P A R T 'B'

SOME TRANSFORMATIONS IN ISOLONGIFOLENE SERIES

CHAPTER I

'STERIC DIVERSION' IN ELECTROPHILIC ADDITIONS

STERIC DIVERSION IN ELECTROPHILIC ADDITIONS

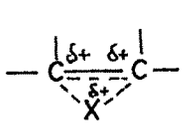
Abstract

Addition of halogens and pseudo-halogens to isolongifolene does not yield any normal addition products due to severe steric hindrance to the approach of the counter ion at C-7. Initially formed halogenonium ions undergo elimination or rearrangement to give a mixture of products 10-12. The term 'Steric Diversion' is suggested to describe all such cases where deviation from normal course occurs due to steric reasons.

STERIC DIVERSION IN ELECTROPHILIC ADDITIONS

1. INTRODUCTION

The addition of electrophilic reagents such as halogens, to simple acyclic and cyclic olefins is usually straightforward and results in trans-stereochemistry. However, it is recognised that many such additions show variable stereoselectivity and the nature of the reactive species is dependent on the nature of the olefin, the electrophile, the solvent and other factors. Details of the mechanism of such electrophilic additions have been extensively investigated during the past several decades and the current position has been ably summarised in some recent review articles[1]. It is generally accepted that addition of halogens, pseudo-halogens and the like proceeds through a 3-membered activated complex (1), which may be strongly bridged (2), weakly bridged (3) or may lead to a fully developed carbonium ion at the more substituted carbon atom.



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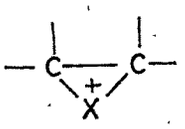

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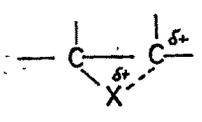

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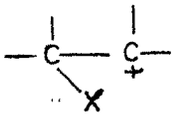

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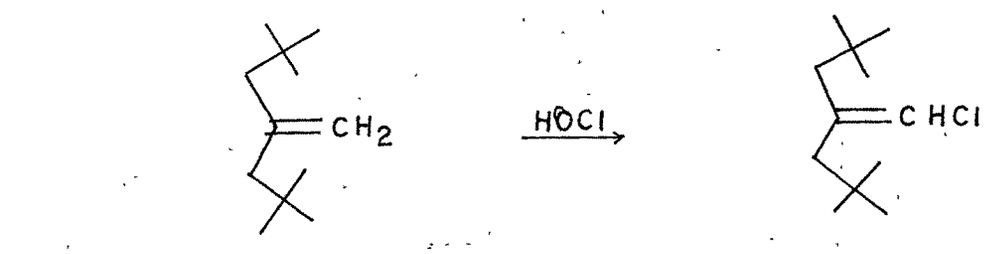
Conceivably, if the more substituted end of the ethylenic linkage is sterically shielded such that the approach of the nucleophile is essentially blocked, the resulting product cannot be expected to be the result of a simple addition reaction, but would be complicated by the intervention of other pathways, such as elimination/rearrangement open to 4 and, the product, in more susceptible cases, may entirely be the result of such alternative pathways. To illustrate this point, the reaction of chlorine-free hypochlorous acid with unsym-dineopentylethylene (5) and 2,4,4-trimethyl-1-pentene (7) may be cited: 5 gave a complex mixture in which 6 predominated (48%) and no oxygen-containing functionality was detected in the total product, while 7, which is comparatively less hindred, furnished 34% of 'normal' product (8) and 46% of elimination product (9)[2]. A literature survey revealed that such 'abnormal'



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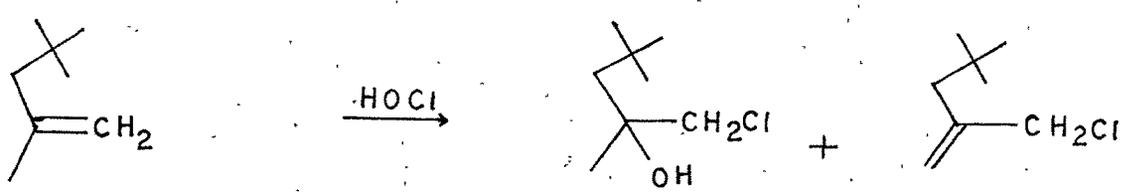

7 8 9

reactions have been often encountered, especially in the area of natural products chemistry and mention may be made of the following olefin reactions: halogen additions[3-9], halogen azide additions[10], Kharasch additions[11,12], ozonolysis[13-16], Chromic acid oxidation[17], and oxirane cleavage[18].

It is felt that this diversion of a 'normal' reaction pathway, because of purely steric hindrance, is a fairly general phenomenon and is responsible for the formation of so-called 'abnormal' products in several reactions, and the general term Steric diversion is proposed to describe this switch over from the 'normal' route*.

2. ELECTROPHILIC ADDITIONS TO ISOLONGIFOLENE

In the context of above description, it was felt that isolongifolene (10a), in which approach at C-7 is severly hindered, could provide a suitable substrate for studying 'Steric diversion'.

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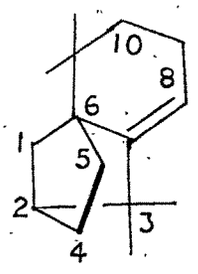
*Steric hindrance to attack at the more substituted carbon atom has been invoked[19] to explain the formation of abnormally oriented adducts in the addition of certain reagents to some olefins. In other similar cases, different explanations have been offered[20] and hence, these cases are not typical examples of steric diversion.

Wagner-Meerwein rearrangements accompanying electrophilic addition to certain olefins and arising from well-recognised stereoelectronic factors are distinct from cases of steric diversion, where purely steric hinderance blocks the 'normal' course of the reaction.

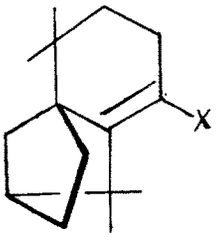
2.1. Reaction with bromine

Isolongifolene, when allowed to react with one molar equivalent of bromine in presence of aqueous sodium carbonate, gave a mixture of products which contained besides unreacted isolongifolene (12.5%), 8-bromoneoisolongifolene (11b, 70%) as the major product along with smaller quantities of the corresponding dibromo derivative 11c (9%) and 8-bromoisolongifolene (10b, 8%). 8-Bromoneoisolongifolene (11b) was clearly monoolefinic : yellow colour with tetranitromethane (TNM); PMR (Fig. 1): -C=C<u>H</u>-CH-, d, 5.65, J = 4.0 Hz, -C<u>H</u>Br, dd, 4.28, J_1, J_2 = 7.5, 8.0 Hz; IR (Fig. 13): C=CH-, 819 cm^{-1}



Isolongifolene (10a)

and could arise by the way of a Wagner-Meerwein rearrangement of the bromonium ion 13. The configuration of bromine atom in 11b is presumed from the known preference of reagents to attack from the endo side of bornyl part of isolongifolene[21].

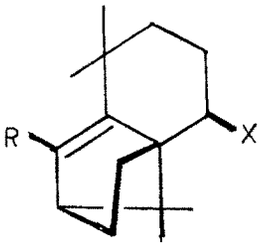


10

a X=H

b X=Br

c X=I



11

a R=X=H

b R=H, X=Br

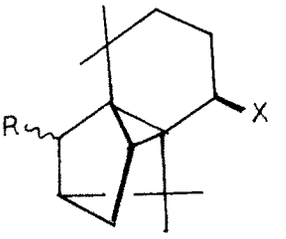
c R=X=Br

d R=H, X=OH

e R=H, X=Cl

f R=X=Cl

g R=H, X=I



12

a R=H, X=Cl

b R=H, X=OH

c R=X=Cl

d R=Cl X=OAc

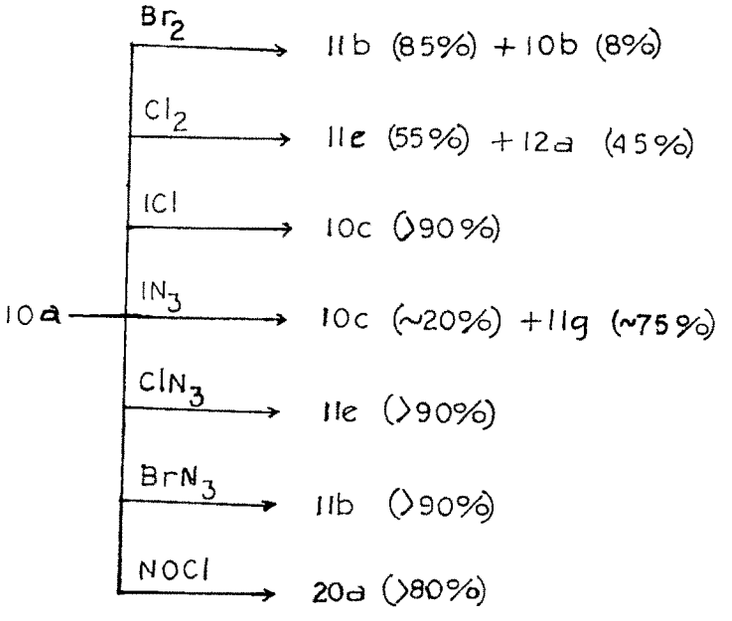


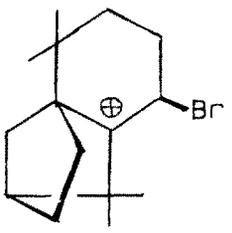
CHART I

Also in the PMR spectrum of 11b, the splitting pattern of proton α to Br is similar to that of proton α to OH in 11d[22] (J_1= 7.0, J_2= 8.0). In the alcohol epimeric to 11d, the vicinal coupling constants for the corresponding proton are small (ill-resolved dd, W_H = 9Hz). The structure of 11b was further confirmed by transformation to known derivatives. On hydrogenation in presence of Raney nickel and alcoholic sodium hydroxide, it furnished the known monoolefinic hydrocarbon, neoisolongifolene[22] (11a). Dehydrobromination of 11b in presence of Li_2CO_3 in refluxing dimethylformamide furnished a nonconjugated diene 14 (orange colour with TNM; PMR (Fig. 6): C=C<u>H</u>-CH-, d, 5.60, J= 3.0 Hz, -CH_2-C<u>H</u>=CH-, ddd, 5.86, J_1, J_2, J_3 = 2.6, 4.6, 10 Hz, -CH_2-CH=C<u>H</u>-, m, 5.47-5.65; IR (Fig. 15): C=CH-1645, 1620, 820, 710 cm^{-1}). The structure of 14 was substantiated by its correlation to neoisolongifolene (11a) by selective hydrogenation of C_8-C_9 double bond over Raney nickel. Dehydrobromination of 11b, in refluxing DMF in absence of Li_2CO_3, provided the known conjugated diene[23] 15. The results are rationalised by assuming that initially formed nonconjugated diene 14 is isomerized by HBr liberated during the reaction to the more stable diene 15. Indeed, the nonconjugated diene 14 on treatment with acetic acid is mostly converted to 15.

The structures of 1,8-dibromoneoisolongifolene [11c, yellow colour with TNM; PMR (Fig. 3): no proton in olefinic region, -CHBr, dd, 4.20, J_1, J_2 = 7.5, 8.0 Hz; IR: (Fig. 4): C=C 1600 cm^{-1}] and 8-bromoisolongifolene (10b, yellow colour with TNM; PMR: no protons in the olefinic or α-to Br regions) were assigned on the basis of spectral data.

2.2. Reaction with Chlorine

Chlorination of isolongifolene in the presence of aqueous sodium carbonate gave a 1:1 mixture of 8-chloroneoisolongifolene [11e, yellow colour with TNM; PMR (Fig. 2): -C=CH-CH, d, 5.67, J = 3.5 Hz, -CHCl, dd, 4.11, J_1, J_2= 7.0, 9.0 Hz; IR (Fig. 14): C=CH-, 1640, 821 cm^{-1}] and a tetracyclic chloride 12a [PMR (Fig. 7): Me's 0.85, 0.96, 0.98, 1.00, -CHCl, t, 4.67, J = 4.5 Hz]. 12a could not be isolated pure as it decomposed even when heated to 50-60° but its presence in the reaction mixture was clearly discernible from the PMR spectrum. Even when the chlorination was carried out in the presence of anhydrous sodium carbonate under the conditions reported in a recent patent[24], only 11e and 12a were formed in the ratio of 2:1. This is in sharp contrast to the reported claim that the major product is the allylic chloride 16. 8-Chloroneoisolongifolene (11e) was isolated pure by fractional distillation of the reaction mixture and the structure was assigned by its dehydrochlorination to



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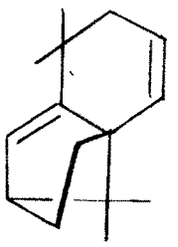

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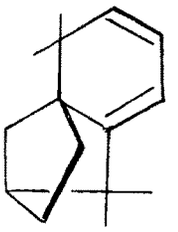

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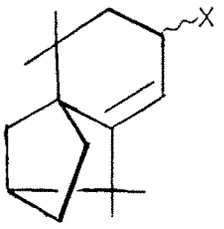
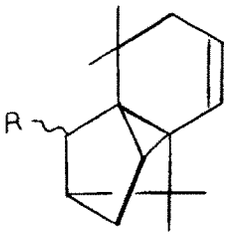


16 a X=Cl
b X=OAc



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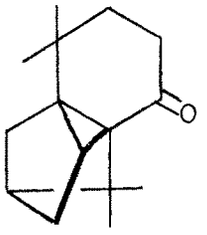
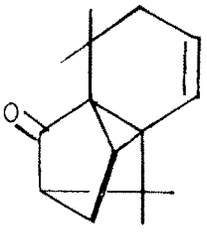


18

a R=H
b R=Cl
c R=OAc
d R=OH



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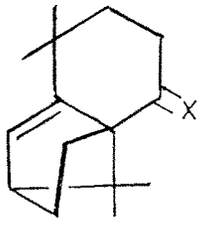
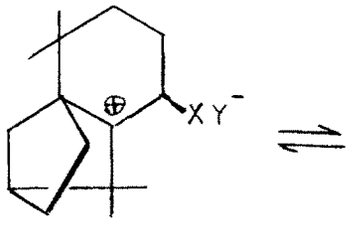


20 a X=NOH
b X=O



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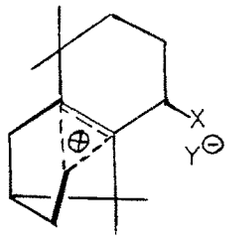

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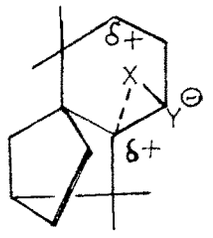

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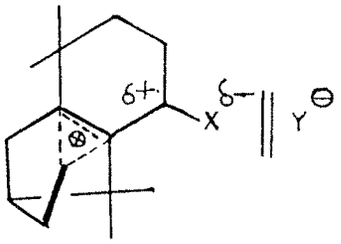
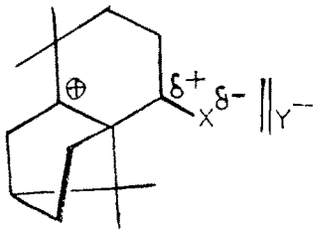


22 A



24

CHART II

nonconjugated diene 15. These results also preclude 16 as the reaction product, as it would have provided the conjugated diene 14 on similar dehydrochlorination. The same patent also describes the acetolysis of the chlorination product which is claimed to give 16b. We, however, observe that acetolysis of neoisolongifolyl halides 11b and 11e gives a rearranged tertiary acetate*.

