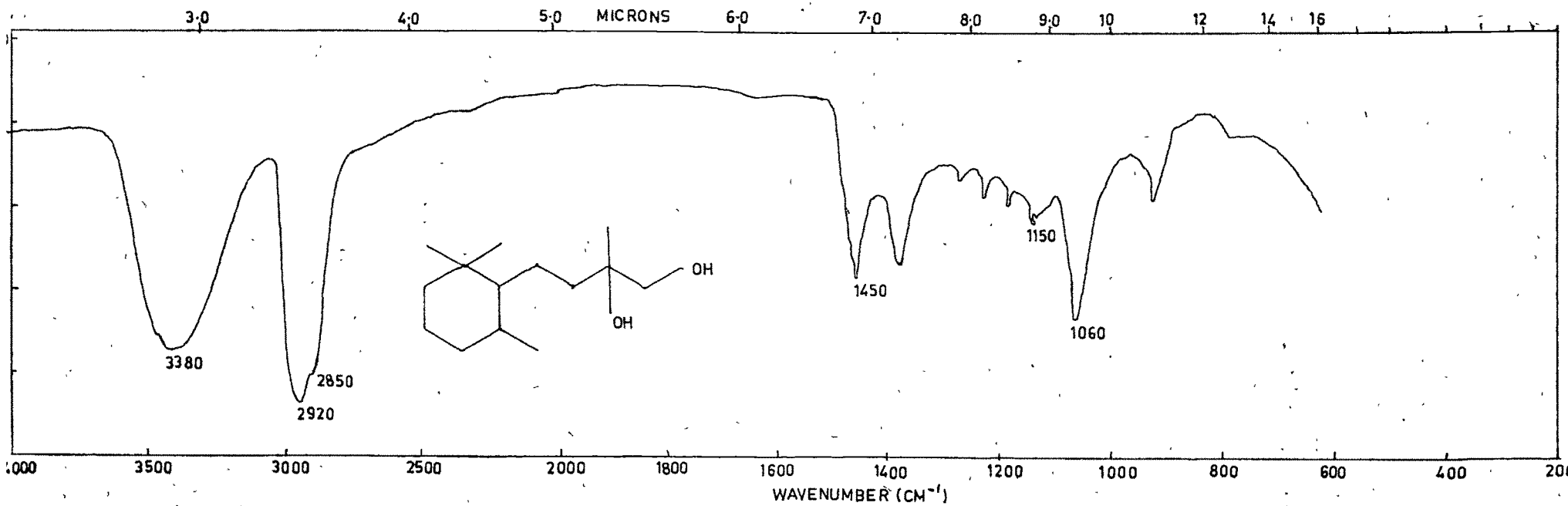


FIG VI-11: IR SPECTRUM OF 4-(2',2',6'-TRIMETHYL-CYCLOHEXYL)-2-METHYL-BUTANE-1,2-DIOL (43)

