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STERIC DIVERSION—I

ADDITION OF HALOGENS AND PSEUDO-HALOGENS TO ISOLONGIFOLENE†

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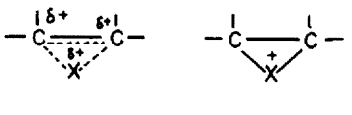
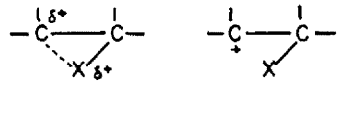
Abstract—Addition of halogens (Cl_2, Br_2) and pseudo-halogens (ICl, halogen azides, NOCl) to isolongifolene does not yield any "normal" addition products due to severe steric hindrance to the approach of counter ion at C-7. Initially formed halogenonium ions undergo elimination or rearrangement to give "abnormal" products. The term *Steric Diversion* is suggested to describe this switch over from the "normal" route.

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 C atom (**4**).

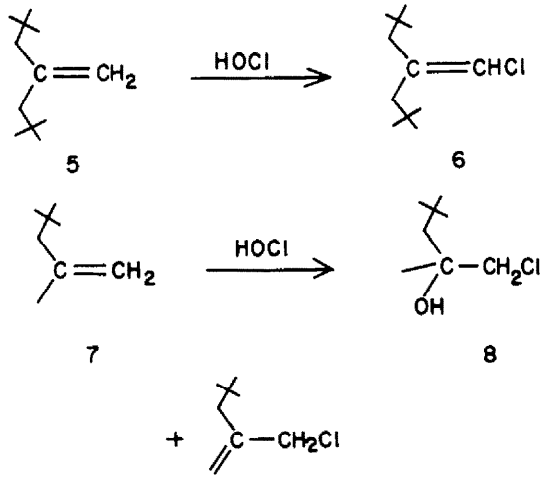


1 **2**



3 **4**

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 arise from 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 hindered furnished 34% of "normal" product (**8**) and 46% of elimination product (**9**).[2] A literature survey revealed that such "abnormal" reactions have been often encountered, especially in the area of natural products chemistry and



5 **6** **7** **8** **9**

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]

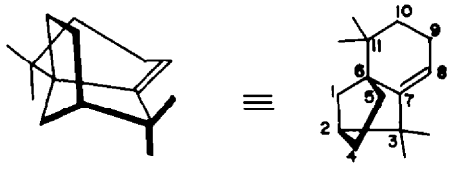
It is felt that this diversion of a "normal" reaction pathway, because of purely steric hindrance, is a fairly general phenomenon and is responsible for the formation of so-called "abnormal" products in several reactions, and the general term *Steric diversion* is proposed to describe this switch over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

†MRC Communication No. 11.

‡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 hindrance blocks the "normal" course of the reaction.

Electrophilic addition to isolongifolene

In the context of the above description, it was felt that isolongifolene[21] (**10**), in which steric crowding at the more substituted end of the ethylenic bond is, at least, as severe as in *unsym*-dineopentylethylene (**5**), should essentially lead to sterically diverted products in reactions such as addition of halogens/pseudo-halogens. This has, indeed, proved to be so in reactions involving its interaction with bromine, chlorine, iodine chloride, halogen azides or nitrosyl chloride.



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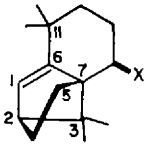
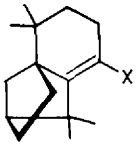
Addition of bromine. Isolongifolene, when allowed to react (~0°) with one mole equivalent of bromine in presence of Na_2CO_3 aq., gave a product, shown by GLC to contain, besides unchanged isolongifolene (RRT = 1.00, 10–13%) and some minor constituents, three compounds having RRT: 4.40 (70–80%), 5.00 (~2%) and 10.40 (~5%). These compounds were separated by fractional distillation.

