CHAPTER III

ACID CATALYSED CYCLISATIONS OF ACYCLIC MONOTERPENES

ABSTRACT

The cyclisation of acyclic monoterpenes catalysed by various acidic reagents is briefly reviewed. Methane sulphonic acid in nitromethane is evaluated as a prospective acidic catalyst for some of these cyclisations. Cyclisation with this reagent was studied with geranic acid (8/9), methyl geraniate (39), geranyl acetate (11), geraniol (12), citral anil, ψ-ionone (17), geranylacetone (20) and cyclic ethylene ketal of geranylacetone (42).

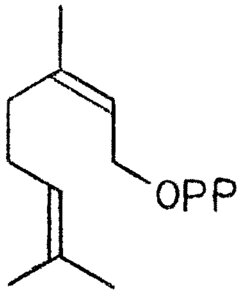
ACID CATALYSED CYCLISATIONS OF ACYCLIC MONOTERPENES

INTRODUCTION

A large number of acyclic and monocyclic monoterpenes occur in nature. The biogenesis of monocyclic monoterpenes was first suggested by Ruzicka[1] to arise from cationic cyclisation of the acyclic monoterpene, neryl pyrophosphate (1). The latter was presumably derived from geranyl pyrophosphate (2) and possesses the requisite Z geometry of the 2,3-double bond. Linaloyl pyrophosphate (3) was also suggested as an alternative species which can undergo the cationic cyclisation.

Various modes of cyclisation are possible[2] leading to several monocyclic carbon skeletons occuring in nature. Some of these cyclisations have been realised in the laboratory.

Most of the naturally occurring acyclic monoterpenes are in the isopropylidene form. Many workers have exploited this double bond in acid catalysed cyclisation reactions to generate derivatives of either *p*-menthane (4) or 1,1,3-trimethylcyclohexane (5). Thus, acyclic terpenes cyclise in acids by a reaction which involves the protonation of the isopropylidene



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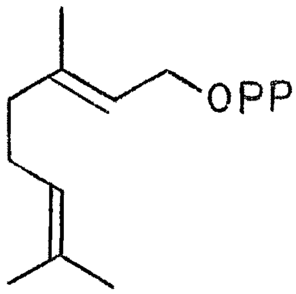

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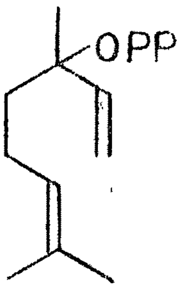

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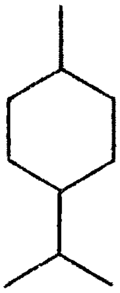

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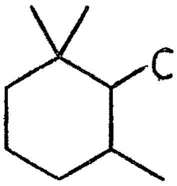

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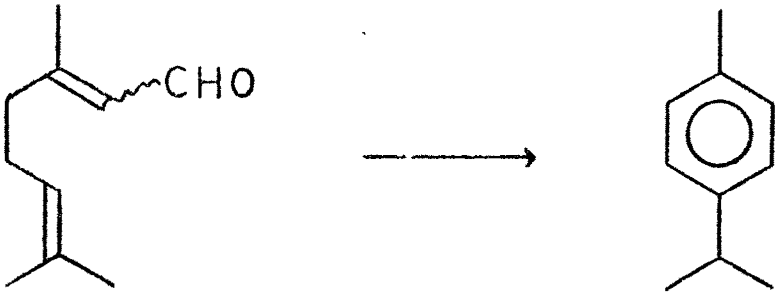
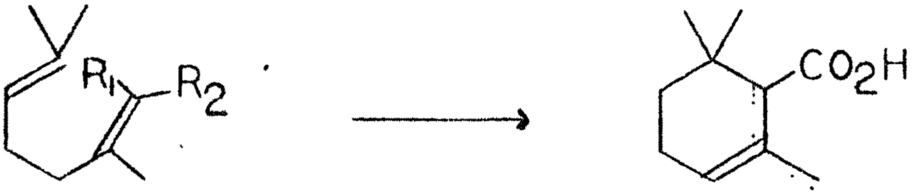


6

7

Eq.1



Eq.2

$\underline{8}$: $R_1 = CO_2H$, $R_2 = H$

$\underline{9}$: $R_1 = H$, $R_2 = CO_2H$

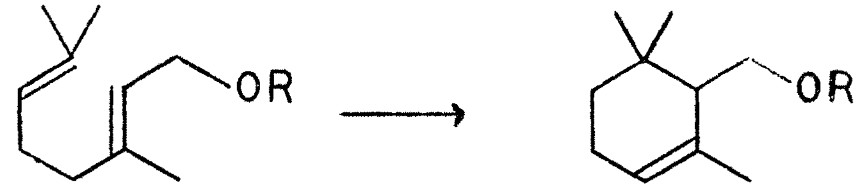
10

double bond followed by attack of the carbonium ion thus generated on the other double bond. Since Semmler's original observation[3] in 1891 of the cyclisation of citral (6) in the presence of potassium hydrogen sulfate to give p-cymene(7) (Eq. 1), a variety of acidic catalysts have been used to carry out similar cyclisations.

1) Sulphuric acid: Conc. H_2SO_4 is the most widely used catalyst for such cyclisations. Cyclisation of cis-geranic acid (8) with conc. H_2SO_4 gave α-cyclogeranic acid (10) in 75% yield, together with small amounts of β- and γ-cyclogeranic acids.[4] Identical result was obtained with trans-geranic acid (9) (Eq. 2). This shows that the difference in stereochemistry at 2,3-double bond has no influence on the course of cyclisation.

Cyclisation of geranyl acetate (11) with 100% H_2SO_4 gave α-cyclogeranyl acetate (13) in 50-60% yield.[5] Cyclisation of geraniol (12) at -60° was reported[6] to give α-cyclogeraniol (14) in 29% yield (Eq. 3).

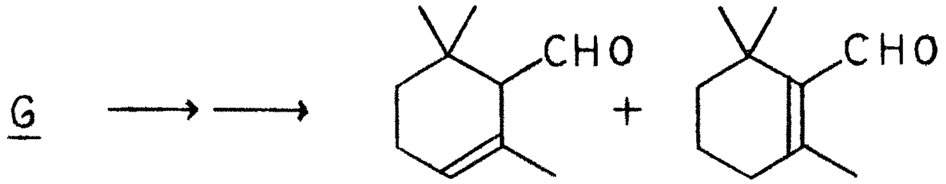
Citral anil[7] and the enamine derived from citral (6) and piperidine[8] were cyclised with conc. H_2SO_4 to give α-(15) and β-cyclocitral (16) in 60 and 40% yields respectively (Eq. 4).