The tetracyclic chloride 12a, due to its labile character, was not isolable. The reaction mixture on heating to 90° for 1 hr gave a mixture of 11e** and dehydrocycloisolongifolene (17a) which could be separated by fractional distillation; the latter was identical in all respects (IR, PMR, GLC on several columns) with an authentic sample prepared by a known method[22]. The formation of 12a was further confirmed by solvolysis of the reaction mixture with CaO and water which provided a mixture of 11e and a secondary alcohol; the two were easily separated by chromatography over alumina. The identity of the secondary alcohol with cycloisolongifolol (12b) was established by IR, PMR, GLC on several columns and

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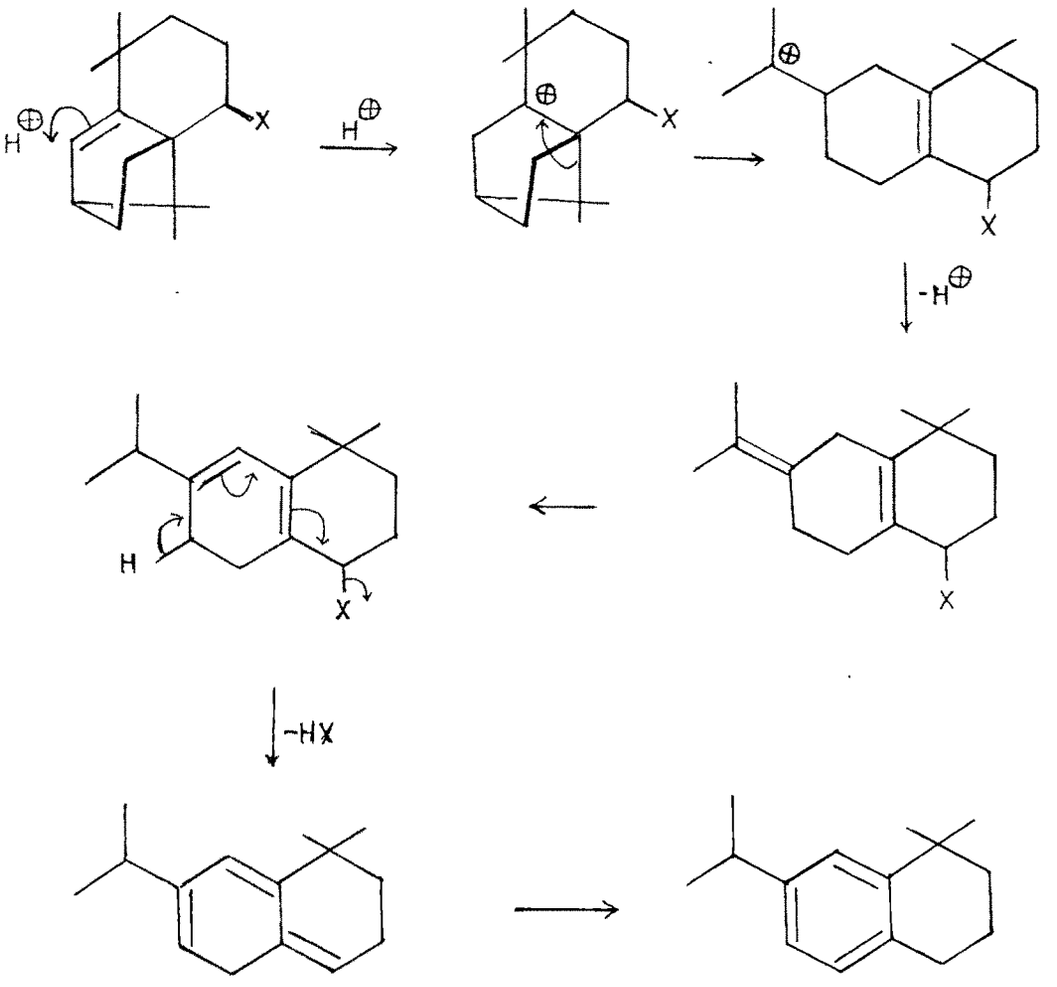
* The structure of this acetate has been elucidated and details are described in the next chapter.

**11e as well as 11b undergoes in interesting rearrangement on treatment with 90% H_2SO_4 or $BF_3 \cdot Et_2O$ to give a tetralin derivative (25), as shown in Chart III.



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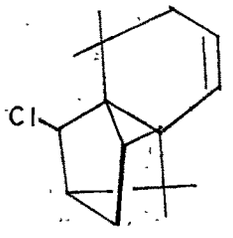
X=Br OR Cl

CHART III FORMATION OF TETRALIN

Jones oxidation to cycloisolongifolene (18; IR: C=O, 1663 cm^{-1}) (see Chart II).

Chlorination of isolongifolene with excess of chlorine in presence of anhydrous Na_2CO_3 yielded mainly the mono- and di-chloro-cycloisolongifolene derivatives 12a and 12c in the ratio of 1:2, along with small quantity of 11f. The dichloride 12c is infact a secondary product derived from 11e by further chlcrination via the corresponding chloronium ion. The mixture of 12a and 12c on heating underwent dehydrochlorination to give



17b

mostly the olefins 17a and 17b which were separated by fractional distillation. The structure of 17b [PMR (Fig. 9): CHCl, d, 4.41, J= 2Hz, CH_2-CH =CH, m, 5.32-5.53, CH_2-CH=CH- dt, 5.90, J_1 = 10 Hz, J_2, J_3 = 1.5 Hz; IR (Fig. 16): C=CH 1640, 690 cm^{-1}] was confirmed by its reduction to 17a with lithium aluminium hydride. The configuration of chlorine atom

at C-1 in 12c or 17b depends on the approach of chlorine molecule from exo or endo side of the bornyl part and is difficult to assign on the basis of present data. However, the location of one chlorine atom at C-1 in 12c was indicated by the following solvolytic experiments. Solvolysis of 12c with NaOAc in acetic acid at 80° resulted in the formation of two acetates, 17c [PMR (Fig. 11): $OCOCH_3$, s, 1.98 -CH OAc, d, 5.24, J = 2.0 Hz, CH_2-CH=CH, m, 5.28-5.50, CH_2-CH=CH-, dt, 5.91, J_1 = 10Hz, J_2= J_3= 1.5 Hz; IR: $OCOCH_3$ 1720, C=C, 1632, 699 cm^{-1}] and 12d (PMR: $OCOCH_3$, s, 1.94, -CHCl, d, 4.30, J= 1.5 Hz, CHOAc, t, 5.34, J= 5Hz; IR: $OCOCH_3$, 1730 cm^{-1}). Hydrolysis of 17c with alcoholic alkali or 17b with CaO in water gave the alcohol 17d [PMR (Fig. 10): CHOH, d, 4.30, J= 1.5 Hz, CH_2-CH=CH-, m, 5.27-5.49, =CH -, dt, 5.91, J= 10Hz, J_2=J_3= 1.5Hz] which was shown to be a secondary alcohol by oxidation with Jone's reagent to the ketone 19.

2.3. Reaction with Pseudohalogens

2.3.1. Iodine chloride: Iodine chloride reacts with isolongifolene in presence of aqueous or anhydrous Na_2CO_3 in CCl_4 or CH_3CN to give exclusively the vinyl iodide 106.

2.3.2. Chlorine azide: On reaction with chlorine azides[25]

isolongifolene yielded mostly the rearranged chloride 11e. Small traces of an azido compound were also formed. Significantly, cycloisolongifolyl chloride 12c was not formed.

2.3.3. Bromine azide: The rearranged bromide 11b was the major product of the reaction of bromine azide[26] with isolongifolene.

2.3.4. Iodine azide: Reaction of isolongifolene with iodine azide[27] in CH_3CN differed from that with iodine chloride in that a 1:3 mixture of 10c and 10a (PMR: -CHI, dd, 4.35, J_1, J_2= 8.0, 9.0 Hz, C=CH-CH, d, 5.48, J = 3.5 Hz; IR: C=C 1632, 815 cm^{-1}) was obtained.

2.3.5. Reaction with nitrosyl chloride: Reaction of nitrosyl chloride with isolongifolene gave the rearranged nitroso derivative corresponding to 11, which existed solely as the oxime 20a. The oxime was identical with that prepared from the ketone 20b.

3. DISCUSSIONS

Irrespective of whether the additions of halogens[28] and pseudohalogens[29] to isolongifolene take place *via* a free radical or ionic mechanism, no normal addition products have been obtained. The etiology of steric diversion in this case

can be ascribed to severe steric hindrance to the approach of addenda at C-7. Three different pathways leading to the sterically diverted products 10, 11 or 12 are followed. But a wide difference in the product composition is observed with different reagents and may be consequent of the involvement of cyclic or acyclic halogenonium ions, intimate or solvent separated ion pairs, the nature of the solvent and other factors. It is not possible to draw rigorous conclusions on the basis of data at hand but the following reasoning may qualitatively explain the product formation in different cases.

The additions of halogens and pseudohalogens to isolongifolene have all been carried out in presence of air so that contributions from the radical pathway can be expected to be minimal. The ionic addition of the addendum X-Y to isolongifolene can give rise to an acyclic carbonium ion (21) which may be stabilised as nonclassical ion 22 or to a cyclic halogenonium ion 23. Whereas carbonium ion 22 can lead to the formation of all three 10, 11 or 12, it is improbable that 23 will undergo deprotonation to 12 or a Wagner-Meerwein rearrangement to 11 because of the lack of antiperiplanar orientation of the dimethylene bridge and C-X bond. It could, however, certainly be a precursor for vinyl halides, 10. Whether the transition state is represented by 22 or 23

will be dependent, besides other things, upon the bridging capacity of the electrophile which increases as Cl < Br < I[30].

Chlorination of isolongifolene in contrast to the addition of other electrophiles is unique in forming cyclo-isolongifolene derivative 12a, which is not formed even with chlorine azide. A similar difference in the reactions of camphene with chlorine[31] and other halogenoids[32] has been observed but no explanation has been offered for the difference. It is generally believed[33] that chlorine additions are better interpreted in terms of mechanisms involving intimate ion pair intermediates, whereas bromine additions also involve solvent separated ions. Further, it is believed[34] that azide ion is very similar to bromide ion in size and nucleophilicity. It is noteworthy that all additions where the gegen ion is either bromide or azide ion viz. addition of bromine or halogen azides; the rearranged products 11 are predominantly formed.

Plausibly, the solvent separated ion pairs 22A primarily rearrange to the ion 24 before forming the derivatives of 11.

In the case of reaction of iodine chloride to isolongifolene, the reactive intermediate may be the iodonium ion 23, which undergoes elimination to give the vinyl iodine 10c.

Similar factors may be operating in the formation of 12c and 11c during the reaction of isolongifolene with excess of chlorine and bromine respectively.

4. EXPERIMENTAL

All m.ps and b.ps are uncorrected. Light petroleum and petroleum refer to the fractions b.ps 40-60° and 60-80° respectively. All solvent extracts were finally washed with brine and dried.

TLC were carried out on SiO_2-gel layers (0.25 mm) containing 15% gypsum and activated at 110-115° (2 hr). $AgNO_3$ (15%)-SiO_2-gel layers without binder were employed[35].

Optical rotations were measured on a Schmidt + Haensch electronic polarimeter model Polatronic I.

The following instruments were used for spectral/analytical data: Perkin-Elmer Infrared Spectrometer, Model 267; Perkin-Elmer model R32 (90 MHz) NMR spectrometer; Varian Mat CH7 Mass Spectrometer (70 eV, direct inlet system); Hewlett-Packard 5712A and 7624A gas chromatographs (column: 360 cm x 5 cm; 3%,6'; 5%,6'; 10%,12'; 12% carbowax 20M and 3%,6' SE-30 on Chromosorb W, 60-80; H_2 as carrier gas). All PMR were taken in 15-20% soln in CCl_4 (unless otherwise stated) with TMS as internal standard; signals are reported in ppm (δ);

while citing PMR data the following abbreviations have been used: s(singlet), d(doublet), t (triplet), q (quartet), m (multiplet), b (broad) and W_H (half width). While summarising mass spectral data, besides the molecular ion, ten most abundant ions (m/e) are reported with their relative intensities.

All temperatures reported were internal temperatures of the reaction mixture. In all chlorination experiments weights reported were the increase in weight after passing chlorine.

4.1. Action of Halogens on Isolongifolene (10a)

4.1.1. Action of Bromine (one mol)

To a stirred slurry of isolongifolene (10a)(180 gm, 0.88 mol) in CCl_4 (750 ml) and 15% aq. Na_2CO_3 (1200 ml) at $-3 \pm 2^{\circ}$ was added dropwise bromine (48 ml, 0.85 mol) in CCl_4 (250 ml) during four hours. When the addition was over it was stirred at room temperature ($\sim 28^{\circ}$) for an additional four hours. The reaction mixture was transferred to a separating funnel and the organic layer was separated. Aqueous layer was extracted with CCl_4 (200 ml x 2) and the combined organic extracts were washed with water (250 ml x 3) and dried ($MgSO_4$). Solvent was removed under reduced pressure and residue (250 gm) was

fractionated. A small sample was distilled and analysed. GLC (carbowax 20M, 3%, 6'; temp. 150°) showed isolongifolene (10a) (12.5%, RRT 1), 8-bromoneoisolongifolene (11b) (60%, RRT 4.4), 8-bromoisolongifolene (10b)(10%, RRT 5.0) and 1,8-dibromoneoisolongifolene (3%, RRT 10.4), besides other minor products.

Frac.	b.p.	weight	Remarks
1	85-87°/1mm	52.5 gm	mostly isolongifolene containing 8-bromoneoisolongifolene.
2	105-110°/1mm	169 gm	8-bromoneoisolongifolene (GLC, 95% pure)
3	110-140°/1mm	14.7 gm	mixture of monobromide and dibromide .

Fraction 3 was redistilled.

Fraction 3a b.p. 110-130°/0.5 mm (4.0gm), mostly 8-bromoisolongifolene

Fraction 3b b.p. 130-132°/0.5 mm (6.2 gm) dibromide 11c

Fraction 3c b.p. 132-137°/0.5 mm (1.5 gm) mixture.

Frac. 2 was characterized as bromide 11b IR (Fig. 13): (liq.): -C=CH- 1610, 831, 819, 810 cm^{-1}. PMR (Fig. 1): -C-Me

each as singlet at 0.83, 0.95, 1.06, 1.09 ppm; C<u>H</u>Br (1H, dd, 4.28 ppm; J_1= 7.5 Hz, J_2= 8Hz); =C<u>H</u> (1H, d, 5.65 ppm, J= 4Hz). Mass: m/e 284 (M^+), 203 (100%), 175 (24%), 159 (12%), 147 (21%), 145 (13%), 133 (12%), 131 (16%), 119 (17%), 105 (19%), 91 (19%). Microanalysis: $C_{15}H_{23}Br$ requires C, 63.60; H, 8.18; Br, 28.21; found C, 64.34; H, 7.71; Br, 27.10%.

Frac. 3a was characterized as bromide <u>10b</u>. PMR: -C(Me)- <u>Me</u> each as singlet at 0.91, 0.91, 1.15, 1.30 ppm.

Frac. 3b was crystallized from pet. ether to give dibromide <u>11c</u> (m.p. 91-92°) $[\alpha]_D \pm 0$, IR (Fig. 4): C=CBr 1600 cm^{-1}, PMR (Fig.3): -C(Me)- <u>Me</u> each as singlet at 0.97, 0.97, 1.10, 1.35 ppm; C<u>H</u>Br (1H, dd, 4.21 ppm, J_1= 7.5 Hz, J_2 = 8Hz). Mass: m/e 364 (M^+), 362 (6%), 283 (51%), 282 (57%), 255 (97%), 253 (100%), 201 (12%), 174 (22%), 159 (37%), 143 (23%), 119 (28%), Microanalysis: $C_{15}H_{22}Br_2$ requires C, 49.75; H, 6.12; Br, 44.13; found C, 50.53; H, 6.71; Br, 43.24%.