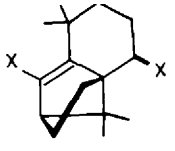
The major product (RRT = 4.40), $C_{15}H_{23}Br$ (M^+: *m/e* 284, 282), is assigned structure **11** because of its structural features: four tert. Me's (PMR: 3H singlets at 0.83, 0.95, 1.06 and 1.09 ppm), =C=CH–CH (PMR: 1H, d, 5.65 ppm, J = 4.0 Hz), =CHBr.CH_2 (PMR: 1H, t, 4.28 ppm, J = 8.5 Hz). On hydrogenation over Raney Ni in presence of alcoholic NaOH, or reduction with LAH, it furnished the known[22] hydrocarbon **14** (neoisolongifolene), thus further securing structure **11**. The configuration for the bromine atom shown in **11** is presumed from the known[23] propensity for *endo* attack at the ethylenic linkage in isolongifolene.



11: X = Br
12: X = Cl
13: X = I
14: X = H



15: X = Br
16: X = I



17: X = Br
18: X = Cl

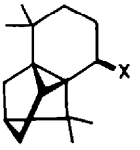
The compound having RRT = 5.00, could not be obtained analytically pure, but from its mass spectrum (M^+: *m/e* 284, 282), PMR spectrum (4 tertiary Me's: 3H singlets at 0.91, 0.91, 1.15 and 1.30 ppm; no olefinic H, no CHBr) and UV end-absorption[24] (ϵ_{220} 4825, ϵ_{230} 2323) is clearly **15**.

The third product (RRT, 10.40), m.p. 91–92° (racemic), $C_{15}H_{22}Br_2$ (M^+: *m/e* 364, 362, 360), from its spectral data (UV, IR, PMR) is assigned structure **17**. When two mole equivalents of bromine were reacted (0°) with isolongifolene, **17** was obtained in over 70% yield. Exposure of 8-bromoneoisolongifolene (**11**) to NBS in buffered aq. dioxane, furnished **17** in good yield. These reactions fully support structure **17**.

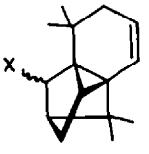
It may also be mentioned that reaction of isolongifolene with NBS in buffered aq. dioxane yielded essentially **11** or **17**, depending on whether one or two mole equivalent of NBS were employed.

Addition of chlorine. Chlorination (1 mole equiv; ~0°) of isolongifolene in presence of Na_2CO_3 aq. gave a product, which from its PMR spectrum and reactions discussed below, could be computed as ~1:1 mixture of the two chloro derivatives **12** and **19**. Compound **12** could be readily isolated by fractionation. Its structure is based on the close similarity of its PMR spectrum (4 tertiary Me's, 3H singlets at 0.83, 0.93, 1.04 and 1.08 ppm; =CHCl.CH_2, 1H, d × d, 4.11 ppm, J_1, J_2 = 7.0, 9.0 Hz; =C=CH–CH, 1H, d, 5.67 ppm, J = 3.5 Hz) with that of **11**.

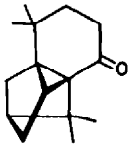
The second compound proved thermally highly labile, eliminating HCl gas even at 50–60° during attempted solvent removal and hence, could not be isolated pure as such. However, it was readily recognised as **19** by indirect means. Thus, by subtracting the PMR spectrum of **12** from the PMR spectrum of the total monochlorination product, PMR signals (4 tertiary Me's 3H singlets at 0.85, 0.96, 0.98 and 1.00 ppm; =CHCl.CH_2, 1H, t, 4.67, J = 4.5 Hz) assignable to the second component and fully consistent with the structure **19** could be readily discerned. In another experiment, the reaction mixture was later, heated at ~90° for 1 hr to complete dehydrochlorination of **19** and the product separated by fractionation to furnish, besides **12**, the known[22] hydrocarbon, dehydrocycloisolongifolene (**21**). In a third experiment, the total monochlorination product, while in solution (CCl_4), was exposed to $Ca(OH)_2$-water, when the much more reactive[25] **19** readily yielded the corresponding alcohol (m.p. 99.5–100°), easily insolable by chromatography, and identified (mixed m.p., IR, PMR) as the known[22] cycloisolongifolol (**20**)†; in an alternative