11: R=Ac
12: R=H

13: R=Ac
14: R=H

Eq.3

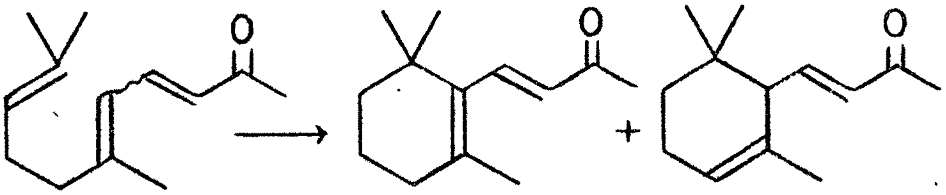


6

15

16

Eq.4

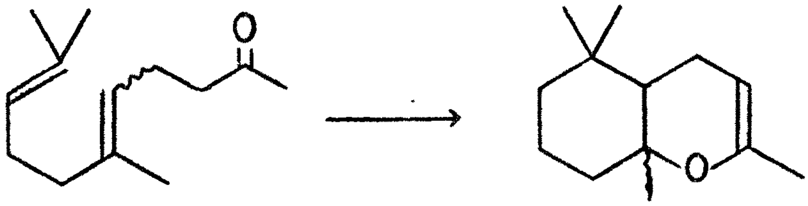


17

18

19

Eq.5



20

21

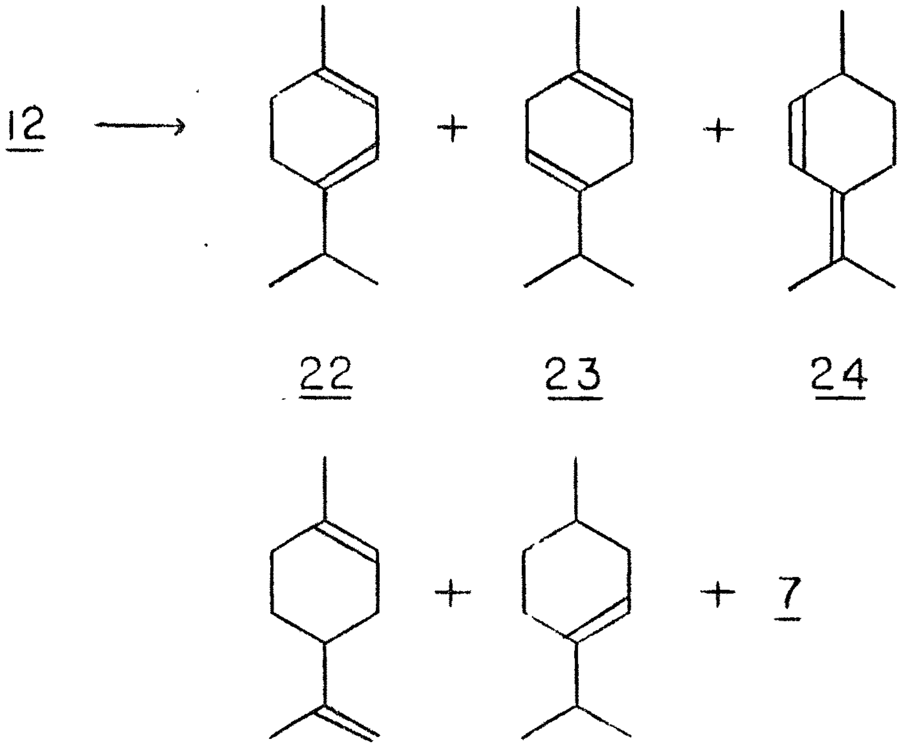
Eq.6

Cyclisation of ψ-ionone (17) with H_2SO_4 was performed in various solvents like ether[9], skellysolve B,[10] liquid MeCl,[11] dichloromethane[12] etc. β-Ionone (18) was the major product if the reaction was carried out at -10° or above. At -70°, α-ionone (19) was the major product (Eq. 5). The yields were around 70%. In addition to α- and β-ionones, other isomers[13] of ionone and bicyclic ethers[13,14] were identified in minor quantities in the cyclisation product of ψ-ionone (17).

Cyclisation of geranylacetone (20) with H_2SO_4 gave 2,5,5,9-tetramethylhexahydrochromene (21).[15] The stereospecificity at the ring junction in 21 is determined by the stereochemistry of the 5,6-double bond in the starting ketone (Eq. 6). Thus, trans-geranylacetone gives trans-21, whereas cis-geranylacetone gives cis-21.

2. Phosphoric acid: Phosphoric acid catalysed cyclisations gave similar results. In the case of ψ-ionone (17), α-ionone (19) was the major product ($\sim$85%).[16] Reaction of geraniol (12) (or geranyl acetate) with 85% H_3PO_4 gave[17] a complex mixture of hydrocarbons, namely, α-terpinene (22), γ-terpinene (23), isoterpinolene (24), limonene (25), p-cymene (7) and p-3-menthene (26) (Eq. 7).

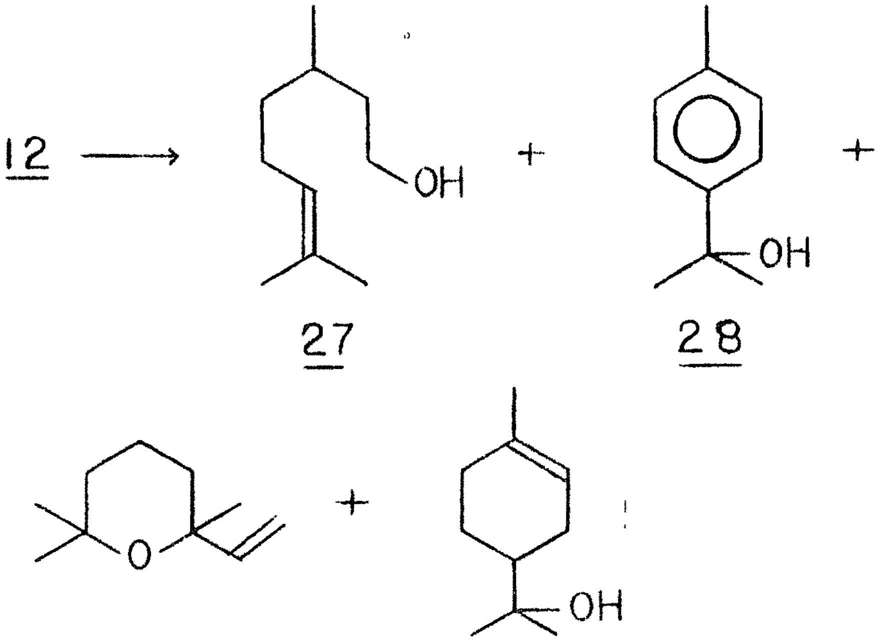
3. Lewis acids: Lewis acids like BF_3, $AlCl_3$, $ZnCl_2$ etc.