4.1.2. <u>With Two Moles of Bromine</u>

Bromine (12 ml, 0.22 mol) in CCl_4 (75 ml) was introduced to a stirred slurry of isolongifolene (22.5 gm, 0.11 mol) in CCl_4 (100 ml) and 10% aq Na_2CO_3 (600 ml) during 3 hrs and the reaction mixture was stirred for 2 more hrs after the addition.

The reaction mixture was then taken into a separating funnel and the organic layer was separated, washed, till neutral, with water and dried. The removal of solvent offered a yellowish residue (31.5 gm) which was distilled, b.p. 132-135°/0.5 mm to give dibromide 11c.

4.1.3. Action of Chlorine

4.1.3.1. With one Mol. of Chlorine in Presence of aq. Na_2CO_3

Chlorine* (7.0 gm, 0.1 mol) was passed into a stirred mixture of isolongifolene (20.5 gm, 0.1 mol) in CCl_4 (100 ml) and $Na_2CO_3H_2O$ (18 gm) in water (130 ml) at $-2\pm1^{\circ}$ for one hour. A small aliquot was drawn from CCl_4 layer and analysed by PMR to check the completion of the reaction. After the completion, approximately half (50 ml) of the CCl_4 soln was pipetted out and kept separately. The rest was hydrolysed by adding calcium oxide (2.5 gm) to it and stirring at room temperature (29-30°) for 16 hours. Then CaO was removed by filtration and washed with CCl_4. The CCl_4 layer was separated and aqueous layer was extracted with CCl_4 (25 ml x 2). The combined

*The absorbed (unreacted) chlorine and CO_2 were driven out by passing a slow stream of nitrogen into the reaction mixture with stirring and the final weight increase was recorded (5.5 gm). Actual weight of chlorine consumed is equal to the sum of the weight increase noted and the weight of CO_2 escaped from the reaction mixture.

organic extracts were washed, till neutral, with water (25 ml x 2), dried ($MgSO_4$) and solvent was removed at room temperature under reduced pressure. A residue (11.5 gm) was obtained. This was divided into three portions:

(i) A sample analysed by GLC (S.E. 30; 3%, 6'; 170°) contained dehydrocycloisolongifolene+ (17a) (46%), 8-chloroneoisolongifolene (11e) (46%), and other minor products (8%). TLC: Solvent, 5% EtOAc in C_6H_6, 8-chloroneoisolongifolene R_f, 6.78 and cycloisolongifolol (12b) R_f, 0.26.

(ii) A portion of the above residue (1.10 gm) was chromatographed over alumina (N/III, 40 gm, 27 cm x 1.5 cm)

Frac. 1 pet ether (30 ml x 2) 483 mg, liquid

Frac. 2 pet. ether (30 ml x 1) nil

Frac. 3 benzene (30 ml x 4) 4.90 solid, m.p. 96-99°.

Frac. 1 was distilled, b.p. 90-95°/2 mm, to give 8-chloroneoisolongifolene (11e). IR (Fig. 14) (liq.): $-\overset{|}{C}=CH-$ 1640, 821, 800, 750 cm^{-1}. PMR (Fig. 2): $-\overset{|}{C}-Me$ each as singlet at 0.83, 0.93, 1.04, 1.08 ppm, C<u>H</u>Cl (1H, dd, 4.11 ppm, J_1= 7Hz, J_2= 9Hz); =C<u>H</u> (1H, d, 5.67 ppm, J = 3.5 Hz). Microanalysis: $C_{15}H_{23}Cl$ requires C, 75.45; H, 9.71; Cl, 14.85; found C, 75.30; H, 9.74; Cl, 14.41%.

+ PMR of the total distilled product does not show the absorption of olefinic protons for dehydrocycloisolongifolene (17a), hence it appears here that cycloisolongifolol is dehydrated on the column.

Frac. 3 was crystallized (pet. ether) to give alcohol 12b (m.p. 99.5-100°). Its PMR and IR were identical with those of the authentic cycloisolongifolol[22] (12b).

(iii) The above crude mixture (1.9 gm) in acetone (10 ml) was oxidized with Jone's reagent (1.5 ml) at 0° and left at 10°C for 3 hrs. The total product was diluted with water (30 ml) and extracted with pet. ether (30 ml x 4). The organic extracts were washed with 10% aq. Na_2CO_3 (20 ml x 2) and water (20 ml x 2) followed by brine (20 ml) and dried ($MgSO_4$). A residue (1.8 gm), was obtained after removal of the solvent. A part of which (600 mg) was distilled, b.p. 110-130°(bath)/1 mm and analysed by GLC (carbowax, 3%, 6',): 8-chloroneoisolongifolene (11e) (45%) and cycloisolongifolene (16) (46%).

The remainder of the above crude mixture (1.2 gm) was chromatographed over alumina (N/III, 40 gm, 27 cm x 1.5 cm).

Frac. 1	pet. ether	(40 ml x 2)	550 mg, liquid.
Frac. 2	pet. ether	(40 ml x 2)	nil
Frac. 3	benzene	(40 ml x 3)	470 mg, liquid

Frac. 1 was distilled, b.p. 110-115°(bath)/2 mm to give 8-chloroneoisolongifolene (11e).

Frac. 3 was distilled, b.p. 110-115°(bath)/2 mm, to give ketone 18 (450 mg). IR (liq.): CO 1665, PMR: -C(Me)- each as singlet at 0.98, 1.06, 1.08, 1.11 ppm.

The CCl_4 (50 ml) drawn out as described above was washed, till neutral, with water (25 ml x 2) and evaporated (at 90°C) on waterbath (most of the chloride 12a had decomposed into hydrocarbon 17a (PMR)). A residue (10.2 gm) obtained, was fractionated, keeping aside a small sample (500 mg) for GLC.

Frac. 1	b.p. 78-80°/2 mm	3.0 gm, dehydrocycloisolongifolene[22] (17a) characterized by IR, PMR, GLC.
Frac. 2	b.p. 80-90°/2 mm	1.0 gm, mixture
Frac. 3	b.p. 90-95°/2 mm	3.5 gm, 8-chloroneoisolongifolene (11e)(PMR, IR, GLC).

The pot residue (1.0 gm), a gummy material, was rejected.

4.1.3.2. With one Mole of Chlorine in Presence of anhy. Na_2CO_3

A slow stream of chlorine (5.5 gm) was passed into a mixture of isolongifolene (22.8 gm; distilled over Na) and Na_2CO_3 (8.6 gm) at 28-30° (by external cooling) for 2 hours. The inorganic salts were filtered off and washed with pet. ether (20 ml x 3). The solvent was removed at room temperature (28°) under reduced pressure. The residue (28.9 gm) obtained

was divided into three parts:

(i) A small sample was distilled, GLC (carbowax, 3%, 6'; temp. 150°) showed dehydrocycloisolongifolene (17a) (30%) and 8-chloroneoisolongifolene (11e) (62%), besides other minor impurities.

(ii) Second portion (3.8 gm) was fractionated:

Frac. 1 b.p. 78-80°/2 mm (620 mg) dehydrocycloisolongifolene (17a) (PMR, IR, GLC).

Frac. 2 b.p. 80-95°/2 mm (830 mg) mixture

Frac. 3 b.p. 95-100°/2 mm(1.7 gm) 8-chloroneoisolongifolene (11e)(GLC, PMR, IR).

(iii) Third portion (4.1 gm) was stirred with AcOH (20 ml) and NaOAc (2 gm) for 36 hrs at 80°. The product was worked up by diluting with water (50 ml) and extracting with pet ether (20 ml x 3). The organic layer was washed free of acid with aq. Na_2CO_3 (20 ml x 3) followed by water (20 ml x 2) and then dried (Na_2SO_4). A part (0.970 gm) of the residue (3.5 gm) obtained after solvent removal was chromatographed over silica gel (35 gm, 40 x 1.5 cm).

Frac. 1 pet. ether (100 ml) 827 mg, liquid

Frac. 2 pet. ether (50 ml) nil

Frac. 3 50% benzene in pet ether (50 ml x 3) 209 mg, liquid.

Frac. 1 was distilled and analysed by GLC and found to be a mixture of hydrocarbon 17a (13.5%) and chloride 11e (73%).

Frac. 3 was distilled, b.p. 120-130°(bath)/1 mm and it was a very bad mixture of acetates (PMR & GLC). Their separation was not attempted.

4.1.3.3. With two Moles of Chlorine

To a well stirred mixture of isolongifolene (10.0 gm, 0.05 mol) in CCl_4 (35 ml) and anhyd. Na_2CO_3 (4.4 gm), chlorine gas (3.5 gm*) was passed over a period of 30 minutes at 28-30°C. A small sample was drawn and analysed by PMR (for the disappearance of protons in olefinic region). Then Li_2CO_3 (3 gm) was added to the reaction mixture and its temperature was raised to 80° where it was stirred for 6 hrs. It was cooled, inorganic salts were filtered off and washed with more of CCl_4 (20 ml x 3). Removal of solvent offered an

*The weight recorded here is the weight increase after the addition of chlorine gas.

only residue (12.0 gm), a portion (9.0 gm) of which was immediately fractionated.

Frac. 1 b.p. 85-90°/2.5 mm (2.35 gm) dehydrocycloisolongifolene (17a) (PMR, IR GLC).

Frac. 2 b.p. 95-100°/2.5 mm (4.45 gm) monochloride (17b)

The pot residue (1.5 gm) was rejected.

Frac. 2 was characterized as 1-chloro-dehydrocycloisolongifolene (17b), IR (Fig. 16) (liq.): -C=CH- 1640, 938, 820, 780 cm^{-1}. PMR (Fig. 9): -C-Me each as singlet at 0.93, 1.01, 1.01, 1.27 ppm; CHCl (1H, d, 4.41 ppm; J = 2Hz); =CH (1H, m, centred at 5.42 ppm; 1H, dt, 5.90 ppm; J_1 = 1.5 Hz, J_2 = 10Hz). Microanalysis: $C_{15}H_{21}Cl$ required C, 77.24; H, 8.50; Cl, 14.27; found C, 76.82; H, 8.65; Cl, 15.17%.

4.1.3.4. Action of Chlorine on Chloride 11e

A slow stream of chlorine gas (1.2 gm) was passed in a well agitated mixture of chloride (11e) (6.98 gm) in CCl_4 (21 ml) and anhyd. Na_2CO_3 (2.8 gm) over a period of 15 minutes at 28.30°. A small sample was drawn and analysed by PMR (for the disappearance of olefinic proton). The inorganic salts

were filtered off and washed with CCl_4 (10 ml x 2). Solvent was removed under reduced pressure at room temperature (25.27°) and the residue (7.1 gm) obtained consisted mostly of a dichloride (~70%) having the structure (12c) as indicated by its PMR (Fig. 8): -C(Me)- each as singlet at 0.96, 1.04, 1.18, 1.16 ppm; CHCl (1H, d, 4.27 ppm, J= 2Hz; 1H, t, 4.56 ppm, J= 4.5 Hz)

4.1.4. Action of Pseudohalogens

4.1.4.1. Iodine Chloride

To a stirred and precooled (5°) mixture of isolongifolene (3.0 gm) in acetonitrile (30 ml) in presence of anhyd. Na_2CO_3 (1.5 gm), was added dropwise, iodine monochloride (3.2 gm) during two minutes and the temperature was brought upto 15° and stirred at that temperature for two and half hours. The reaction mixture was diluted with 10% aq. $Na_2S_2O_3$ (20 ml) and extracted with pet. ether (20 ml x 2). Pet. ether layer was washed with brine and dried ($MgSO_4$). The residue (3.3 gm) was distilled, b.p. 135-140°(bath)/ 1 mm (2.8 gm) to give 8-iodoisolongifolene (10c). PMR: -C(Me)- each as singlet 0.93, 0.93, 1.19, 1.29 ppm; $-CH_2-CI=C-$ (2H, m, spanned between 2.49-2.64 ppm). IR (liq.): -C=C- 1635 cm^{-1}.

The above experiment was carried out with ICl (1.5 gm) and isolongifolene (1.4 gm) in CCl_4 (15 ml) in presence of anhyd. Na_2CO_3 (1 gm); the product isolated was 8-iodoisolongifolene (10c) (1.5 gm).

4.1.4.2. Iodine Azide

Sodium azide (2.6 gm, 40 mmol) and acetonitrile were charged in a 100 ml three necked round bottomed flask fitted with reflux condenser, dropping funnel and thermometer. The flask was covered with black paper and cooled to 0°. Iodine monochloride (4.80 gm, 30 mmol) was introduced slowly during 10 min and stirred for an additional half an hour to ensure the formation of iodine azide. Then isolongifolene (3.5 gm, 17 mmol) was added and the temperature of reaction mixture was brought to 15° over one hour and stirred at the same temperature for an additional six hours. Most of the acetonitrile was removed under reduced pressure, then it was diluted with 10% aq. $Na_2S_2O_3$ (30 ml) and extracted with CCl_4 (20 ml x 3). The solvent was removed at low temperature ($35 \pm 3^{\circ}$) under reduced pressure. The product (4.6 gm, brown coloured) was distilled, b.p. $140-145^{\circ}$(bath)/1 mm (3.7 gm) and analysed by GLC (S.E-30, 3%, 6', temp. 180°, flow rate 60 m/min.), iodides 11g (60%, RT 2.4 min), and 10c (30%, RT 2.8) and other minor products (10%, RT 1.8 & 2.0). Iodide (11g) could be

recognized easily from its PMR: -C-Me each as singlet at 0.71, 0.86, 0.95, 0.99 ppm; CHI (1H, dd, 4.35 ppm, J_1= 8Hz, J_2= 9Hz), =CH (1H, d, 5.48 ppm, J= 3.5 Hz). IR (liq.): -C=CH- 1610, 815 cm^{-1}.

When the above experiment was repeated in CCl_4 (30 ml) with NaN_3 (3.0 gm), ICl (3.2 gm) and isolongifolene (2.8 gm), a mixture containing iodides 11a and 10c in the ratio of 1:1 was obtained.

4.1.4.3. Chlorine Azide

ClN_3 (775 mg) in CH_2Cl_2 (30 ml) was introduced to a cooled (0°) solution of isolongifolene (2.08 gm) in CH_2Cl_2 (10 ml) in presence of Na_2CO_3 (1 gm) during 2 min. and the reaction mixture was stirred for 15 min. The inorganic salts were filtered off and washed with CH_2Cl_2 (5 ml x 2). The solvent was removed under reduced pressure and the residue (2.1 gm) obtained was analysed by PMR which showed mostly 8-chlorone-isolongifolene (11c) while the signals due to cyclopropyl chloride 12a were absent.

4.1.4.4. Nitrosyl Chloride

To a cooled (0.5 ± 2°) and agitated mixture of isolongifolene (1.0 gm) and isoamyl nitrite (1 ml) in gl. AcOH (1 ml)

was added dropwise conc. HCl (0.5 ml) during 3 min. and then the reaction mixture was stirred for 2 hrs. Then it was diluted with water (10 ml) and extracted with CH_2Cl_2 (10 ml x3). The organic layers were washed, till neutral with water and dried. Removal of solvent offered a brown coloured pasty solid which was crystallized (MeCN) to get pure oxime 20a (560 mg, m.p. 141-143°). IR (nujol): OH 3250, NO 940, 920, C=N 1655, -C=CH-1610, 870, 830 cm^{-1}. PMR ($CDCl_3$): -C-Me each as singlet at 0.88, 1.01, 1.05, 1.11 ppm, =CH (1H, d, 5.64 ppm, J = 4Hz); OH (1H, s, 9.47 ppm). Microanalysis: $C_{15}H_{23}ON$ requires C, 77.25; H, 9.87; N, 6.01; found C, 77.57; H, 9.52; N, 6.22%.