19: X = Cl
20: X = OH



21: X = H
22: X = Cl
23: X = OH
24: X = OAc



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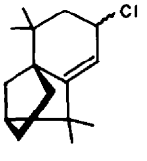

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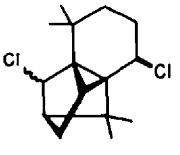

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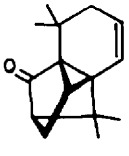

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†Configuration of the OH given in ref. 22 is opposite to that shown in **20**. The latter represents the corrected configuration arising from the revised[23] stereochemistry for isolongifolene epoxide. The total retention of configuration in this solvolytic reaction requires that σ-bridged ions,[26] such as a bicyclobutonium cation, are unimportant in this reaction.

sequence, the crude product after hydrolysis and consisting essentially of 8-chloroneoisolongifolene (**12**) and **20**, was oxidised (CrO_3/H_2SO_4) and the product separated to get the expected ketone **25** (IR: C=O 1667 cm^{-1}).[27] All these transformations serve to delineate the second product of chlorination as **19**.

In a recent patent[28] it has been claimed that action of Cl_2 on isolongifolene in presence of anhyd. Na_2CO_3 gives as the major product, the allylic chloride **26**. On repetition of this reaction according to the directions of the patent, we got a product consisting essentially of **12** and **19** in the ratio of 2:1 and none of the alleged allylic chloride **26** was detected.

The olefinic linkage in 8-chloroneoisolongifolene (**12**) is even more sterically shielded than that in isolongifolene and hence it was of interest to examine its further reaction with chlorine. Exposure of **12** to another mole equivalent of Cl_2 (at 28–30°) furnished a product, consisting mostly (~80%) of a compound, recognised indirectly (and PMR) as **27**. When isolongifolene was straightaway reacted at 28–30° with two mole equivalents of Cl_2, the product was computed (PMR) as consisting of the monochloride **19** (30%) and dichlorides **27** (60%) and **18** (5%). The latter material was heated to get dehydrochlorinated products **21** and **22**, which could be separated by fractionation and suitably characterised. Pure **22** on reduction with LAH furnished dehydrocycloisolongifolene (**21**); on hydrolysis (lime/water) it yielded alcohol **23**, which on oxidation (CrO_3/H_2SO_4) gave ketone **28** (IR: C=O 1745 cm $^{-1}$).[29] Reaction of crude **27** with NaOAc/AcOH yielded, amongst other products, the olefine acetate **24**. Spectral data of all these products are fully consistent with the assigned structures, which in turn help to characterise the major dichloride as **27**.

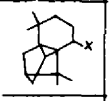
Action of pseudohalogens. Next, action of pseudohalogens, such as iodine chloride, halogen azides, nitrosyl chloride, on isolongifolene was investigated to see what type of products result. No attempt was made to separate components, as with the knowledge of the PMR spectral features of the chlorine and bromine addition products described above, the PMR spectrum of the total product from these reactions sufficed to furnish a semi-quantitative analysis of the product. These results have been summarised in Table 1, which also displays, for comparison, the composition of reaction products from halogen addition.

DISCUSSION

Irrespective of whether the addition of halogens[30] and pseudohalogens[31] to isolongifolene takes place via a free radical or ionic mechanism, no "normal" addition products have been observed. The steric diversion in these cases can be ascribed to severe steric hindrance to the approach of addenda at C_7 or, at C_6 in the case of 8-haloneoisolongifolene (e.g. **11**). Three different pathways leading to sterically diverted products (Table 1) are followed. But a wide difference in the product composition is observed with different reagents and may be a consequence of the involvement of cyclic or acyclic halogenonium ions, and intimate or solvent separated ion pairs, which in turn are governed by such factors as the bridging capacity of the electrophile, nature of the counter ion, nature of the solvent, etc.[1] At this stage it is not possible to offer any rigorous explanation for product development in different cases, but the following reasoning suffices to rationalise the results.