22 23 24

25 26

Eq.7



27 28

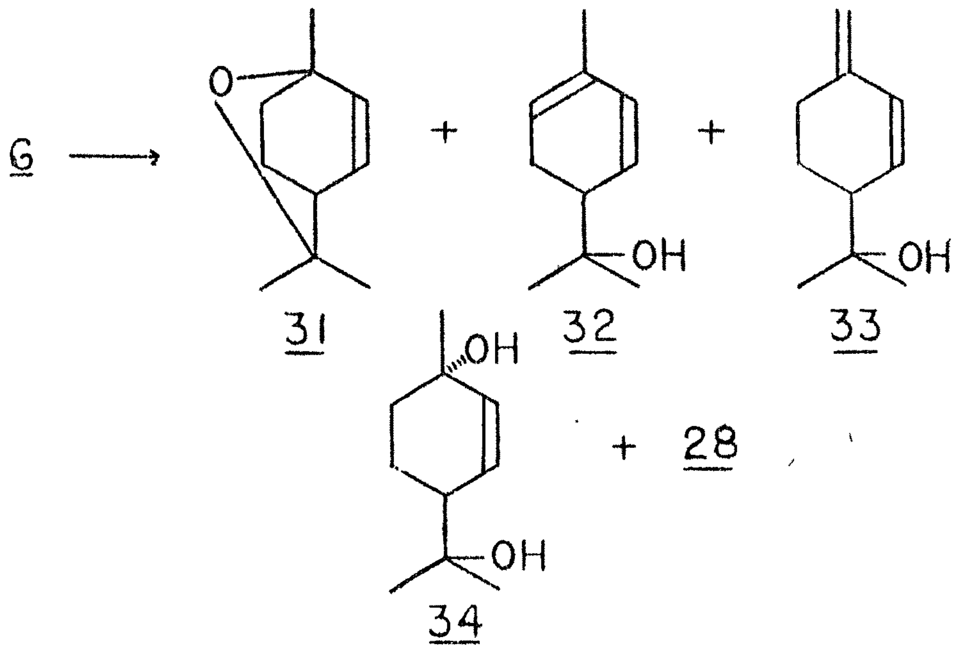
29 30

Eq.8

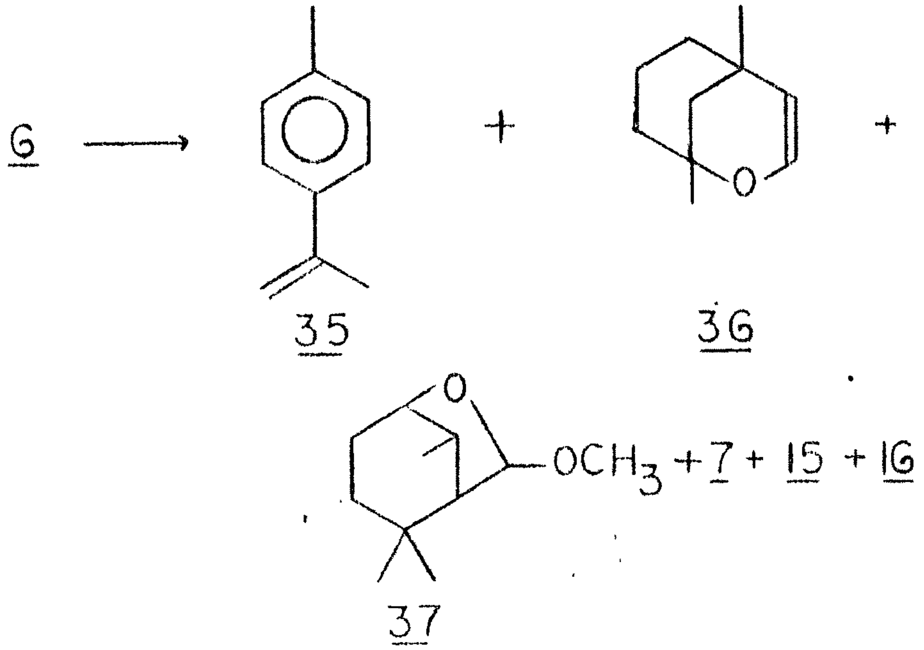
were also reported to give similar results. With BF_3-etherate, ψ-ionone (17) gave γ-ionone as a major product.[18]

4. Aqueous acids: There is no preparative use for aqueous acids for these cyclisation reactions, since they invariably led to complex mixtures. Geraniol (12), when treated with aq. oxalic acid,[19] gave 23 identified products, most of which result from simple hydration and proton-transfer reactions. The major products were citronellol (27), cymenol (28), 2,6,6-trimethyl-2-vinyl tetrahydropyran (29) and α-terpineol[20] (30) (Eq. 8). Fourteen compounds were identified from the acid catalysed cyclisation of citral (6) under aqueous conditions. The major products were 1,8-epoxy-*p*-menth-2-ene (31), *p*-menth-1,5-dien-8-ol (32), *p*-menth-1(7),2-dien-8-ol (33), *p*-cymenol (28) and *cis*-*p*-menth-2-ene-1,8-diol (34) (Eq. 9).

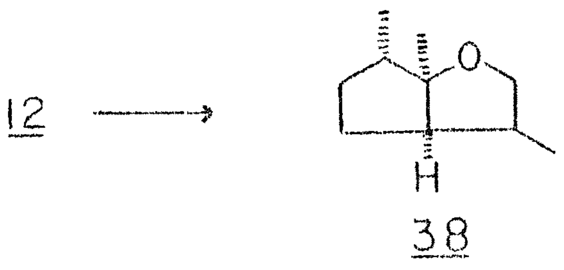
5. Super acids: Treatment of acyclic monoterpenes with super acids gave completely different products from those of conventional acid-catalysed process. Treatment of citral (6) with FSO_3H gave[21] considerable quantities of high-boiling materials and only low (15-30% at most) recoveries of monoterpenoids. The latter fraction comprised *p*-cymene (7), 1-isopropenyl-4-methylbenzene (35), α-cyclocitral (15),



Eq.9



Eq.10



Eq.11

β-cyclocitral (16) and two novel products (36) and (37) (Eq. 10). Similar treatment of geraniol (12) gave[22] a novel iridoid ether, 3β, 6α, 6aα-trimethyl-*cis*-perhydrocyclopenta(b)furan (38) (Eq. 11). However, Smit and co-workers[23] report that cyclisation of ψ-ionone (17) with FSO_3H gave α-ionone (19) as the major product and that of geranic acid (8/9) gave α-cyclogeranic acid (10).

In these super acid catalysed cyclisations, despite all precautions to ensure rapid, intimate mixing of the acid and the reactants and quenching at lowest possible temperature, polymers and tars were formed in substantial amounts.

6. Ion exchange resins: Cyclisations effected by ion exchange resins were not satisfactory. Cyclisation of geranic acid (8/9) with Amberlite IR-120 in dioxane gave α-cyclogeranic acid (10) in 70% yield.[24] Cyclisation of ψ-ionone (17) with KRS 10 TN gave[25] 93% pure α-ionone (19) in 37% yield.

Applications: Acid catalysed cyclisation of acyclic monoterpenes is a viable synthetic tool. For example, α-cyclocitral (15) is a key intermediate in the synthesis of several terpenes like α-ionone and α-damascone.[26] β-Ionone (18), which is the starting material for the synthesis of vitamin A, is made by cyclisation of ψ-ionone (17).

PRESENT WORK

From the above details, it is obvious that H_2SO_4 is the most useful reagent for these cyclisations to date. We planned to evaluate methane sulphonic acid and p-toluene sulphonic acid as prospective reagents for such cyclisations. We hoped that these will have all the advantages associated with H_2SO_4 and yet be bereft of the drawbacks of the super acid, FSO_3H.