4.2. Some transformations of 8-Haloneoisolongifolene.

4.2.1. Neoisolongifolene (11a)

8-Bromoneoisolongifolene (34 gm) in EtOH (300 ml) and 40% aq. NaOH (20 ml) was hydrogenated over Raney nickel catalyst (14 gm) at room temperature (25°) and atmospheric pressure, with vigorous shaking over reciprocating shaker. After the absorption of one mole equivalent of hydrogen (in 2 hrs), the ethanol layer was decanted and Raney nickel

was washed with pet. ether (50 ml x 4). Then the EtOH layer was diluted with water (900 ml) and saturated with NaCl and extracted with pet. ether (100 ml x 3). The combined organic extracts were washed with water (50 ml x 2) and dried (Na_2SO_4). The residue (23.8 gm), after removal of solvent, was distilled, b.p. 78-81°/1 mm to give neoisolongifolene (11a) (21.8 gm, 91%) (Single -$AgClO_4$-SiO_2[35], GLC 95% pure). IR (liq.): -C=CH-1610, 815 cm^{-1}. PMR (Fig. 5): -C-Me each as singlet at 0.73, 0.77, 1.02, 1.10 ppm; =CH (1H, d, 5.61 ppm, J= 4Hz).

4.2.2. 8-Dehydroneoisolongifolene (14)

A mixture of 8-bromoneoisolongifolene (11b) (4.5 gm) and Li_2CO_3 (7.6 gm) was refluxed in DMF (25 ml) for 1 hr. Most of the DMF was then removed under reduced pressure. The product was diluted with water (20 ml), extracted with pet. ether (20 ml x 3) and washed with water (20 ml x 2) and then dried (Na_2SO_4). The residue (3.2 gm), after removal of solvent, was distilled, b.p. 80-85°/3 mm to give hydrocarbon 14 (2.64 gm, 98% pure). IR (Fig. 15) (liq.): -C=CH-1645, 1610, 887, 810, 775 cm^{-1}. PMR (Fig. 6): -C-Me each as singlet at 0.74, 0.83, 1.01, 1.12 ppm; =CH (2H, m, spanned between 5.48-5.73 ppm, 1H, m, spanned between 5.73-5.99 ppm); Mass: m/e M^+ 220; Microanalysis: $C_{15}H_{22}$ requires C, 89.04; H, 10.96; found C, 89.00; H, 11.18%.

4.2.3. Action of Li_2CO_3/DMF on Chloride(11e)

A mixture of chloride 11e (500 mg) and Li_2CO_3 (400 mg) in DMF (10 ml) was refluxed under nitrogen for 10 hrs. Usual work up (described above) gave 8-dehydroneoisolongifolene (14) (350 mg).

4.2.4. Partial Reduction of 8-Dehydroneoisolongifolene (14)

A mixture of hydrocarbon (14) (4.5 gm) and Raney nickel (1.2 gm) in ethanol (20 ml) was stirred under H_2 atmosphere at room temperature (29.30°) and atmospheric pressure, for about 2 hrs. After the absorption of one mole equivalent of hydrogen, Raney nickel was filtered off and washed with pet. ether (10 ml x 3) keeping the catalyst always covered with solvent. Ethanol was removed under reduced pressure and the residue was mixed with the residue obtained from pet. ether washings. The total residue (4.4 gm) was distilled bp. 90-92°/ 2.3 mm (4.2 gm) and was found to be neoisolongifolene (11a).

4.2.5. 9-Dehydroisolongifolene (15)

A solution of bromide 11b (5.3 gm) was refluxed in DMF (25 ml) for one hour. Most of the DMF was removed under reduced pressure. Then it was diluted with water (25 ml) and extracted

with pet. ether (20 ml x 3). The organic extract was washed with water (20 ml x 3) followed by brine and dried ($MgSO_4$). The residue (3.1 gm) was distilled, b.o. 85-90°/1 mm (2.42 gm), to give 15 (2.42 gm). IR (liq.):-C=CH- 1652, 1585, 855 cm^{-1}, PMR:-C-Me as singlet at 0.90, 1.03, 1.07, 1.13 ppm; =CH (1H, d, 5.18 ppm, J= 10Hz; 1H, d, 5.43 ppm, J= 6Hz; 1H, dd, 5.72 ppm, J_1= 6Hz, J_2 = 10Hz).

4.2.6. Solvolysis of Bromide (11b) in KOAc/AcOH

A mixture of KOAc (4.02 gm) and bromide 11b (6.4 gm) in gl. AcOH (40 ml) was refluxed for 5 hrs. The progress of the reaction was monitored by GLC (disappearance of bromide 11b). Then most of the AcOH was removed under reduced pressure, The remaining residue was diluted with water (25 ml) and extracted with pet. ether (25 ml x 3) followed by brine and dried ($MgSO_4$). Out of the residue (4.5 gm) obtained, a small sample (200 mg) was distilled b.p. 100-140°(bath)/ 2 mm and analysed by GLC (carbowax, 3%, 6', temp. 160°). It showed dehydroneoisolongifolene (14) (4.2%, RRT 1), 9-dehydroisolongifolene (15) (32.5%, RRT 1.5), tetralin (25) (0.5%, RRT 2.5), tertiary acetate (50%, RRT 7.8). Then rest (4.1 gm) of the residue was chromatographed over silica gel (IIB, 120 gm, 2.5 x 55 cm^2).

Frac. 1	pet ether	(50 ml x 3)	2.43 gm, liquid.
Frac. 2	pet ether	(50 ml x 3)	100 mg liquid, mixture
Frac. 3	5% benzene in pet ether	(50 ml x 3)	1.43 gm, liquid
Frac. 4	50% benzene in pet ether	(50 ml x 1)	nil

Frac. 1 was distilled, b.p. 85-90°/1 mm (2.4 gm) and found to be 15 (PMR, IR, GLC).

Frac. 3 was distilled, b.p. 118-120°/1 mm (1.43 gm) to give a tertiary acetate*. IR (liq): Acetate 1740, 1240; -C=CH- 1620, 870, 820, 810 cm^{-1}. PMR: -C-Me each as singlet at 0.98, 1.15, 1.17, 1.22 ppm; CH_3CO (3H, s, 2.00 ppm); =CH (1H, d, 5.37 ppm, J= 4 Hz). Mass: m/e 262 (M^+, 24%), 219 (94%), 202 (21%), 187 (39%), 164 (100%), 159 (47%), 149 (31%), 148 (30%), 123 (22%), 105 (25%). Microanalysis: $C_{15}H_{26}O_2$ requires C, 77.82; H, 9.99; found C, 78.29; H, 9.64%.

In one of the experiments, bromide 11b (9.63 gm) was refluxed with KOAc (10.1 gm) in gl. AcOH (50 ml) for 5 hrs. Usual work up (described above) gave a residue (7.8 gm), which was refluxed with KOH (4 gm), in 15% aq. MeOH (35 ml) for 36 hrs. At the end most of the MeOH was removed under reduced pressure and the product was worked up by diluting

*The structural elucidation of tert. acetate is discussed in the next Chapter.

with water (25 ml), extracting with diisopropyl ether (25 ml x 3) and washing the organic extracts with water (20 ml x 3). A residue (6.79 gm) was obtained, a part (200 mg) of which was distilled, b.p. 100-140°(bath)/1 mm and analysed by GLC (carbouax, 3%, 6', Temp. 150°). It showed dehydroneoisolongifolene (14) (11.5%, RRT 1), dehydroisolongifolene (15)(38%, RRT 1.5), tetralin (25) (4.5%, RRT 3), tertiary alcohol (40%, RRT 7) and a secondary alcohol (2%, RRT 9). The rest (6.5 gm) of the above residue was chromatographed, (silica gel IIB, 180 gm, 3 x 30 cm .

Frac. 1	pet. ether	(50 ml x 2)	3.103 gm, hydrocarbons 14 and 15 (GLC)
Frac. 2	5% benzene in pet. ether	(50 ml x 2)	218 mg, mixture, rejected.
Frac. 3	5% benzene in pet ether	(50 ml x 4)	2.01 gm, solid m.p. 41-48°
Frac. 4	benzene	(50 ml x 3)	861 mg, semisolid

Frac. 4 was rechromatographed over silica gel (IIB, 45 gm, 1.3 x 60 cm).

Frac. 4a	pet ether	(50 ml x 1)	nil
Frac. 4b	10% benzene in pet ether	(20 ml x 5)	510 mg, solid, m.p. 42-48°.

Frac. 4c	10% benzene in pet ether	(20 ml x 4)	50 mg, rejected
Frac. 4d	25% benzene in pet ether	(20 ml x 5)	35 mg, solid
Frac. 4e	50% benzene in pet ether	(30 ml x 4)	75 mg, mixture, rejected.

Frac. 3 and 4b were mixed and crystallized (pet ether) to give a tertiary alcohol*; m.p. 54.5-55.5°, IR (CCl_4): OH 3608, 3495, -C=CH- 1615, 810 cm^{-1}. PMR: -C-Me each as singlet at 0.93, 0.98, 1.20, 1.27 ppm; =CH (1H, d, 5.28 ppm, J= 4Hz). Mass: m/e 220 (M^+, 100%), 205 (86%), 177 (23%), 163 (19%), 151 (29%), 149 (39%), 138 (30%), 135 (17%), 121 (19%), 107 (22%), 95 (18%), 91 (26%). Microanalysis: $C_{15}H_{24}O$ requires C, 81.76; H, 10.98; found C, 82.01; H, 11.05%.

Frac. 4d was crystallized (pet ether) to get a secondary* alcohol m.p. 40-42°. IR (CCl_4): OH 3610, 3460, -C=CH- 1605, 815, 810 cm^{-1}. PMR ($CDCl_3$): -C-Me each as singlet at 0.95, 1.02, 1.05, 1.15 ppm; CHOH (1H, idd, 4.11 ppm, W_H = 9Hz); =CH (1H, d, 5.72 ppm J = 3.5 Hz). Microanalysis: $C_{15}H_{24}O$ requires C, 81.76; H, 10.98; found C, 82.01; H, 11.05%.

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*The secondary alcohol and tertiary alcohol have been designated as alcohol A and B, their structures are discussed in the next Chapter.

4.2.7. Solvolysis of Chloride 11e with NaOAc/AcOH

Chloride 11e (2.5 gm) was refluxed with NaOAc (2.5 gm) in AcOH (15 ml) for 36 hrs and the usual work up (described above) gave a residue (2.4 gm), which was chromatographed over silica gel. Hydrocarbons 14 and 15 (1.150 gm) were eluted out with pet ether and the tertiary acetate (705 mg) was eluted out with benzene. The product obtained from solvolysis of chloride 11e and bromide 11b were found to be the same by GLC comparison.

4.2.8. Action of AcOH on Dehydroneoisolongifolene (14)

A soln of hydrocarbon 14 (1.87 gm) in gl. AcOH (15 ml) was refluxed for 8 hrs. Then most of the AcOH was removed under reduced pressure and the product was worked up by diluting with water (25 ml) and extracting with diisopropyl ether (20 ml x 3). Then organic layer was washed with 10% aq. Na_2CO_3 (25 ml x 2) and water (25 ml x 2) followed by brine and dried (Na_2SO_4). The residue (21 gm) obtained was charged on chromatographic column (SiO_2, IIB, 90 gm, 2.3 x 55 cm) and hydrocarbon (1.39 gm) was eluted out with pet ether (25 ml x 3); the (more polar) mixture of compounds (450 mg) was eluted out with benzene (25 ml x 2). The hydrocarbon was found to be 15 (PMR, IR, GLC).

4.2.9. Action of $BF_3.Et_2O$ on Chloride 11e

The chloride 11e (3.0 gm) with BF_3Et_2O (two drops) was stirred at 90-95° for 3 hrs, when the evolution of HCl gas was stopped and it was cooled to room temperature. The product was taken in pet. ether (40 ml) and worked up by washing with 10% aq. Na_2CO_3 (15 ml x 2) followed by water (15 ml x 2) and then dried (Na_2SO_4). A black residue (2.6 gm) was obtained after solvent removal and a part of it (2.2 gm) was distilled, 100-110°(bath)/3 mm (1.3 gm); the solid, undistallable residue (800 mg) was rejected. The distillate was found to be tetralin (25) by comparison with authentic sample[36].

4.2.10. Action of H_2SO_4 on Halides 11b and 11e

Chloride 11e (400 gm) was added in one lot to a well stirred and cooled (0°) 90% aq. H_2SO_4 (4ml). The evolution of HCl ceased after 5 min. and it was worked up by pouring it into ice cold water (25 ml) and extracting with pet ether (15 ml x 3). The pet. ether extract was washed with 10% aq. Na_2CO_3 (15 ml x 4), followed by water (15 ml x 2) and brine. After solvent removal a gummy residue (3.5 gm) was obtained. A portion of it (2.2 gm) was distilled; 100-110° (bath)/3 mm to yield tetralin (25) (1.2 gm).

Similarly treatment of bromide 11b (1.4 gm) with 90% aq. H_2SO_4 (5 ml) gave tetralin (25) (680 mg).

4.3. Some Transformations in 1-Chlorocycloisolongifolane Derivatives

4.3.1. Solvolysis of Dichloride 12c

The total dichloride 12c (2.0 gm, vide section 4.1.3.4) was taken in a two necked r.b. flask fitted with reflux condenser, thermometer and $CaCl_2$ guard tuble. AcOH (25 ml) and NaOAc (1.0 gm) were added to this, then it was plunged in an oil bath at 80°. The reaction mixture was stirred at the same temperature for 24 hrs. After cooling to room temperature (25-26°), it was worked up by diluting with water (60 ml) and extracting with pet. ether (25 ml x 3). The pet. ether extract was washed with 10% aq. Na_2CO_3 followed by water (15 ml x 2), dried (Na_2SO_4) and solvent was removed. An oily residue (2.4 gm) was obtained, which was a mixture of atleast five compounds having R_f 0.88, 0.50 (major), 0.37 (minor), 0.19 (trace) and 0.11 (trace); (TLC-SiO_2, solvent: benzene; solvent front, 16 cm). A small portion (1.24 gm) of it was chromatographed (SiO_2, 40 gm, 1.5 x 50 cm).

Frac. 1	pet. ether	(50 ml x 2)	308 mg, tlc single
Frac. 2	50% benzene in pet. ether	(50 ml x 1)	nil

Frac. 3	50% benzene in pet ether	(50 ml x 2)	450 mg, tlc single
Frac. 4	50% benzene in pet ether	(50 ml x 1)	60 mg
Frac. 5	50% benzene in pet ether	(50 ml x 2)	108 mg
Frac. 6	benzene	(150 ml)	95 mg, bad mixture

Frac. 1 was distilled, b.p. 120-135°(bath)/1.5 mm, It was a very bad mixture of several compounds, the major identifiable portion having the structure 11f. PMR: $-\overset{|}{C}-$Me each as singlets at 0.96, 0.96, 1.09, 1.33 ppm; CHCl (1H, dd, 4.06 ppm; J_1 = 7 Hz, J_2= 9.5 Hz), no olefinic protons.