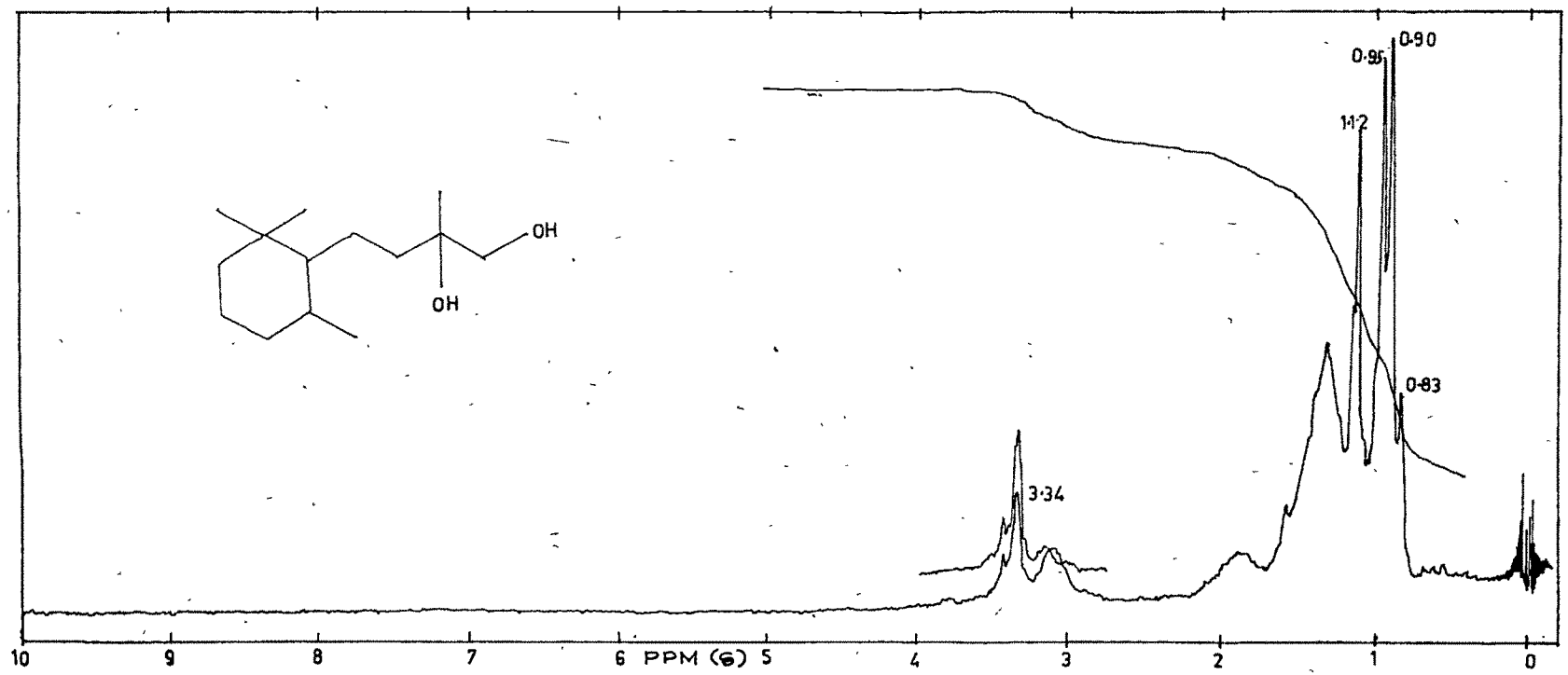


FIG VI-12: PMR SPECTRUM OF 4-(2',2'-6'-TRIMETHYL-CYCLOHEXYL)-2-METHYL-BUTANE-1,2-DIOL (43)