We chose two solvents initially for conducting these cyclisations. They are nitromethane and sulfolane. Both these solvents are very similar to each other in many respects. Both possess high dielectric constants —— 39 for nitromethane and 44 for sulfolane. Both are aprotic dipolar solvents of very low basicity. Cryoscopic studies of Hammett[27] and Arnett[28] show that ions are poorly solvated in these solvents, so that acid solutions in them have enormously greater effective acidity at lower acid concentrations than aqueous solutions of the same concentration. The two solvents also have good thermal and chemical stability.

We first studied the cyclisation of geranic acid (8/9) in both these solvents using $MeSO_3H$ and p-toluene sulphonic acid as catalysts. The results are summarised in Table 1.

TABLE 1 : Cyclisation of geranic acid

Entry	Geranic acid (g/mmol)	Catalyst (g/mmol)	Solvent (ml)	Time* h	Result
1	1/5.95	Me SO_3H (0.1/1.04)	Me NO_2 (3.3)	5.5	α-Cyclogeranic acid+ (<u>10</u>) (98% yield).
2	"	"	Sulfolane (3.3)	"	Geranic acid + α-cyclogeranic acid (1:1) (86% yield).
3	"	PTS.H_2O (0.2/1.04)	$MeNO_2$ (3.3)	10	α-Cyclogeranic acid+ (<u>10</u>) (98% yield).
4	"	"	Sulfolane (3.3)	"	Geranic acid + α-cyclogeranic acid (1:1) (86% yield).

* Reaction temperature = 30°

\+ The product contains a small amount of β- and γ-cyclogeranic acids (PMR).

From these results, it became evident that nitromethane was the solvent of choice and PTS.H_2O is as effective as $MeSO_3H$. The rest of the study with other monoterpene derivatives was restricted to $MeSO_3H/MeNO_2$.

Methyl geraniate (39) underwent smooth cyclisation with $MeSO_3H/MeNO_2$ at room temperature (∼30°) to give methyl α-cyclogeraniate (40) in almost quantitative yield (Eq. 12).

Cyclisation of citral anil at -15° led to extensive (75%) polymerisation. Also, the distillate (25%) was a complex mixture containing α-(15) (16%) and β-cyclocitral (16) (16%) (PMR). No attempt was made to separate the components of the mixture.

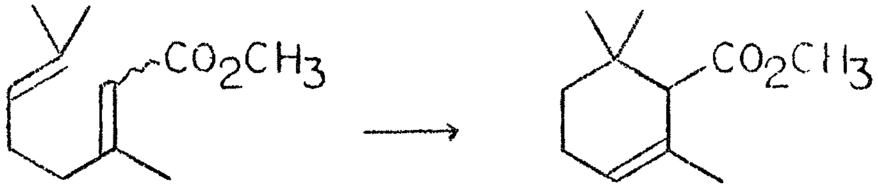
In the cyclisation of geranyl acetate (11) also, extensive resinification was noticed. After a series of experiments, the best conditions under which minimum resinification takes place, were found. Thus, cyclisation with 0.33 mole eq. of $MeSO_3H$ in $MeNO_2$ at -15° for 1 h gave α-cyclogeranyl acetate (13) in 50% yield.

Cyclisation of geraniol (12) with 0.2 mole eq. of $MeSO_3H$ in $MeNO_2$ at -10° for 45 min. gave 30% of the distillate, the rest being polymeric material. This distillate was a complex mixture and contained 33% of α-cyclogeraniol (14) as evident from a co-injection on GLC (10% carbowax, chromosorb W, 6', 170°, 60 ml/min) with an authentic sample obtained by alkaline hydrolysis of α-cyclogeranyl acetate (13).

Cyclisation of ψ-ionone (17) with molar eq. of $MeSO_3H$ at -5° for 24 h gave 60% product, which contained 67% α- (19) and 12% β-ionone (18), identified by co-injection with authentic samples on GLC (10% SE-30 on chromosorb W, 6', 170°, 60 ml/min.) In view of the commercial importance of this cyclisation it was studied with some more acidic catalysts. Cyclisation by refluxing with the super acid Nafion H[29] in nitromethane at 105° for 2 h. gave a complex mixture containing α- (33%) and β-ionone (4%). At lower temperatures (for example, refluxing with 60-80° pet. ether), there was no reaction.

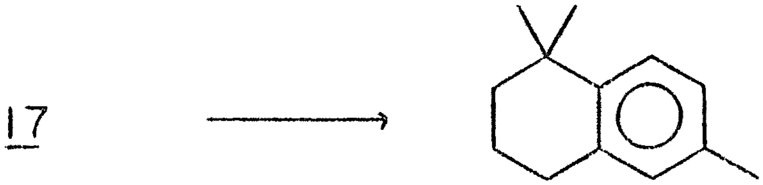
Cyclisation of ψ-ionone with PPA in xylene at room temperature (~30°) gave a single product in 60% yield. From its spectral data (IR: C=C 1615, 1500 cm^{-1}; ArH 820 cm^{-1}. PMR: C-Me's, 6H, s, 1.24 ppm, Ar-$C\underline{H}_3$, 3H, s, 2.21 ppm; Ar-$C\underline{H}_2$, 2H, t, 2.66 ppm, J = 6 Hz; Ar$\underline{H}$, 3H, m, 6.7-7.2 ppm), it was identified as ionene (41). This was further confirmed by synthesising ionene by cyclodehydration of β-ionone using iodine as catalyst.[30] The present method of PPA cyclisation of ψ-ionone to ionene (41) is superior to the older procedure in terms of ease of operation and yield.

Ionene is obviously derived from the further cyclisation of initially formed α- and or β-ionone. When the same reaction was carried out at much lower temperature (5-10°) for less time (15 min.), the product contained ionene (8%), α-(35%) and



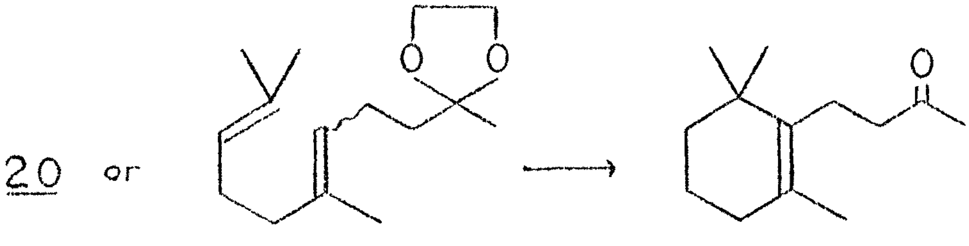
39 40

Eq. 12



41

Eq. 13



42 43

Eq. 14

β-ionone (44%). Attempts to find out conditions in which β-ionone is the sole product were unsuccessful.

Finally, cyclisation of geranylacetone (20) (cis/trans) with molar equivalent of $MeSO_3H$ at -5° for 12 h gave dihydro-β-ionone (43) in 50% yield. Similar cyclisation of geranylacetone cyclic ethylene ketal (42) gave dihydro-β-ionone (43) in 60% yield (Eq. 14). Obviously, the ketal was hydrolysed during aqueous work-up.