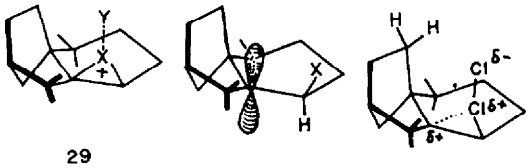
The additions of halogens and pseudohalogens to isolongifolene have all been carried out in presence of air and hence, contributions from the radical pathway can be expected to be minimal. The ionic addition of addendum X – Y to isolongifolene can, in principle, lead to the fully bridged ion **29** or the ion **30** with the fully developed carbonium ion, or to intermediate situations with varying degree of bridging. Whereas carbonium ion **30** can conceivably lead to all three types of products, it is improbable that **29** will undergo deprotonation to a cyclopropane derivative (e.g. **19**) or Wagner–Meerwein rearrangement to type of product exemplified by **11**, because of lack of antiperiplanar orientation of the dimethylene bridge and C–X bond. It could, however,

Table 1. Some electrophilic additions to isolongifolene

Reagent	Solvent	Reaction temp. (~)	Product(s)			
			Addendum (X)	% Composition*		
						
Cl_2/Na_2CO_3 aq	CCl_4	0°	Cl	55	0	45
Br_2/Na_2CO_3 aq	CCl_4	0°	Br	95	5	0
ICl/Na_2CO_3	CH_3CN or CCl_4	5→15°	I	0	> 90	0
IN_3	CH_3CN	0→15°	I	60	30	0
BrN_3/Na_2CO_3	CH_2Cl_2	0°	Br	> 90	0	0
ClN_3/Na_2CO_3	CH_2Cl_2	0°	Cl	> 90	10	0
NOCl	AcOH	0°	NO†	> 80	0	0

* Refers to the composition of the monoaddition product only

† Isolated in oxime form.



29 30 31

certainly be a precursor for vinyl halides (e.g. **15**). It has been stated[32] that the bridging capacity of halogens increases in the order $Cl_2 < Br_2 < I_2$, and the above reasoning would predict increased yields of the vinyl halide as X varies from Cl to Br to I, and this, indeed, is the case (Table 1). Chlorine, amongst all the reagents studied, is unique in generating cycloisolongifolane derivatives,[33] which are not formed with chlorine azide and this highlights the importance of the gegen ion; conceivably, Cl_2 reaction, for which mechanisms involving intimate ion-pairs have been preferred,[34] passes through a geometrically optimal transition state such as **31** wherein elimination of proton from C-5 is facilitated by proximity of Cl (δ-) atom.[35]

EXPERIMENTAL

All m.ps and b.ps are uncorrected. Light petroleum refers to the fraction b.p. 60–80°. All solvent extracts were finally washed with brine and dried (Na_2SO_4).

The following instruments were used for spectral/analytical data: Perkin–Elmer Infrared Spectrophotometer, model 267; Perkin–Elmer model R 32 (90 MHz) NMR spectrometer; Varian Mat CH7 Mass spectrometer (70 eV, direct inlet system); Hewlett–Packard 5712 A and 7624 A gas chromatographs (Al columns, 180 × 0.6 cm; support, 60–80 mesh Chromosorb W; carrier gas, H_2). All PMR spectra were taken in 15–20% soln in CCl_4 (unless stated to the contrary) with TMS as internal reference; 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; br, broad. While summarising mass spectral data, besides the molecular ion, ten most abundant ions (*m/e*) are reported with their relative intensities.

Alumina used for chromatography was neutral and was graded according to Brockmann.[36] Silica gel for column chromatography (−100, +200 mesh) was washed with hot water till sulphate-free, dried, activated at 125–130° for 6–8 h, and standardised.[37] TLC was carried out on SiO_2-gel layers (0.25 mm) containing 15% gypsum and activated at 110–115° (2 h).