Frac. 3 was distilled, b.p. 120-130°(bath)/ 1 mm to give acetate 17c (420 mg). IR(CCl_4): Acetate 1730, 1235; $-\overset{|}{C}=CH-$ 1631 cm^{-1}. PMR (Fig. 11): $-\overset{|}{C}-$Me each as singlet at 0.98, 0.98, 0.98, 1.04 ppm; CH_3CO (3H, s, 1.26 ppm); CHOAc (1H, d, 5.24 ppm, J= 2Hz); =CH (1H, m, spanned between 5.24-5.64 ppm; 1H, dt, 5.91 ppm, J_1= 2Hz, J_2= 10Hz). Microanalysis: $C_{17}H_{24}O_2$ requires C, 78.41; H, 9.29; found C, 78.20; H, 9.44%.

Frac. 5 was distilled, b.p. 130-140°(bath)/1 mm, (70 mg) to give chloroacetate 12d. IR(CCl_4): Acetate 1730, 1235 cm^{-1}. PMR: $-\overset{|}{C}-$Me each as singlet at 0.87, 0.98, 1.12, 1.18 ppm; CH_3CO (3H, s, 1.94 ppm); CHCl (1H, d, 4.30 ppm, J= 2 Hz), CHOAc (1H, t, 5.34 ppm, J_1= 5Hz).

4.3.2. Action of LAH on Chloride 17b

A mixture of LAH (300 mg) and chloride 17b (250 mg) in THF (15 ml) was refluxed for 12 hrs under N_2. The reaction mixture was cooled to 0 5° and excess of LAH was destroyed by dropwise addition of water (0.3 ml) with stirring followed by 15% aq. NaOH (0.3 ml) and water (1 ml). The salts were filtered off and washed with pet. ether. Removal of solvent offered a residue (225 mg), which was distilled, b.p. 90-100° (bath)/1 mm. The distillate (200 mg) was found to be dehydrocycloisolongifolene (11a) (PMR, IR, GLC).

4.3.3. Hydrolysis of Chloride 17b

A mixture of chloride 17b (1.2 gm) and calcium oxide (500 mg) in water (20 ml) was stirred at 85-90° for 16 hrs. The product was cooled to room temperature, CaO filtered off and washed with water (10 ml x 2) followed by pet. ether (20 ml x 2). The combined pet. ether was washed, till neutral, with water (10 ml x 1), dried (Na_2SO_4) and then solvent was removed under reduced pressure. An oily residue (1.10 gm) was obtained which was filtered through a small column (SiO_2, 40 gm, 2 x 40 cm) to remove traces of less polar inpurities, then distilled, b.p. 110-125°(bath)/2 mm (850 mg) to give dehydrocycloisolongifol-1-ol (17d). IR (Fig. 17) (liq): OH 3400, 1040; -C=CH-

1630, 940, 743, 705 cm^{-1}. PMR (Fig. 10): -C(Me) each as singlet at 0.89, 0.96, 1.01, 1.20 ppm; CHOH (1H, d, 4.30 ppm, J= 1.5 Hz); =CH (1H, m, spanned between 5.26-5.54 ppm; 1H, dt, 5.91 ppm, J= 1.5 Hz, J= 10Hz). Microanalysis: $C_{15}H_{22}O$ requires C, 82.51; H, 10.16; found C, 82.28; H, 9.40%.

4.3.4. Oxidation of Alcohol 17d with Jones Reagent

To a cooled soln (0^{o}) of alcohol 17d (390 mg) in acetone (2ml) was added dropwise, Jone's reagent (0.5 ml) with shaking till the orange colour of chromic acid persisted. It was left at this temperature for 4 hrs and then worked up by diluting with water (6 ml) and extracting with pet ether (10 ml x 3). The pet. ether layer was washed, till neutral, with water (10 ml x 2) and dried (Na_2SO_4). Solvent was removed and the residue (350 mg) distilled, b.p. 120-130^{o}(bath)/1 mm (305 mg) to give ketone 19. IR (Fig.18) (liq.): CO 1745, -C=CH- 1661, 1630, 853, 830, 700 cm^{-1}. PMR (Fig. 12): -C(Me) each as singlet at 1.00, 1.00, 1008, 1.19 ppm; =CH (1H, m, spanned between 5.40-5.60 ppm; 1H, dt, 6.04 ppm; J= 1.5 Hz, J_2= 10Hz). Microanalysis: $C_{15}H_{20}O$ requires C, 83.30; H, 9.85; C, 83.45; H, 10.53%.

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FIG.1

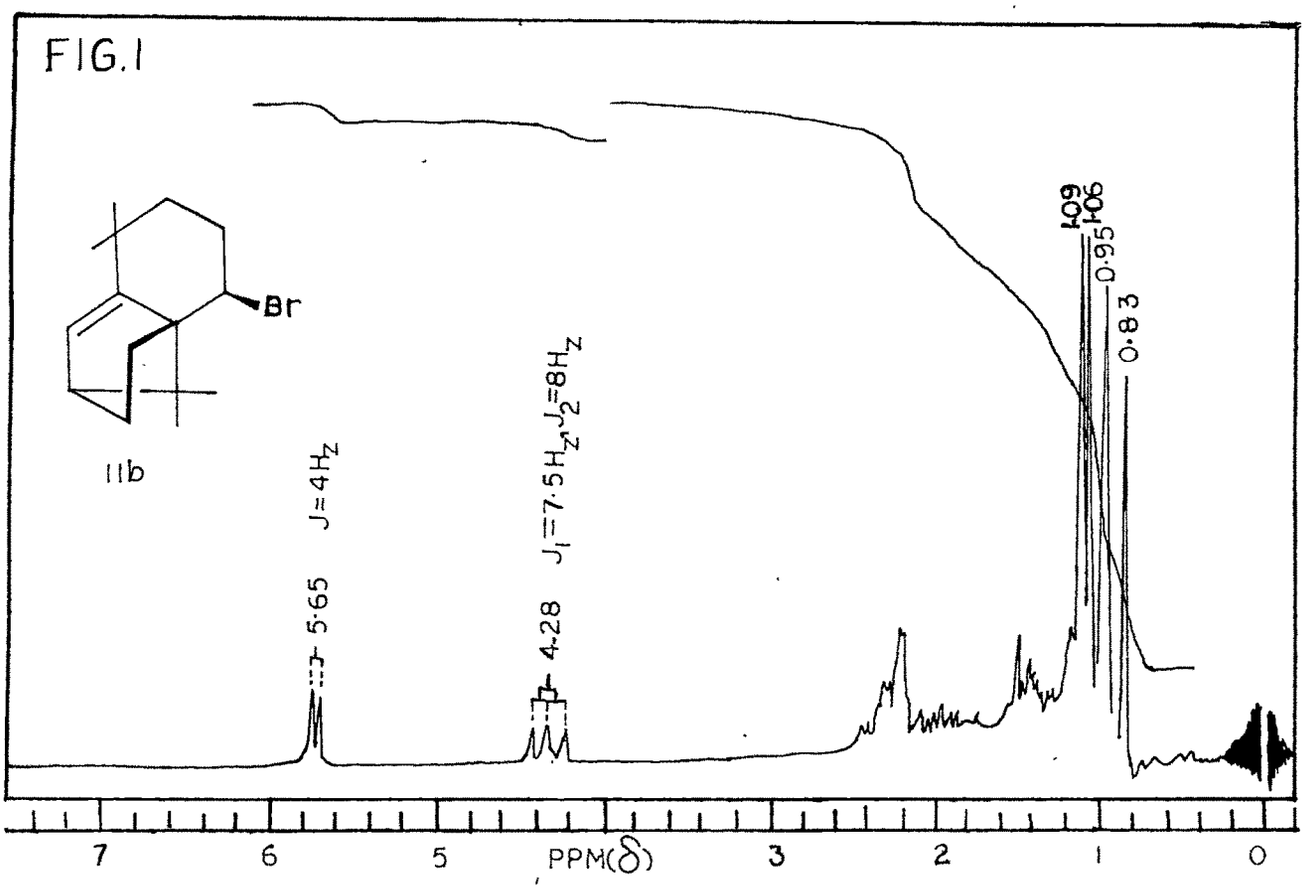

Br
IIb
J=4Hz
5·65
J1=7·5Hz, J2=8Hz
4·28
1·09
1·06
0·95
0·83
7
6
5
PPM(δ)
3
2
1
0

FIG.2

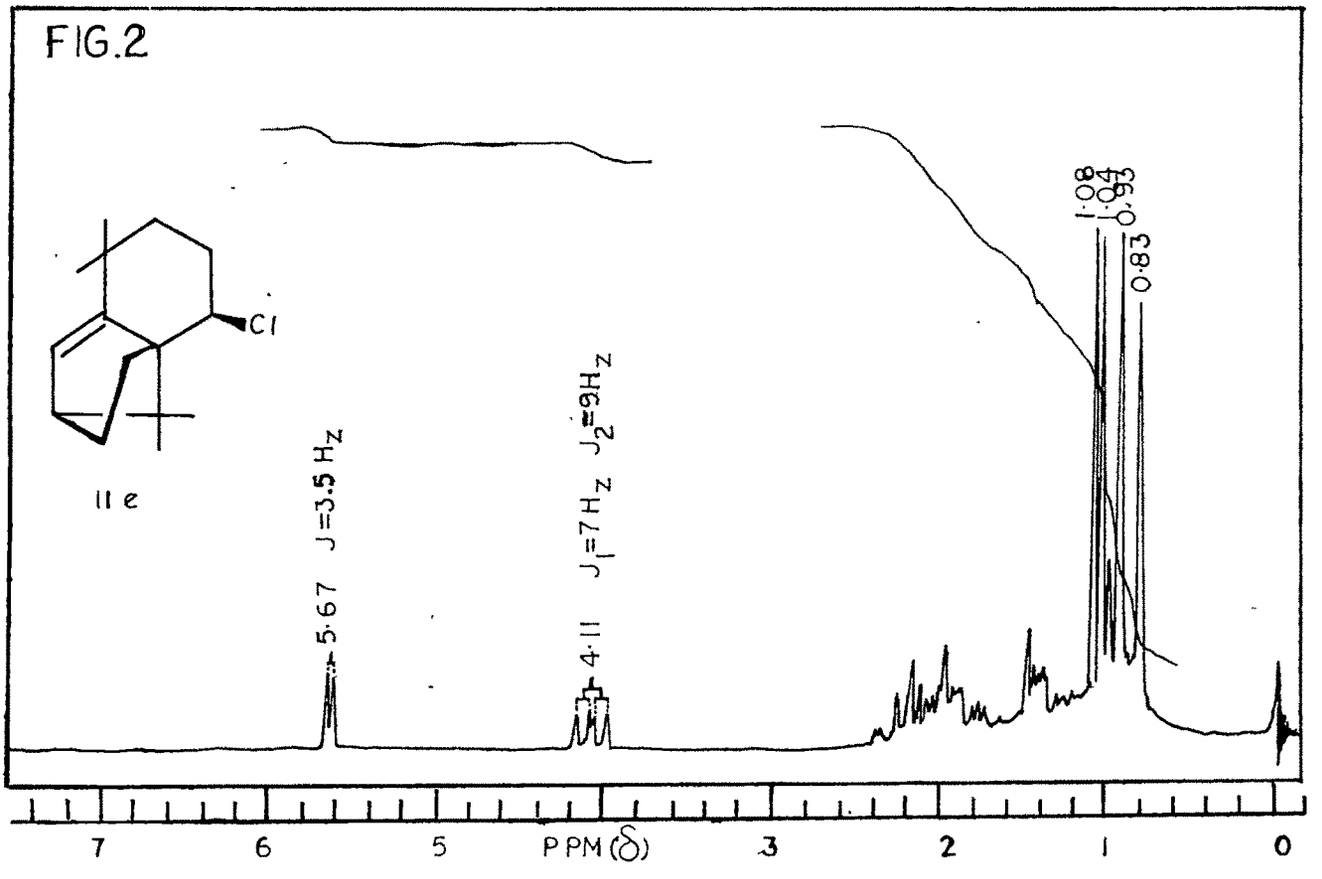

Cl
IIe
J=3.5Hz
5·67
J1=7Hz J2=9Hz
4·11
1·08
1·04
0·93
0·83
7
6
5
PPM(δ)
3
2
1
0

FIG. 3

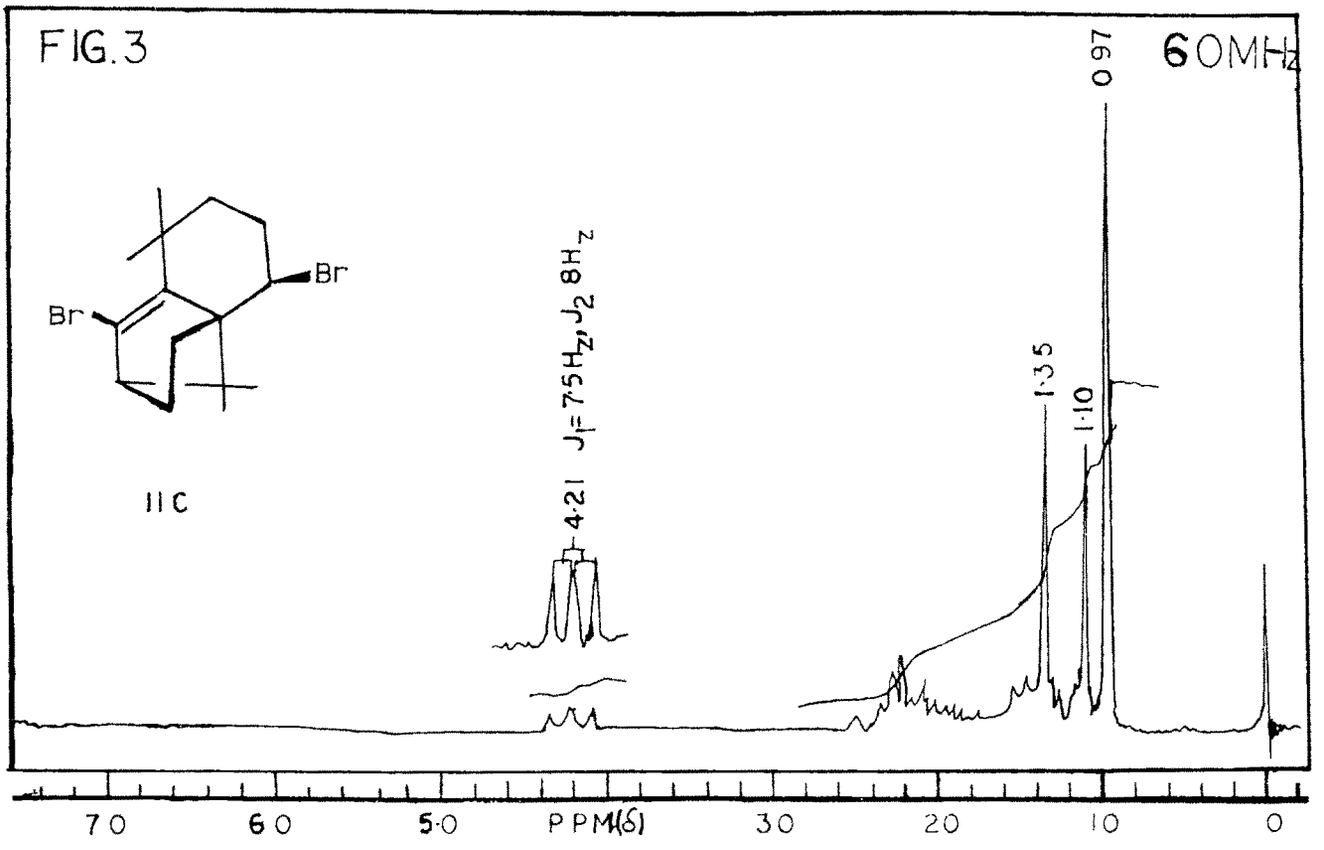

60MHz
0·97
1·35
1·10
4·21
J=7·5Hz, J 8Hz
Br
Br
II C
7·0
6·0
5·0
PPM(δ)
3·0
2·0
1·0
0