This cyclisation of geranylacetone and its cyclic ethylene ketal is distinct from the known cyclisations (see introduction) in that it gives dihydro-β-ionone (43) rather than the bicyclic ether (21). The former is a useful intermediate in the synthesis of monocyclofarnesol.[31]

EXPERIMENTAL

For general remarks, see Chapter I, Section I.

Materials

1. **Sulfolane:** The commercial solvent was dried by passing through a column of molecular sieves (3A). The material was then distilled through a spinning band column. The middle cut (85% yield) was collected and stored over molecular sieves.

2. **Nitromethane:** The commercial solvent was purified as follows:[32] It was washed thrice with a solution containing 25 g. of $NaHCO_3$ and 25 g. of $NaHSO_3$ per liter, then with water, 5% H_2SO_4 aq, water, 5% $NaHCO_3$ aq and dried overnight over Na_2SO_4, then passed through a column of molecular sieves (3A) and distilled from a small amount of sieve powder.

3. **Methane sulfonic acid:** The bench reagent (Fluka) was purified by distillation; b.p. 120-2°/0.1 mm.

4. **Nafion H:** The super acid Nafion H[29] was liberated from its potassium salt, Nafion K (Du Pont) by washing with Conc. HNO_3 and water and dried at 120° for 6 h.

5. **Citral (6):** Lemon grass oil was rectified twice and the fraction containing >95% (GLC) citral was used.

6. *Geranic acid (8/9)*: Oxidation of citral with Ag_2O[33] furnished geranic acid (8/9) in 94% yield; b.p. 112-6°/0.7 mm (lit.[33] b.p. 153°/11 mm).

IR (neat): CO_2H 3040-3500, 2660, 2580, 1690 cm^{-1};
C=C 1640 cm^{-1}.

PMR (CCl_4): C=C Me_2, 3H, singlets at 1.60, 1.68 ppm;
C=C-CH_3, s, 1.92 ppm for *cis*- and s, 2.16 ppm for *trans*-isomer; C=CH-, 1H, m, 5.1 ppm; C=CH-CO-, 1H, s, 5.66 ppm;
CO_2H, 1H, bs, 12.75 ppm.

7. *Methyl geraniate (39)*: Esterification of geranic acid with diazomethane gave methyl geraniate (39) in quantitative yield; b.p. 118-20°/15 mm (lit.[34] b.p. 117°/14 mm).

IR (neat): CO_2CH_3 1730 cm^{-1}; C=C 1660, 860 cm^{-1}.

PMR (CCl_4): C=CMe_2, 3H, singlets at 1.62, 1.68 ppm; HC=C-CH_3,
d, 1.87 for *cis*- and d, 2.12 ppm for *trans*-isomer,
J = 1.5 Hz; OCH_3, 3H, s, 3.61 ppm; C=CH, 1H, m, 5.1
ppm; C=CH-CO-, 1H, s, 5.6 ppm.

8. *ψ-Ionone (17)*: Condensation of acetone with citral in presence of NaOH aq gave ψ-ionone (17) in 85% yield;[35] b.p. 120-2°/3 mm (lit.[35] b.p. 124-6°/4 mm).

IR (neat): CO 1670 cm^{-1}; C=C 1630, 1590, 980 cm^{-1}

PMR (CCl_4): $C{=}C\ \underline{Me}_2$, 3H, singlets at 1.62, 1.70 ppm;
$C{=}C{-}C\underline{H}_3$, 3H, s, 1.93 ppm; $COC\underline{H}_3$, 3H, s, 2.18 ppm;
$C_9{-}\underline{H}$, 1H, bm, 5.1 ppm; $C_3{-}\underline{H}$ and $C_5{-}\underline{H}$, 2H, m, 5.88-6-15 ppm;
$C_4{-}\underline{H}$, 1H, m, 7.15-7.51 ppm.

9. α-Ionone (19): An authentic sample of α-ionone was prepared by cyclisation of ψ-ionone with H_3PO_4;[16] b.p. 78-80°/2 mm.

IR (neat): CO 1670 cm^{-1}; C=C 1615, 980 cm^{-1}.

PMR (CCl_4): $C\underline{Me}_2$, 3H, singlets at 0.88, 0.95 ppm; $C{=}C{-}C\underline{H}_3$
3H, s, 1.6 ppm; $COC\underline{H}_3$, 3H, s, 2.18 ppm; $C{=}C\underline{H}$, 1H, bs,
5.5 ppm; $C{=}C\underline{H}{-}CO{-}$, 1H, m, 5.88-6.12 ppm; $C\underline{H}{=}CH{-}CO$,
1H, m, 6.38-6.68 ppm.

10. β-Ionone (18): An authentic sample of β-ionone was prepared by cyclisation of ψ-ionone with H_2SO_4 in CH_2Cl_2;[12] b.p. 100-2°/2 mm (lit.[12] b.p. 127-8°/10 mm).

IR (neat): CO 1670 cm^{-1}; C=C 1615, 980 cm^{-1}.

PMR ($CDCl_3$): $C\underline{Me}_2$, 6H, s, 1.08 ppm; $C{=}C{-}C\underline{H}_3$, 3H, s, 1.68 ppm;
$COC\underline{H}_3$, 3H, s, 2.18 ppm; $C{=}C\underline{H}{-}CO{-}$, 1H, d, 6.1 ppm,
J = 17 Hz; $C\underline{H}{=}CH{-}CO{-}$, 1H, m, 7.10-7.40 ppm.

11. Geraniol (12): Commercial sample (Koch-Light) was purified by distillation.

12. Geranyl acetate (11): Acetylation of geraniol with Py/Ac_2O gave geranyl acetate (11) in 93% yield; b.p. 110-4°/10 mm (lit.[36] b.p. 110-5°/10 mm).

IR (liq. film): CO 1740 cm^{-1}; C=C 1670, 830 cm^{-1}.

PMR (CCl_4): C=C-Me's, 3H, singlets at 1.58, 1.65, 1.68 ppm; $OCOCH_3$, 3H, s, 1.95 ppm; CH_2OAc, 2H, d, 4.48 ppm, J = 7Hz; $(CH_3)_2$ C=CH, 1H, bs, 5.05 ppm; CH_2-CH=C-, 1H, t, 5.3 ppm, J = 7Hz.

13. Citral anil: This was prepared from aniline and citral according to the known[7] method and used without further purification.

14. Geranylacetone (20): Condensation of linalool with methyl acetoacetate, according to the method of Carroll,[37] gave 20 in 80% yield; b.p. 120-3°/ 10 mm (lit.[37] b.p. 120-4°/10 mm).

IR (liq. film): CO 1710 cm^{-1}.

PMR (CCl_4): C=C-CH_3's, 3H, singlets at 1.60, 1.68, 1.68 ppm; $COCH_3$, 3H, s, 2.05 ppm; two olefinic protons, 2H, bm, 5.05 ppm.

15. Cyclic ethylene acetal of geranylacetone (42): A mixture of geranylacetone (1.g, 5.2 mmol), ethylene glycol (0.64 g, 10.4 mmol) and PTS.H_2O (20 mg) was refluxed in dry benzene for 6 h. with continuous removal of water. The reaction

mixture was poured in water (50 ml) and extracted with ether. The combined ether extracts were washed with 5% $NaHCO_3$ aq (10 ml), water (10 ml) and brine (10 ml) and dried (Na_2SO_4). Removal of solvent followed by distillation gave the acetal 42 as a colorless oil (1.08 g, 88%), b.p. 130°(bath)/ 2 mm.