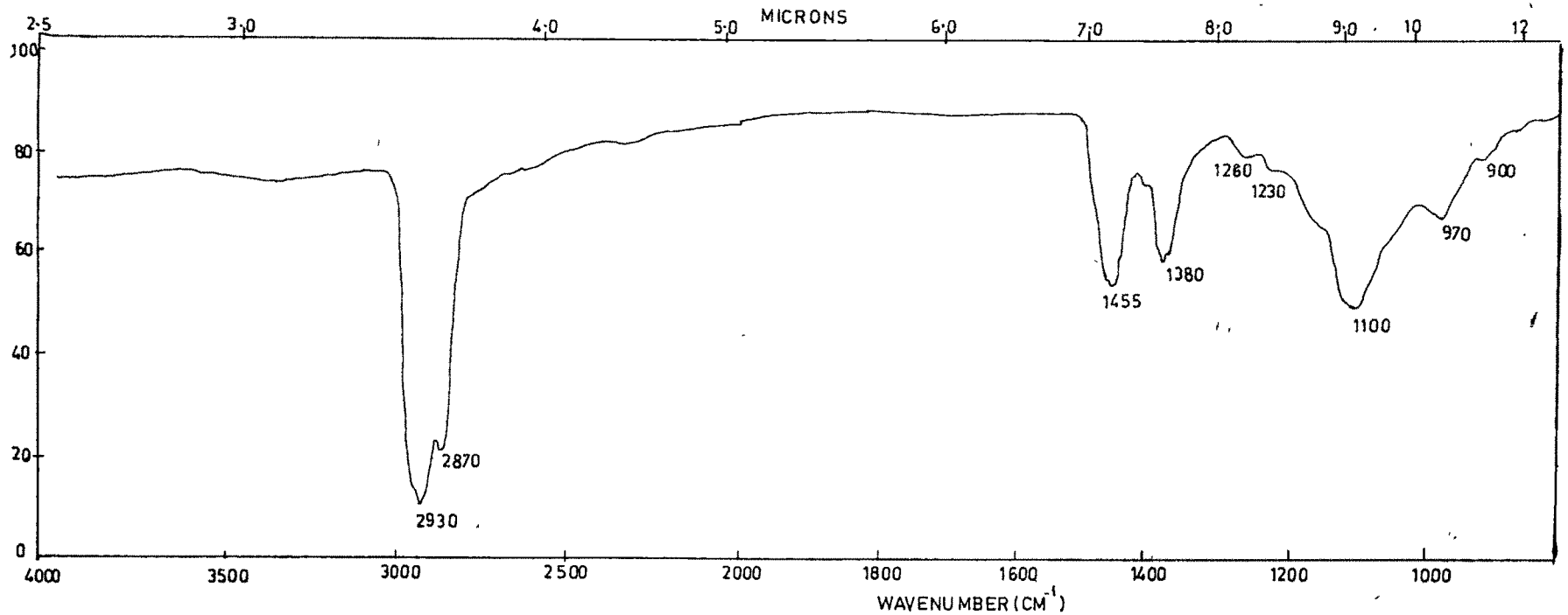


FIG VI-13: IR SPECTRUM OF DIMER

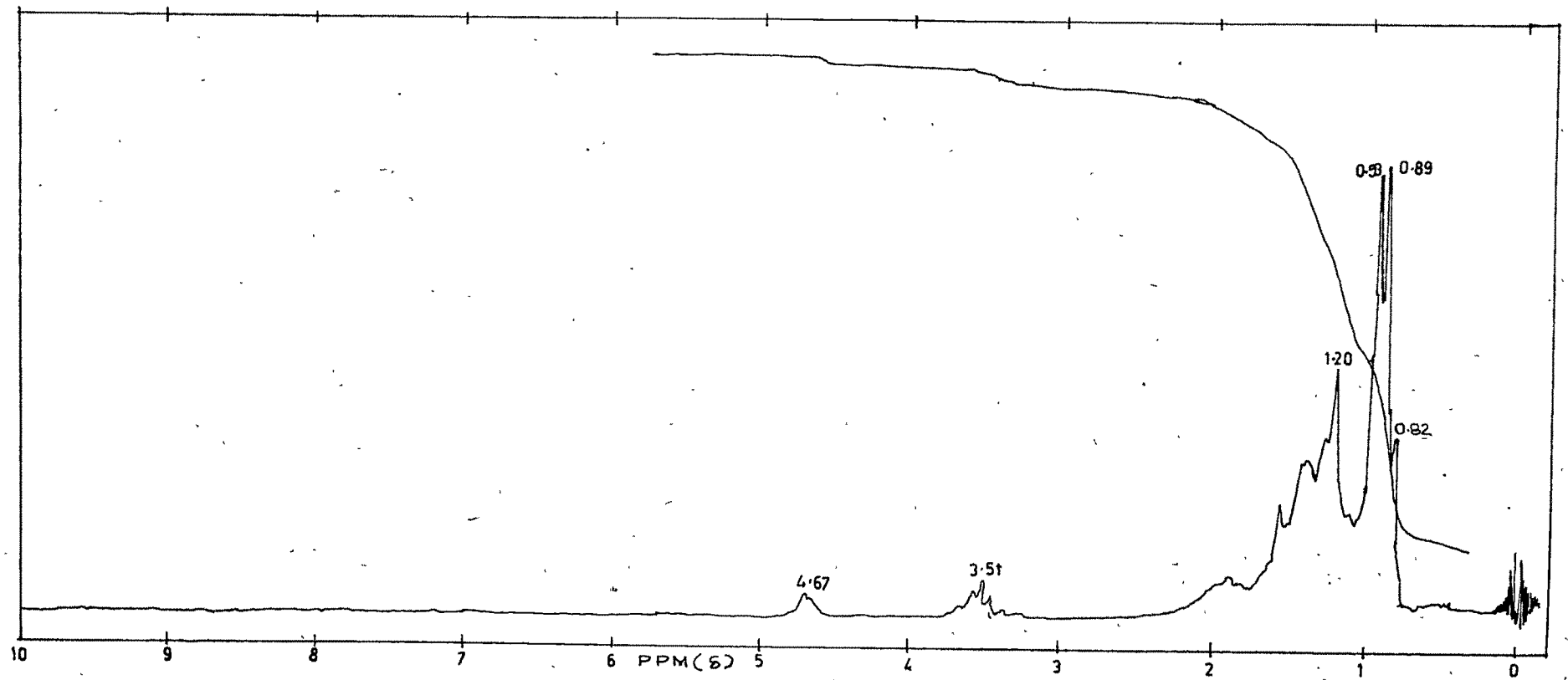


FIG VI-14: PMR SPECTRUM OF DIMER

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