FIG 4

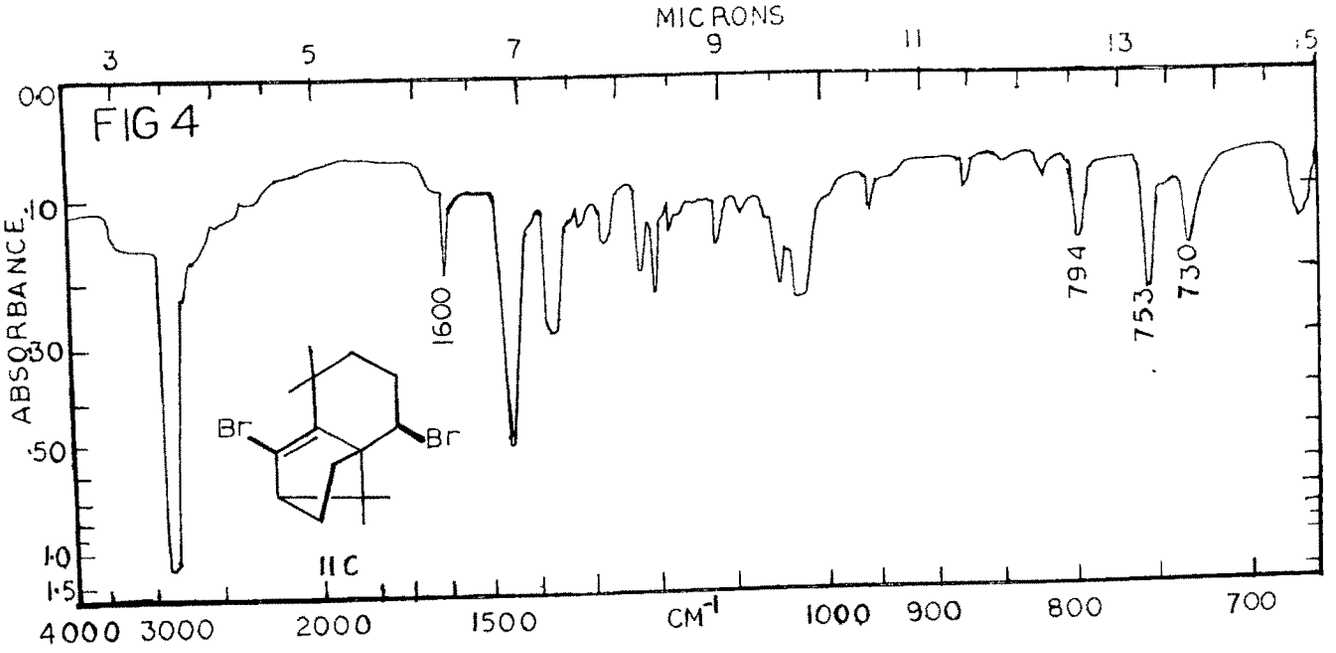

MICRONS
3
5
7
9
11
13
15
0·0
1·0
2·0
3·0
5·0
1·0
1·5
ABSORBANCE
1600
794
753
730
Br
Br
II C
4000
3000
2000
1500
CM⁻¹
1000
900
800
700