IR (liq. film) (Fig. 1): C=C 1670, 865, 835 cm^{-1}.

PMR (CCl_4) (Fig. 2): $\overset{\text{O O}}{\text{C}} - \underline{CH_3}$, 3H, s, 1.24 ppm; C=C $\underline{Me}_2$, 3H, singlets at 1.60, 1.68 ppm; $\underline{C-O-C\underline{H}_2C\underline{H}_2-O}$, 4H, s, 3.88 ppm; two olefinic protons, 2H, bm, 5.1 ppm.

Cyclisation of geranic acid (8/9).

Geranic acid (3 g, 0.018 mole) was taken up in dry CH_3NO_2 (7.5 ml). $MeSO_3H$ (0.3 g, 3.1 mmol) in CH_3NO_2 (2.5 ml) was added slowly (0.5 h) and the mixture allowed to stir at room temperature (~30°) for 5 h, when solid α-cyclogeranic acid (10) separated out. Excess CH_3NO_2 was flashed off, the concentrate was taken up in ether (10 ml), washed with water (5 ml x 2), brine (5 ml) and dried (Na_2SO_4). Removal of solvent gave a solid (2.86 g, 96%). This solid was recrystallised from $CHCl_3$/pet. ether to give α-cyclogeranic acid (10); m.p. 105-6° (lit.[4] m.p. 105-6°).

IR (nujol): CO_2H 3070-3400, 2700, 2620, 1690 cm^{-1}; C=C 1650, 820 cm^{-1}.

PMR (CCl_4): C-$\underline{Me}$'s, 3H, singlets at 0.96, 1.02 ppm;
$C=C-C\underline{H}_3$, 3H, s, 1.7 ppm; $C\underline{H}CO_2H$, 1H, s, 2.54 ppm;
$C=C\underline{H}$, 1H, bs, 5.55 ppm, W_h=8Hz; $CO_2\underline{H}$, 1H, bs, 11.45 ppm.

Similar result was obtained with PTS.H_2O.

Cyclisation of methyl geraniate (<u>39</u>).

Methyl geraniate was cyclised as described above to give methyl α-cyclogeraniate (<u>40</u>) in 96% yield; b.p. 95-100° (bath)/3.5 mm.

IR (liq. film): CO_2CH_3 1735, 1235 cm^{-1}; C=C 825 cm^{-1}.

PMR (CCl_4): $C\underline{Me}_2$, 3H, singlets at 0.91, 0.93 ppm; $C=C-C\underline{H}_3$,
3H, s, 1.63 ppm; $C\underline{H}CO_2CH_3$, 1H, bs, 2.52 ppm, W_h = 4.5 Hz;
$OC\underline{H}_3$, 3H, s, 3.63 ppm; C = C$\underline{H}$, 1H, bs, 5.51 ppm, W_h = 8 Hz.

Cyclisation of geranyl acetate (<u>11</u>).

A solution of $MeSO_3H$ (0.085 g, 0.89 mmol) in nitromethane (0.35 ml) was added dropwise to a solution of geranyl acetate (<u>11</u>) (0.5 g, 2.6 mmol) in the same solvent (1.1 ml), being stirred at -15°. The stirring was continued at -15° for 1 h. Usual work-up gave α-cyclogeranyl acetate (<u>13</u>) (0.25 g, 50%); b.p. 110-5°(bath)/4 mm (lit.[5] b.p. 85-7°/1 mm).

IR (liq. film): $OCOCH_3$ 1745, 1240 cm^{-1}; C=C 1640 cm^{-1}.

PMR (CCl_4): C$\underline{Me}_2$, 3H, singlets at 0.93, 0.97 ppm; C=C-C$\underline{H}_3$, 3H, s, 1.74 ppm; OCOC$\underline{H}_3$, 3H, s, 1.97 ppm; C$\underline{H}_2$OAc, 2H, m, 4.0-4.15 ppm; C=C$\underline{H}$, 1H, bs, 5.43 ppm.

Cyclisation of ψ-ionone (17):

(i) With $MeSO_3H$: A solution of $MeSO_3H$ (0.5 g, 5.2 mmol) in nitromethane (4.2 ml) was added dropwise to a stirred and cooled (-5°) solution of ψ-ionone (1 g, 5.2 mmol) in nitromethane (2.2 ml) and the reaction mixture was kept at -5° for 24 h. Usual work-up gave a colorless liquid (b.p. 110-5° (bath)/4 mm) (0.6 g), which contained 67% α- and 12% β-ionone, identified by co-injection on GLC (10% SE-30 on chromosorb W, 6', 170°, 60 ml/min) with authentic samples.

(ii) With PPA: ψ-Ionone (1.17 g, 6.1 mmol) in xylene (2.5 ml) was added dropwise to polyphosphoric acid (prepared by dissolving 1.3 g of P_2O_5 in 0.65 ml of orthophosphoric acid) at 20° with stirring. Stirring was continued at room temperature (~30°) for 1 h. The reaction mixture was quenched with ice-cold water and extracted with ether (10 ml x 3). The combined ether extracts were washed with water (10 ml) and brine (10 ml) and dried (Na_2SO_4). Removal of solvent followed by distillation gave ionene (0.637 g, 60%); b.p. 115-20°(bath)/10 mm (lit.[30] b.p. 107-8°/10 mm).

UV (Ethanol):				
	λ_{max}	227.5	270	278 nm
	ϵ_{max}	2740	1410	1440.

IR (liq. film): C=C 1615, 1500, 820 cm^{-1}; C$\underline{Me}_2$ 1365, 1385 cm^{-1}.

PMR (CCl_4): C-$\underline{Me}$'s, 6H, s, 1.24 ppm; $C\underline{H}_2C\underline{H}_2$, 4H, m, 1.66 ppm; Ar-$C\underline{H}_3$, 3H, s, 2.21 ppm; Ar-$C\underline{H}_2$, 2H, t, 2.66 ppm, J = 6 Hz; Ar$\underline{H}$, 3H, m, 6.7-7.2 ppm.

Cyclisation of geranylacetone.

Methane sulphonic acid (0.5 g, 5.2 mmol) in nitromethane (4.2 ml) was added to a stirred and cooled (-5^o) solution of geranylacetone (1.01 g, 5.2 mmol) in nitromethane (2.2 ml). The reaction mixture was kept at -5^o for 24 h. Usual work-up gave dihydro-β-ionone (43) (0.25 g, 50% yield); b.p. 120-5^o(bath)/3 mm (lit.[31] b.p. 60-4^o/0.2 mm).

IR (liq. film) (Fig. 3): CO 1720 cm^{-1}.

PMR (CCl_4) (Fig. 4): C-$\underline{Me}$'s, 6H, s, 0.99 ppm; C=C-$C\underline{H}_3$, 3H, s, 1.57 ppm; CO$C\underline{H}_3$, 3H, s, 2.06 ppm.