FIG. 5

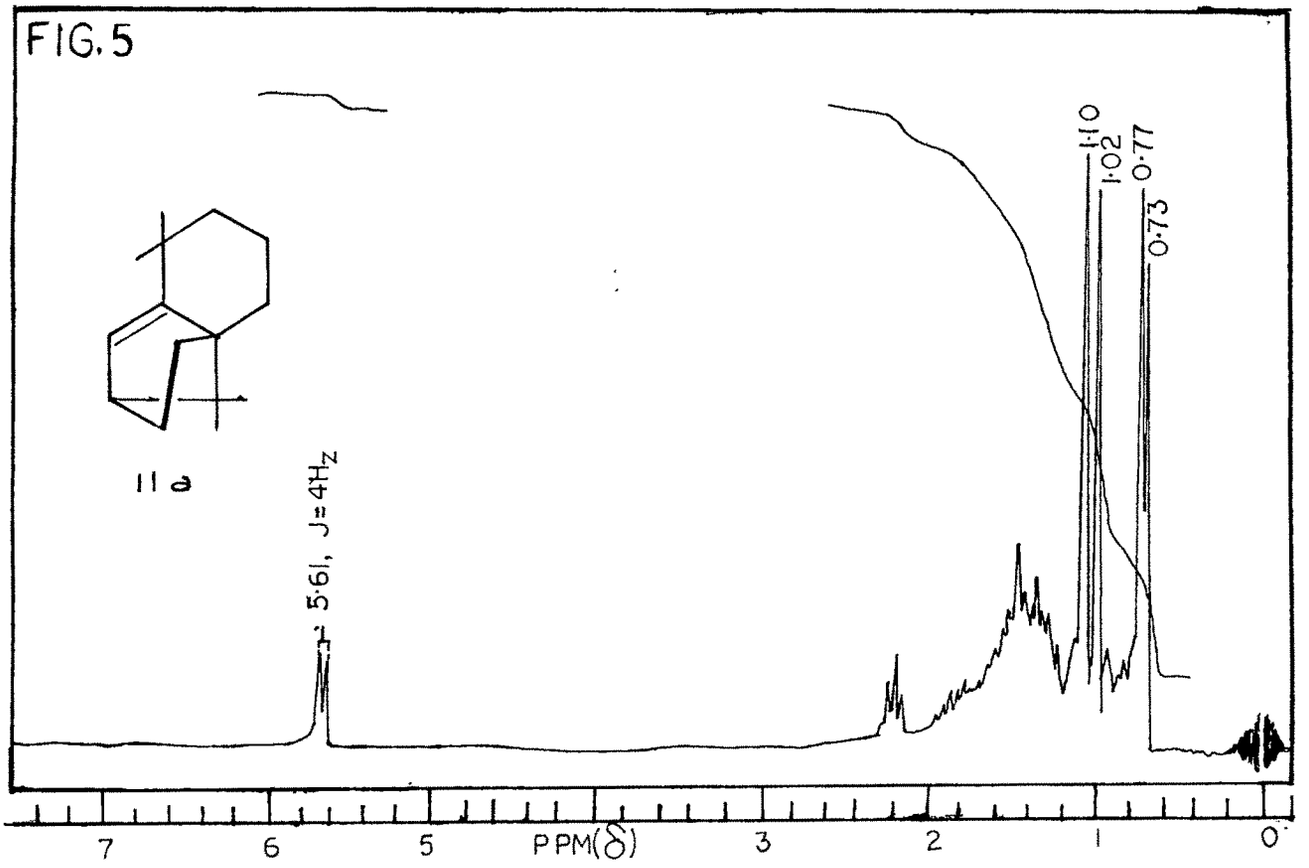

11 a
5·61, J=4Hz
1·10
1·02
0·77
0·73
7
6
5
PPM(δ)
3
2
1
0

FIG. 6

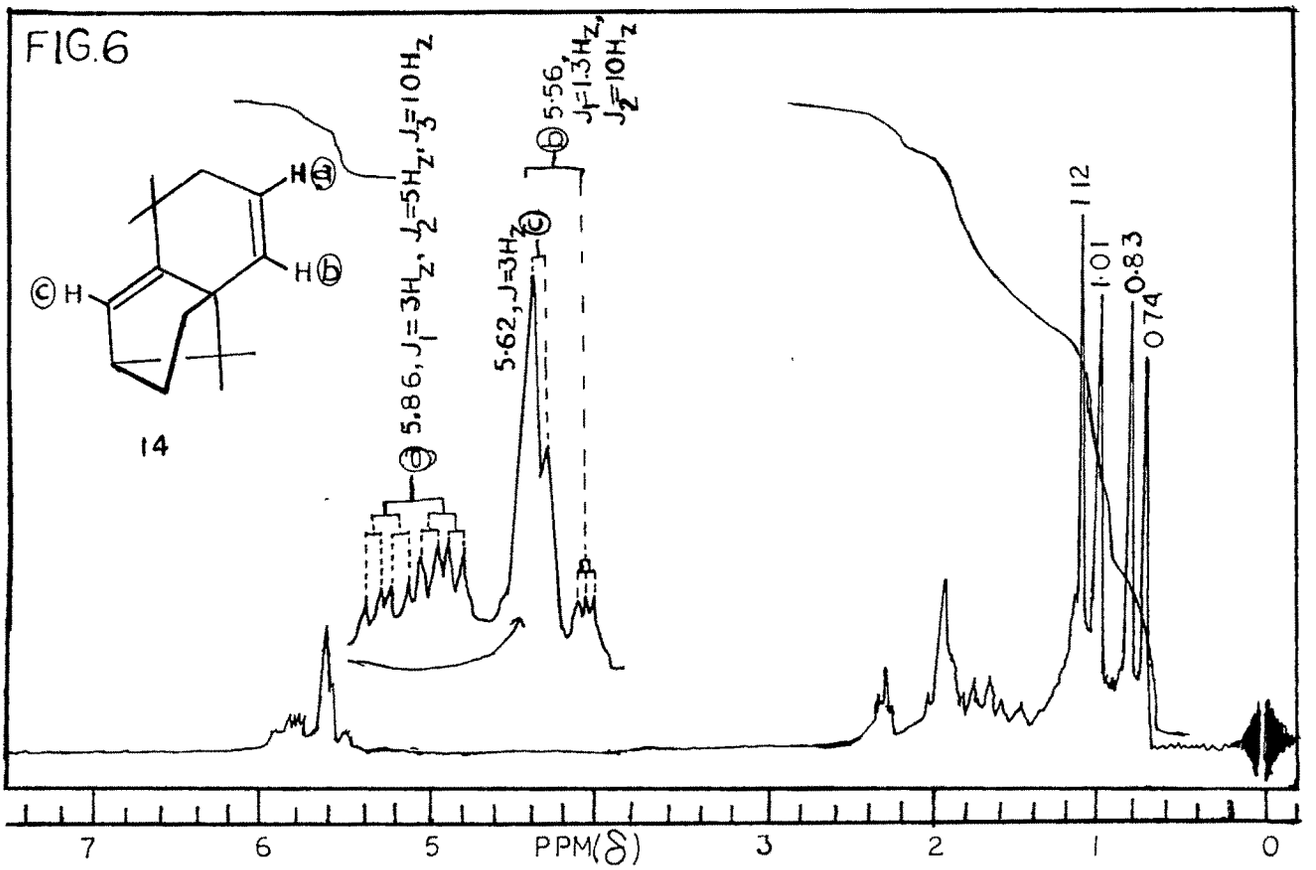

14
Ha
Hb
Hc
5·86, J1=3Hz, J2=5Hz, J3=10Hz
5·62, J=3Hz
5·56, J1=1·3Hz, J2=10Hz
1·12
1·01
0·83
0·74
7
6
5
PPM(δ)
3
2
1
0

FIG.7

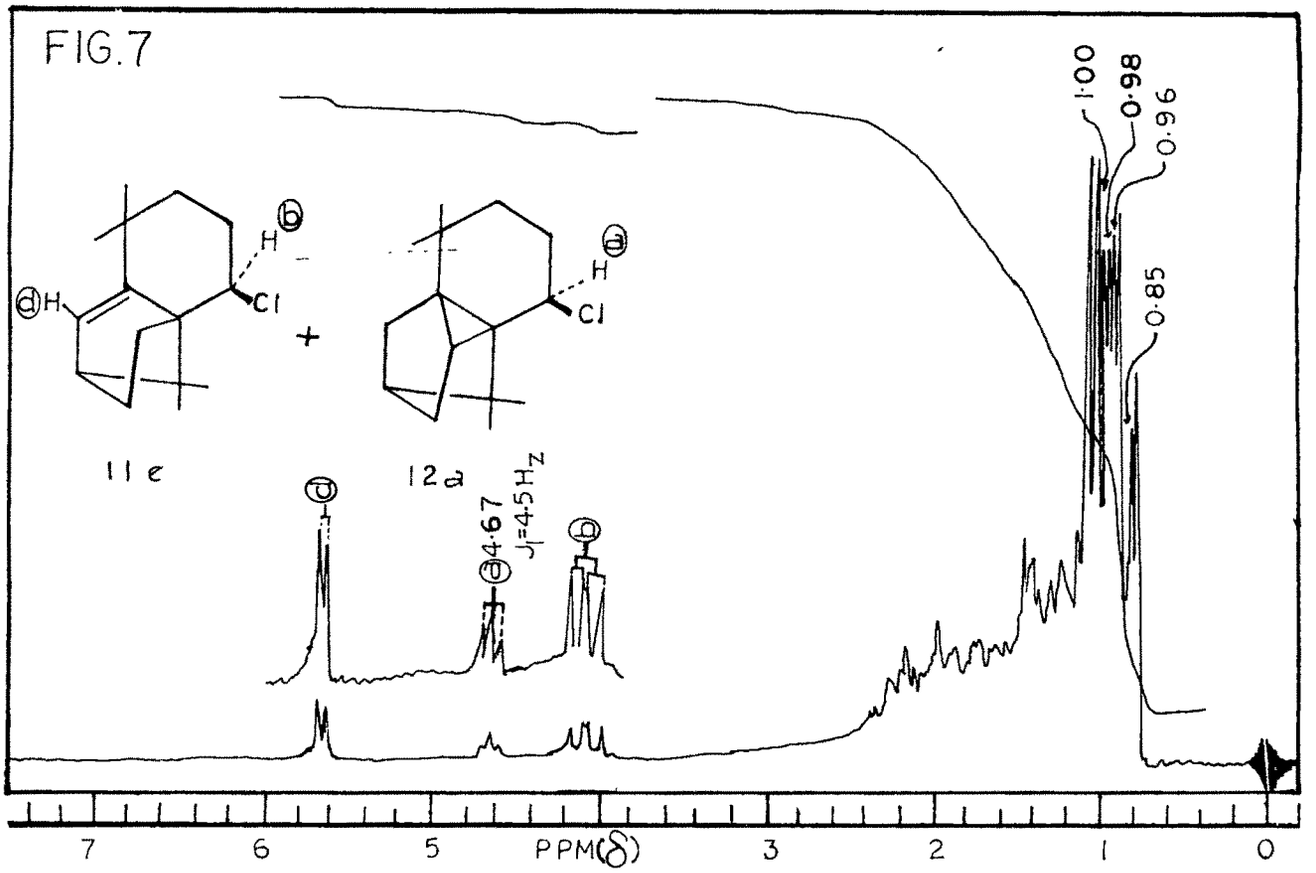

1·00
0·98
0·96
0·85
11e
12a
4·67
J=4·5Hz
7
6
5
PPM(δ)
3
2
1
0

FIG 8

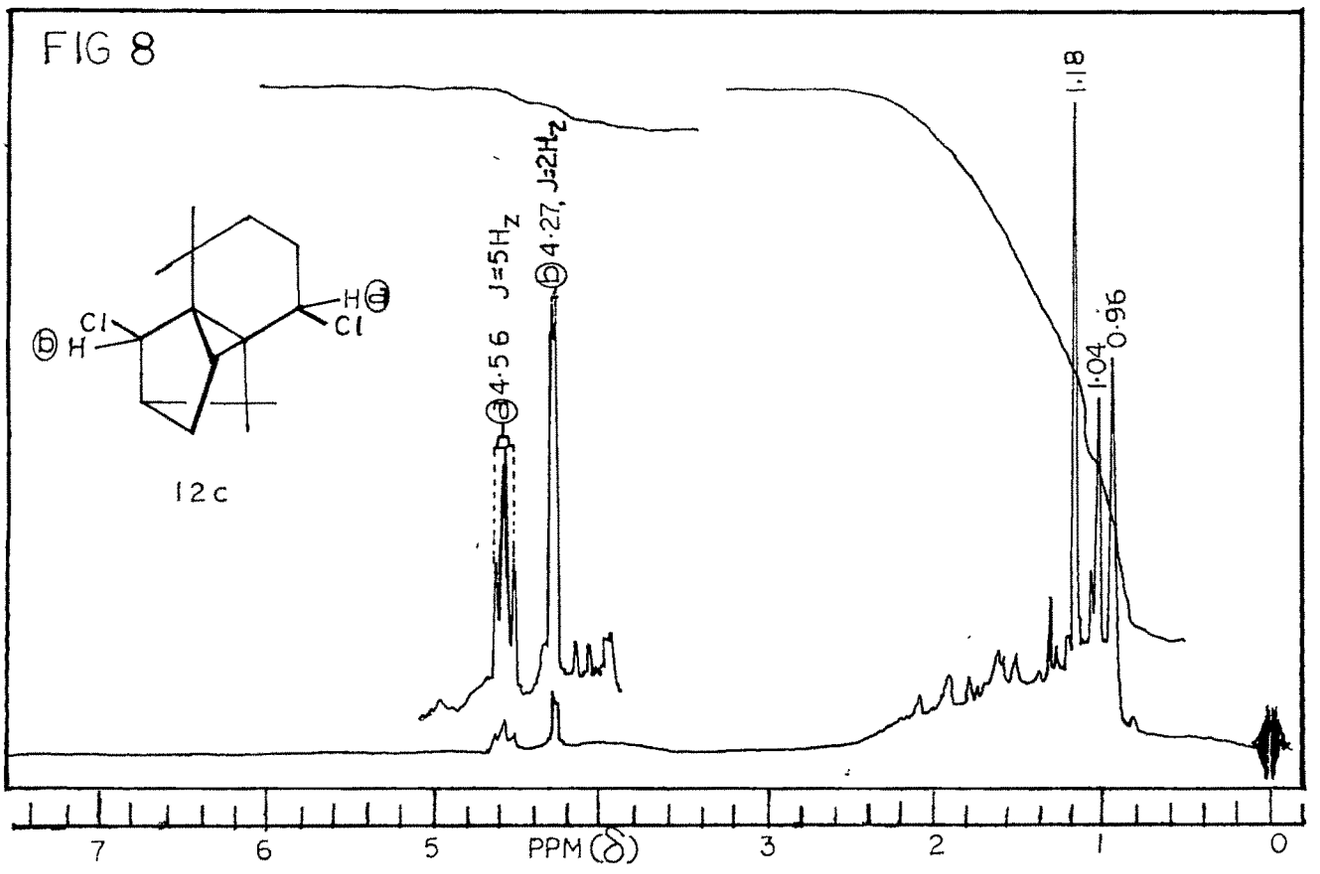

1·18
4·27, J=2Hz
J=5Hz
4·56
1·04
0·96
12c
7
6
5
PPM(δ)
3
2
1
0

FIG. 9

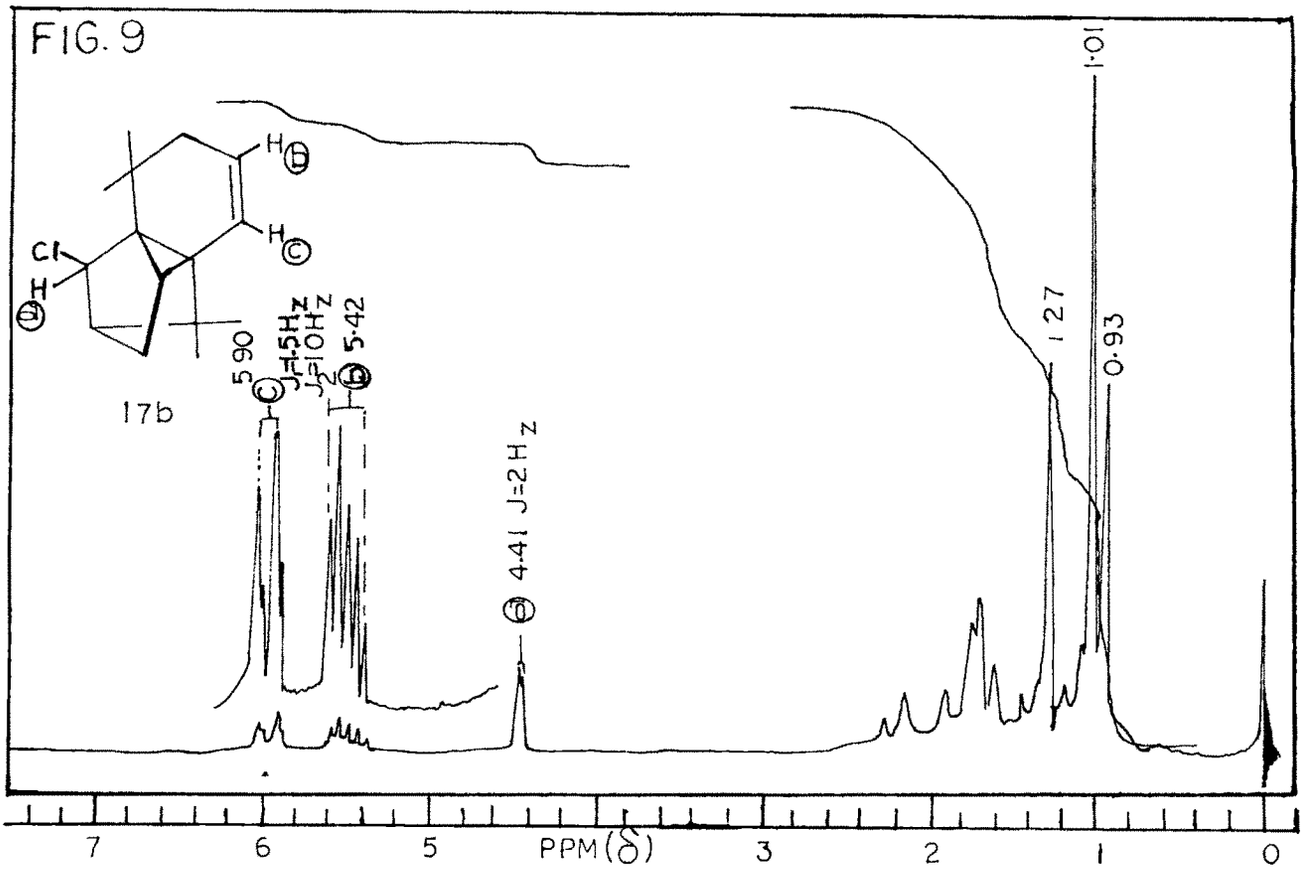

17b
5·90
J=1·5Hz
J=10Hz
5·42
4·41 J=2Hz
1·27
1·01
0·93
7
6
5
PPM(δ)
3
2
1
0

FIG 10

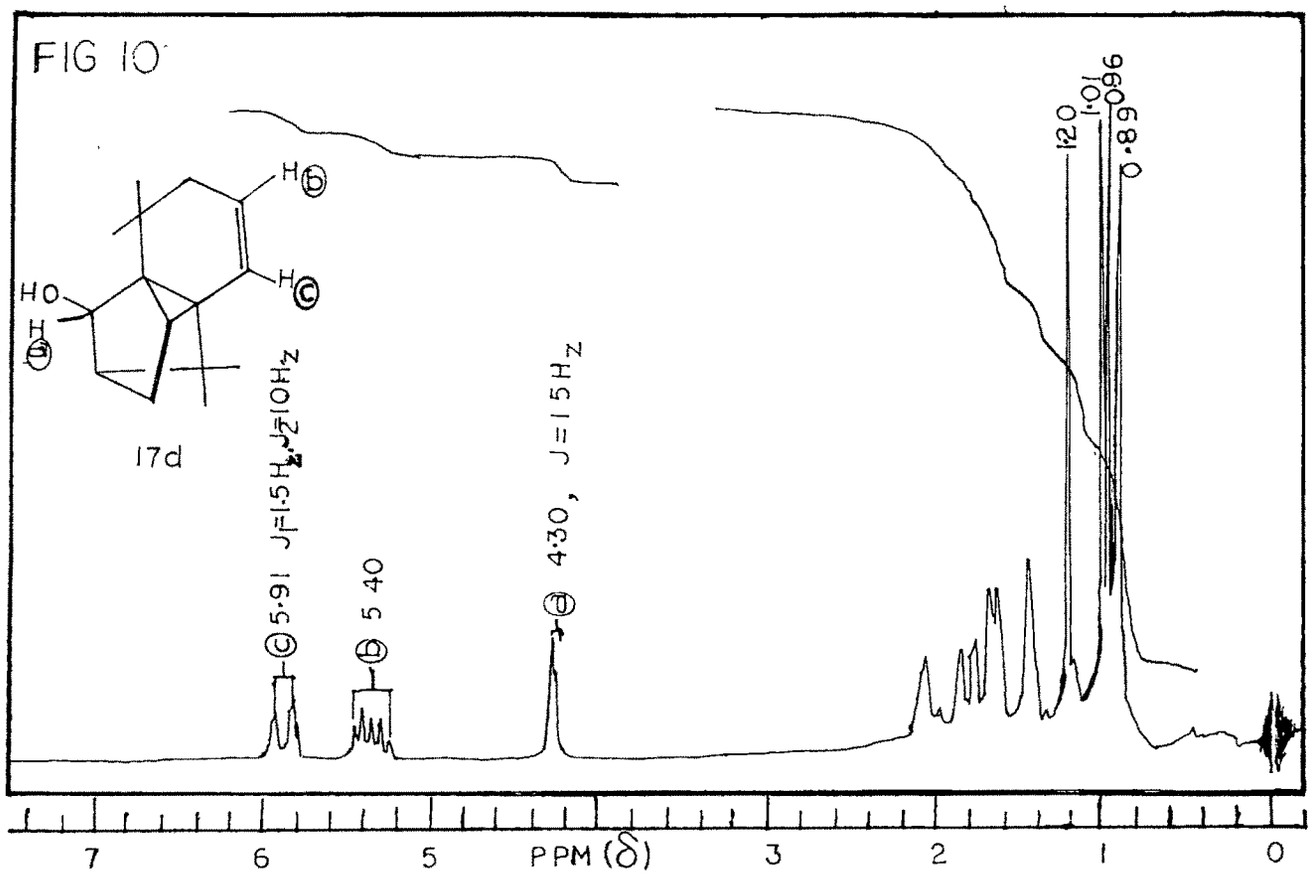

17d
5·91 J=1·5Hz, J=10Hz
5·40
4·30, J=1·5Hz
1·20
1·01
0·96
0·89
7
6
5
PPM (δ)
3
2
1
0