The ketal 42 was cyclised with $MeSO_3H$ in $MeNO_2$ exactly as described above. The product was dihydro-β-ionone obtained in 60% yield.

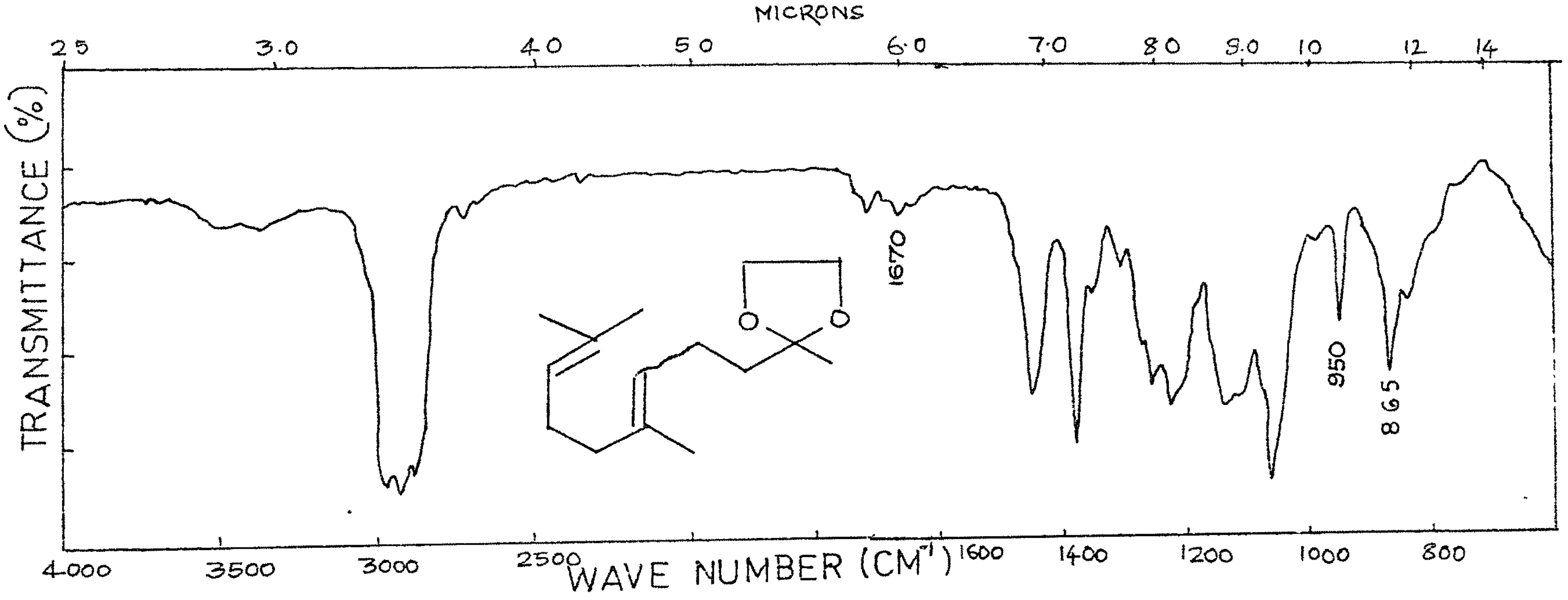


FIG.1:IR SPECTRUM OF THE KETAL 42

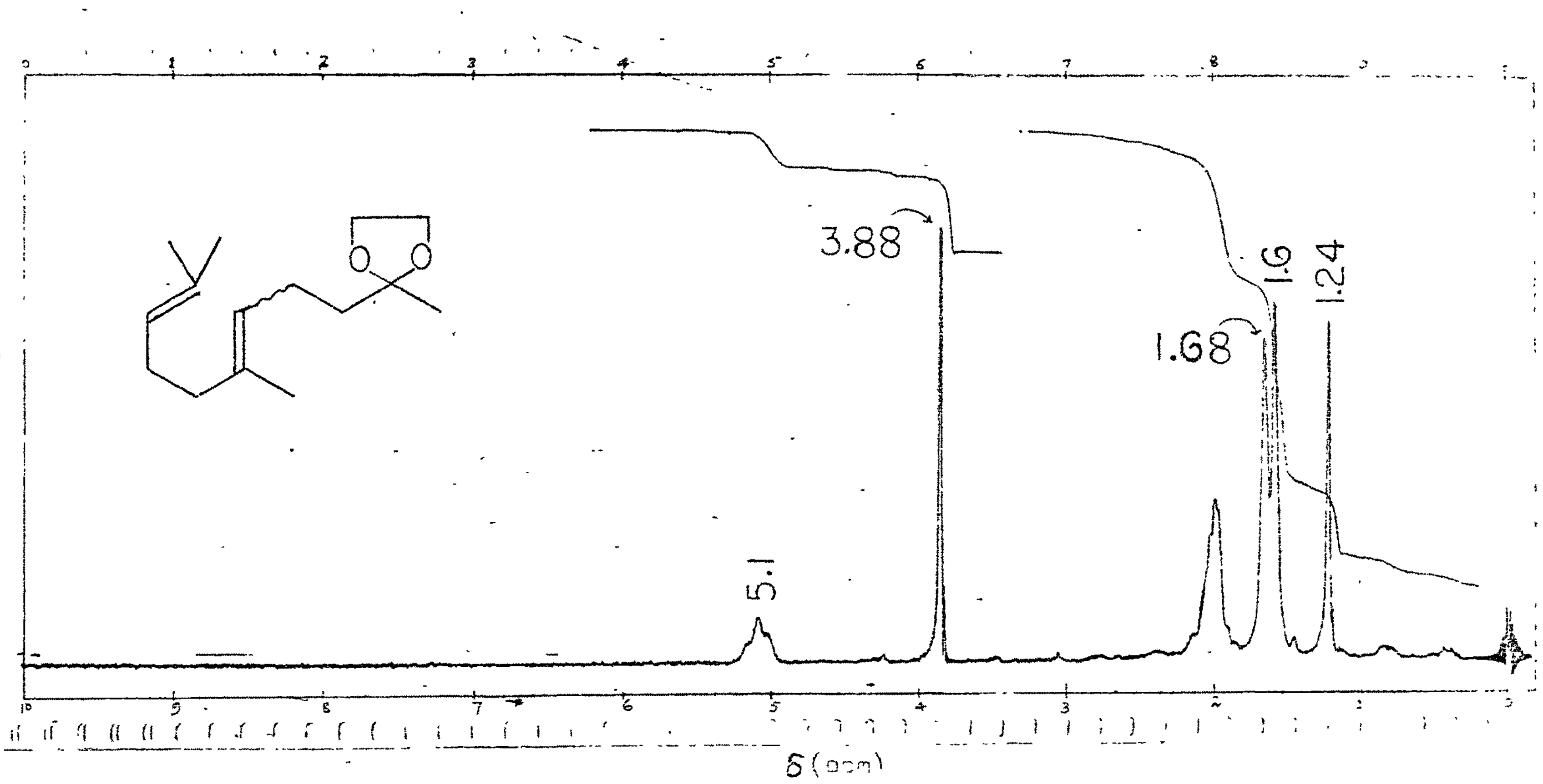


FIG. 2 : NMR SPECTRUM OF THE KETAL 42

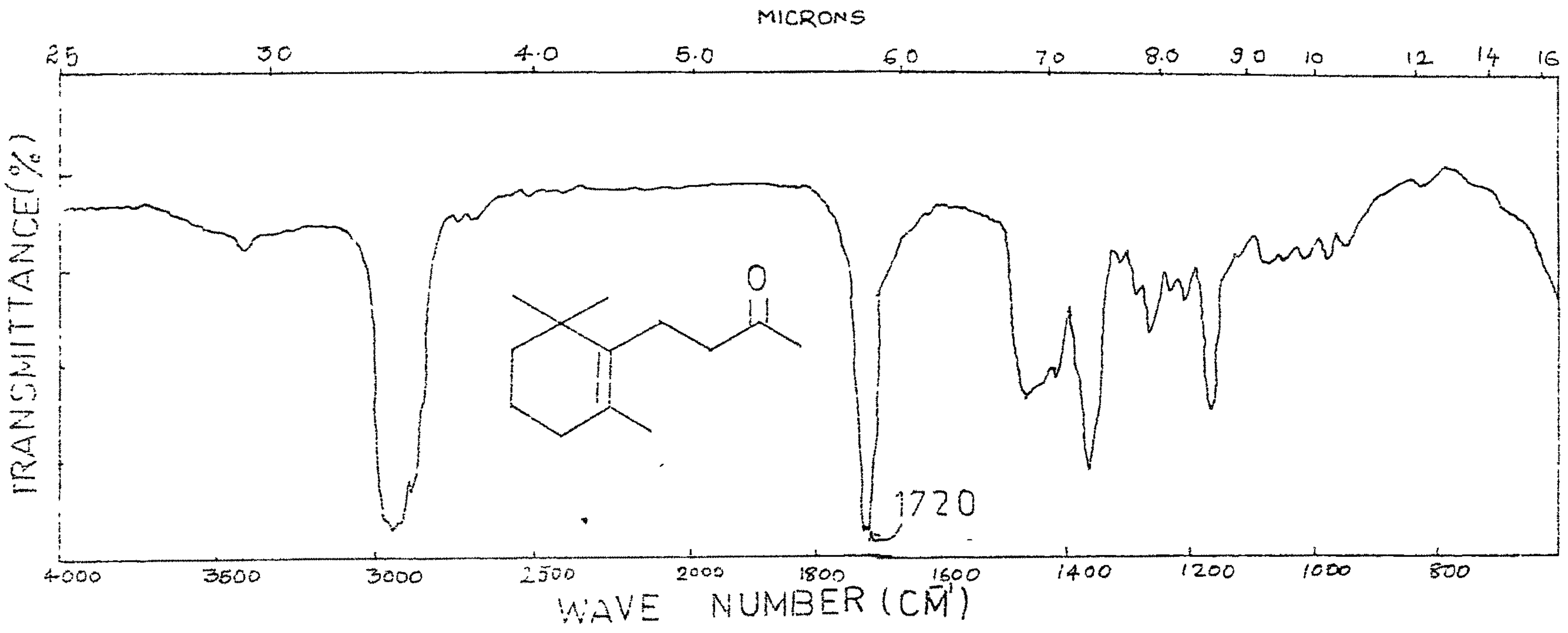


FIG.3: IR SPECTRUM OF DIHYDRO-β-IONONE (43)

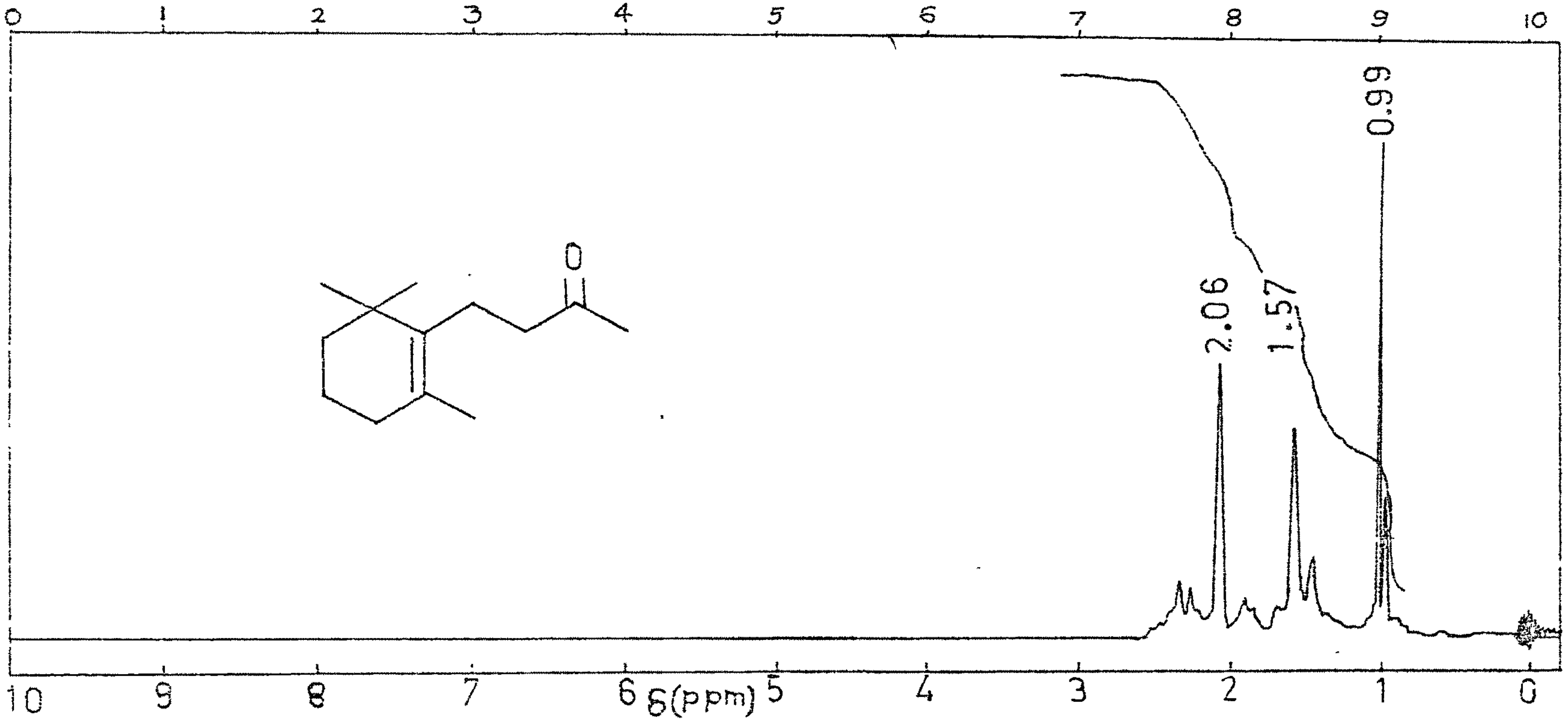


FIG.4 : PMR SPECTRUM OF DIHYDRO-β-IONONE (<u>43</u>)

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