FIG.11

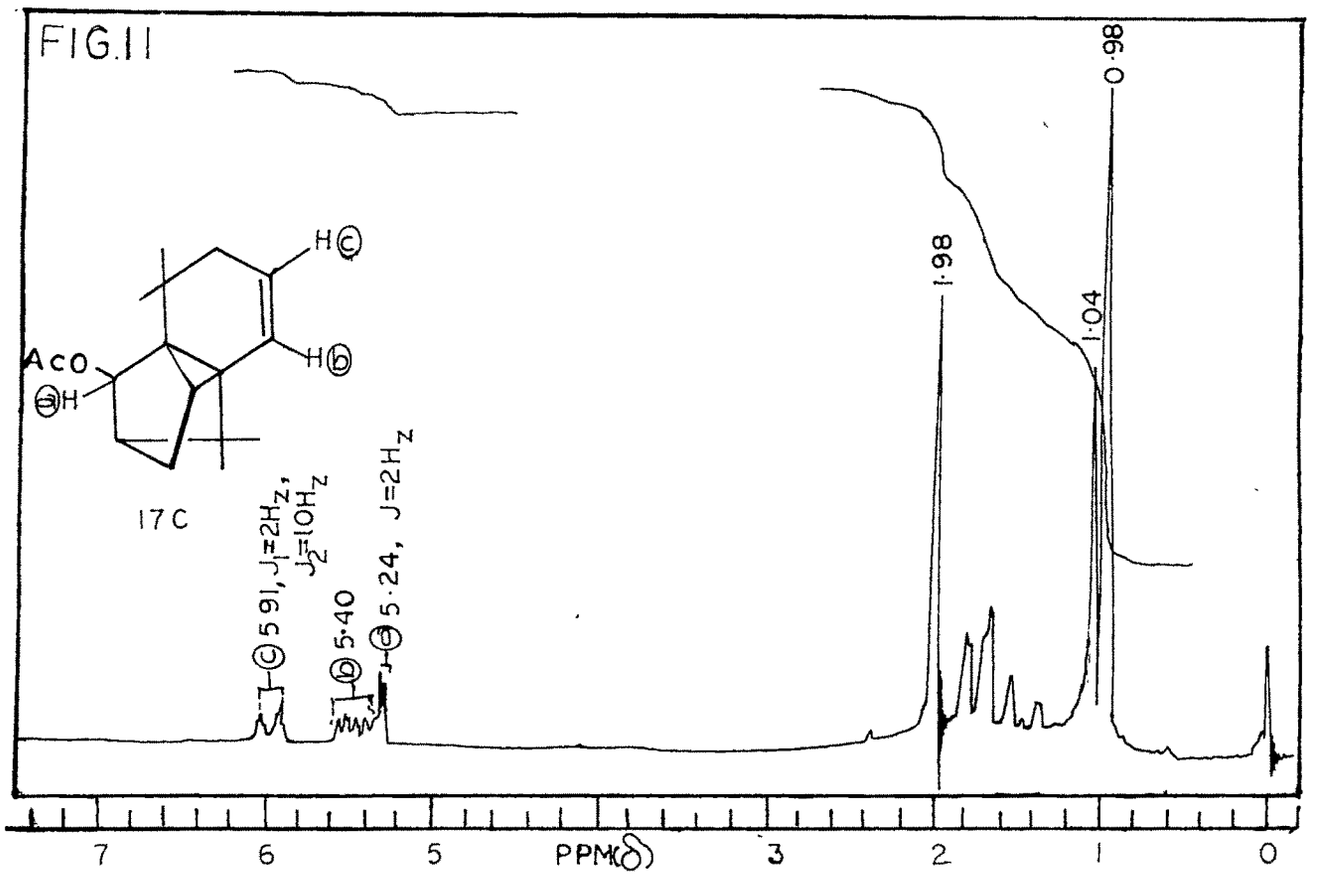
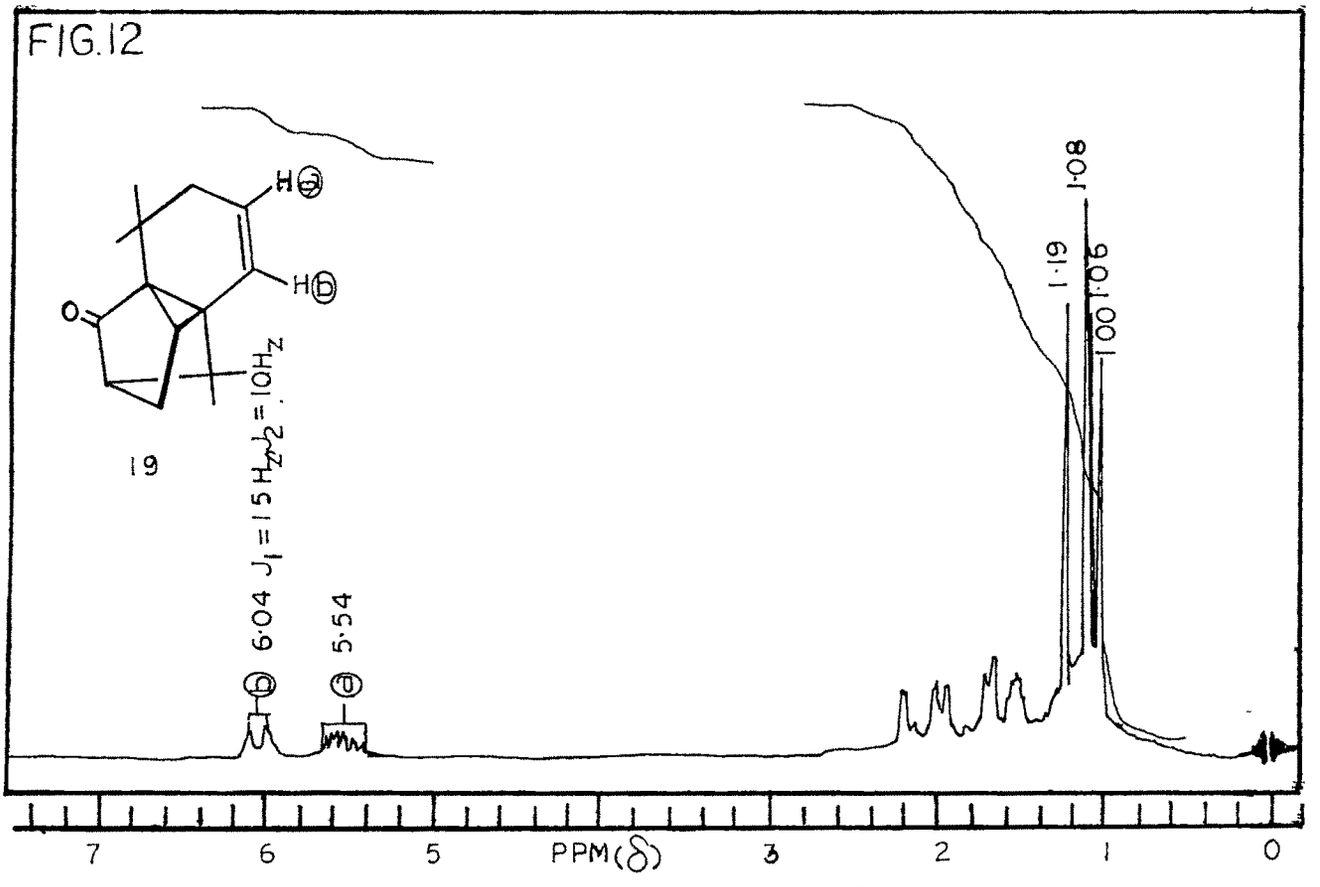
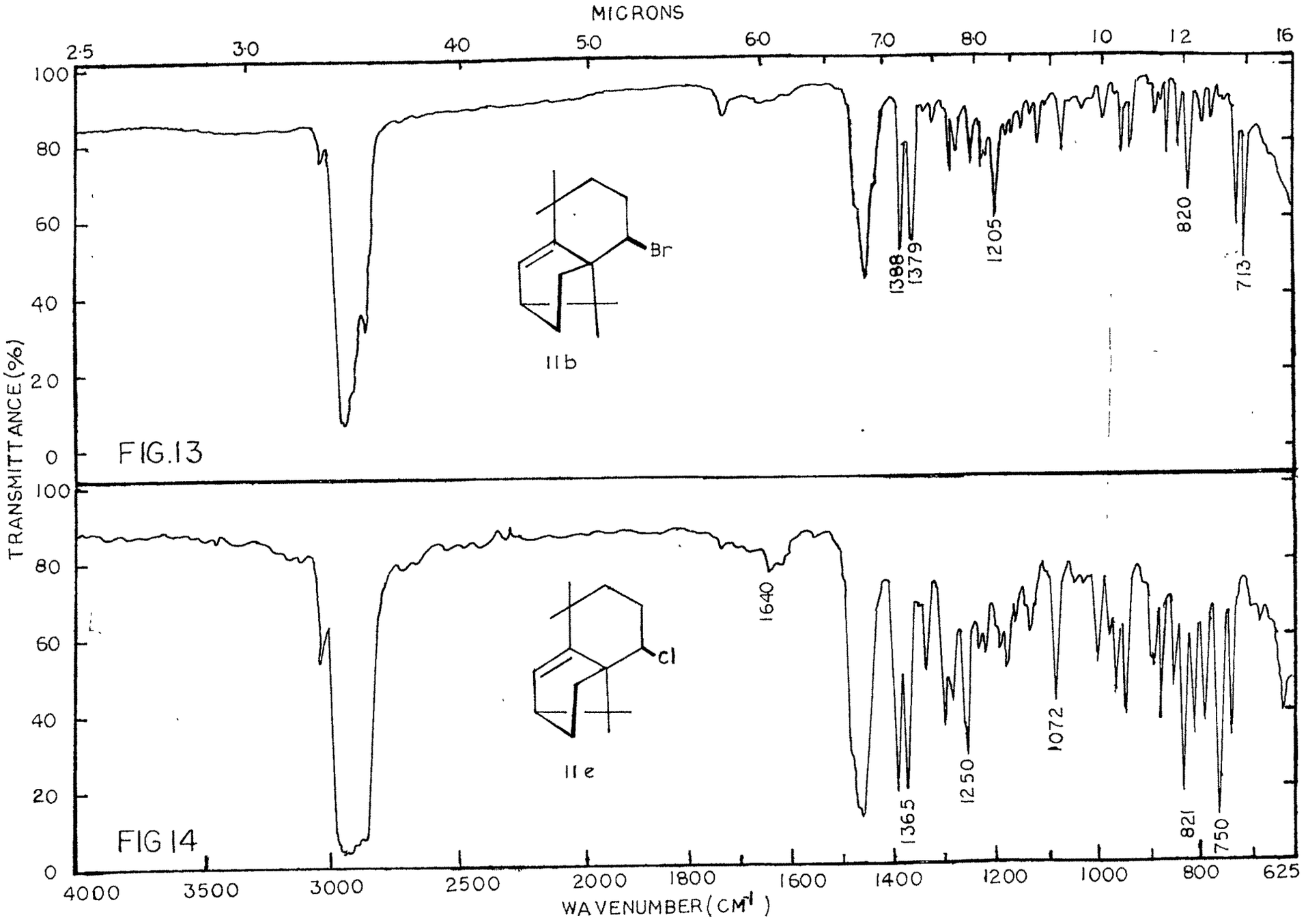
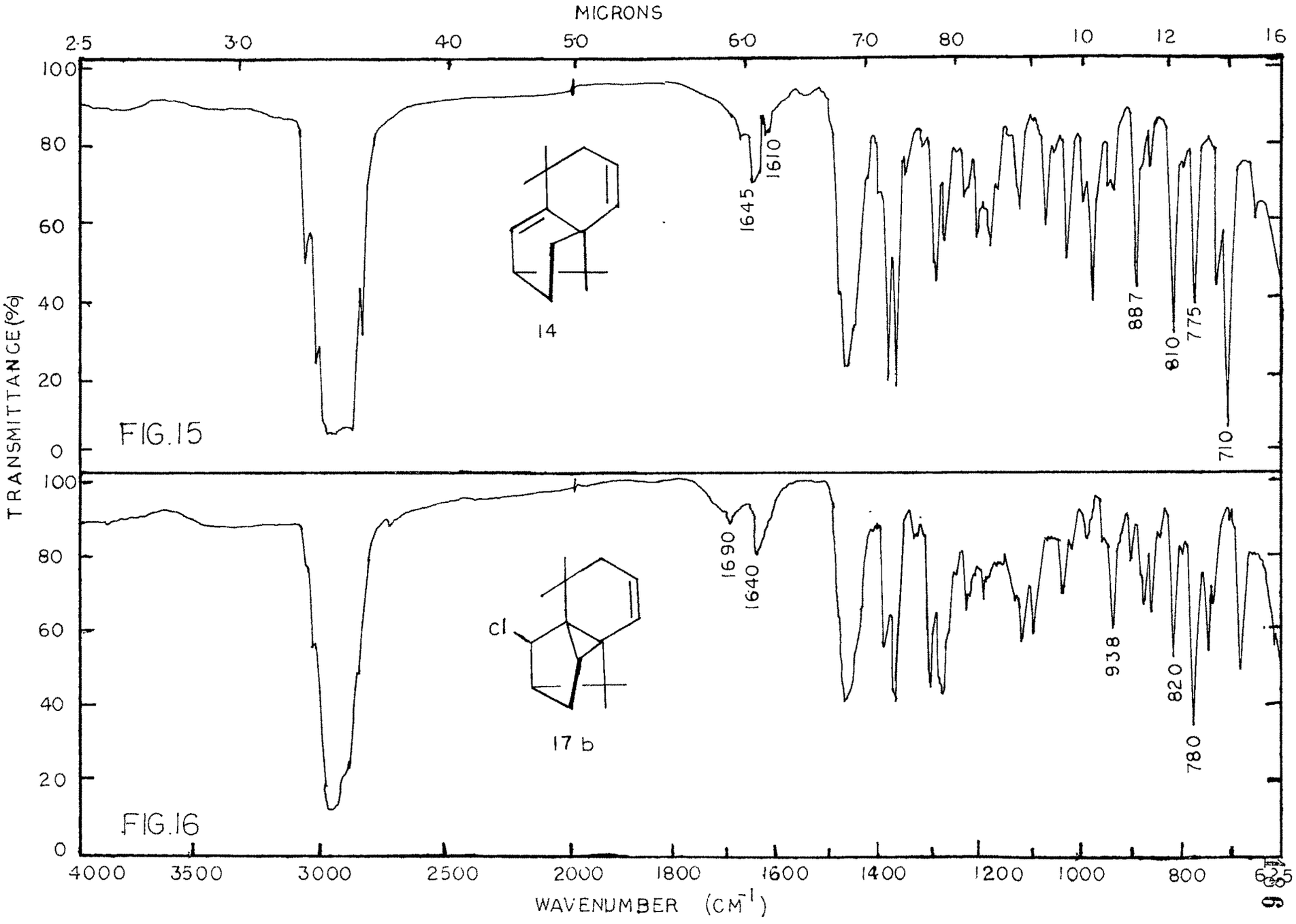
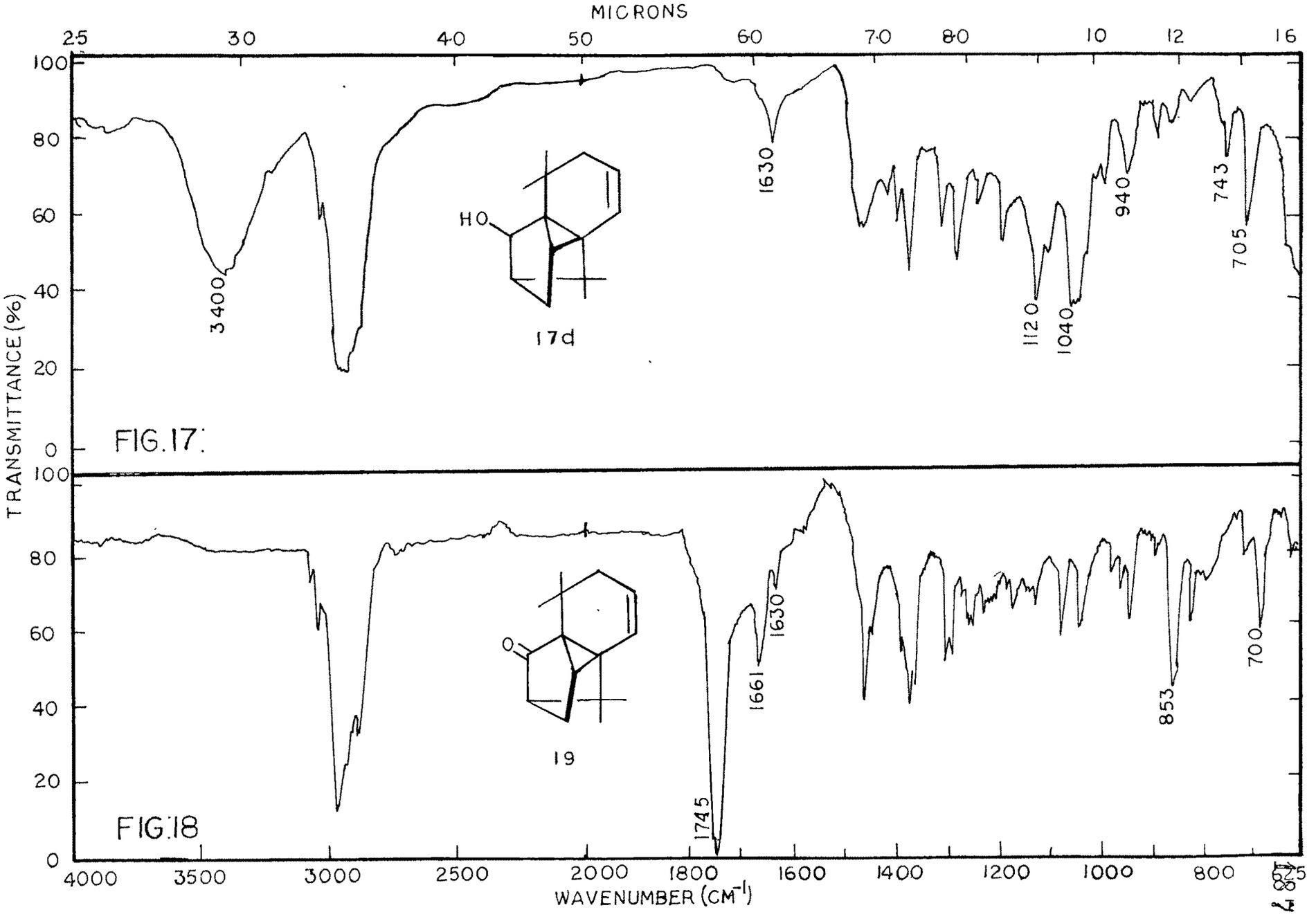

H©
H⓫
AcO
⊖H
17C
⓬ 5·91, J=2Hz, J=10Hz
⓫ 5·40
⓪ 5·24, J=2Hz
0·98
1·04
1·98
7
6
5
PPM(δ)
3
2
1
0

FIG.12


H⓪
H⓫
O
19
⓫ 6·04 J=15Hz, J=10Hz
⓪ 5·54
1·08
1·19
1·00
0·95
7
6
5
PPM(δ)
3
2
1
0


MICRONS
2·5
3·0
4·0
5·0
6·0
7·0
8·0
10
12
16
100
80
60
40
20
0
TRANSMITTANCE (%)
Br
11b
1388
1379
1205
820
713
FIG.13
Cl
11e
1640
1365
1250
1072
821
750
FIG 14
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
625
WAVENUMBER (CM⁻¹)


MICRONS
2·5
3·0
4·0
5·0
6·0
7·0
8·0
10
12
16
TRANSMITTANCE (%)
100
80
60
40
20
0
1645
1610
887
810
775
710
14
FIG. 15
1690
1640
938
820
780
Cl
17 b
FIG. 16
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
625
WAVENUMBER (CM⁻¹)


MICRONS
25
30
40
50
60
70
80
10
12
16
100
80
60
40
20
0
TRANSMITTANCE (%)
3400
1630
1120
1040
940
743
705
HO
17d
FIG. 17.
1745
1661
1630
853
700
O
19
FIG. 18
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
WAVENUMBER (CM⁻¹)