Isolongifolene used in this investigation was 80% racemised.[21]

Reaction with bromine/NBS (one mole equivalent)

(i) *Action of bromine.* To a stirred mixture of isolongifolene (180 g, 0.88 mole) in CCl_4 (750 ml) and 15% Na_2CO_3 aq (1200 ml) at $-3 \pm 2°$, a soln of Br_2 (136 g, 1.7 g. atom) in CCl_4 (250 ml) was introduced at a rate such that the reaction temp. was maintained at ~0° (4 h). After the addition, the temp. was allowed to reach room temp. (28°) and stirring continued at that temp. for an additional 4 h. Usual work up gave a product (240 g), a small sample from which was distilled and analysed by GLC (carbowax 20M, 3%; temp. 150°) (see text). The main product was carefully fractionated (Vigreaux column) to furnish, besides a fore-run (52.5 g, b.p. 85–87°/1 mm, essentially isolongifolene) and residue (4.5 g), three main cuts.

Fraction b.p. 105–110°/1 mm (169 g, 95% purity by GLC) was characterised as 8-*bromoneoisolongifolene* (**11**).† IR (liq.): 1292, 1205, 1119, 1071, 952, 938, 865, 840, 820, 730, 712 cm^{-1}. Mass: *m/e* 284 (M^+, 6%), 282 (M^+, 6%), 203 (100%), 175 (24%), 159 (12%), 147 (21%), 145 (13%), 133 (12%), 131 (16%), 119 (17%), 105 (19%), 91 (19%). (Found: C, 64.34; H, 7.71; Br, 27.10. $C_{15}H_{23}Br$ requires: C, 63.60; H, 8.18; Br, 28.21%).

Fraction b.p. 115–120/1 mm (4.0 g) was characterised as 8-bromoisolongifolene (**15**).

Fraction b.p. 138–140°/1 mm (6.2 g) was characterised as 1,8-*dibromoneoisolongifolene* (**17**). The product slowly partly crystallised and the crystals, m.p. 91–92° (light petrol), $[\alpha]_D = \pm 0°$, had spectral characteristics identical with those of the total material. IR (Nujol): 1600, 1220, 1200, 1118, 1042, 1020, 952, 875, 795, 752, 730 cm^{-1}. UV (EtOH): ϵ_{220} 5150, ϵ_{225} 3580, ϵ_{230} 2460. PMR: tert. Me's 0.97, 0.97, 1.10, 1.35 ppm; CHBr, t, 4.21 ppm, J = 8.5 Hz. Mass: *m/e* 364 (M^+, 6%), 362 (M^+, 13%), 360 (M^+, 7%), 283 (51%), 281 (57%), 255 (97%), 253 (100%), 174 (16%), 159 (28%), 143 (16%), 129 (20%), 128 (20%), 91 (22%). (Found: C, 50.53; H, 6.71; Br, 43.24. $C_{15}H_{22}Br_2$ requires: C, 49.75; H, 6.12; Br, 44.13%).

(ii) *Reaction with NBS.* To a mixture of isolongifolene (2 g), dioxane (20 ml), water (10 ml) and $CaCO_3$ (1 g), NBS (2 g) was added with stirring at 0–5°. After stirring at this temp. for 2 h, the reaction mixture was diluted with water (50 ml) and worked up with ether in the usual manner, to give after solvent removal, 2.75 g of a pale yellow oil, identified (GLC, PMR) as essentially **11**.

Reaction with bromine/NBS (two mole equivalent)

(i) *Action of bromine.* To a stirred mixture of isolongifolene (22.5 g, 0.11 mole) in CCl_4 (100 ml) and 10% Na_2CO_3 aq (600 ml) at ~0°, a soln of Br_2 (35.2 g, 0.44 g atom) in CCl_4 (75 ml) was introduced (3 h), keeping the reaction temp. ~0°. The reaction mixture was stirred for another 2 h at room temp. (28°) and then worked up in the usual manner to furnish essentially **17** (31.5 g), b.p. 132–135°/0.5 mm.

(ii) *Action of NBS.* To a stirred mixture of isolongifolene (40 g), water (200 ml), dioxane (400 ml) and $CaCO_3$ (20 g) at 20°, NBS (80 g) was added rapidly (10 min). The mixture was stirred for 2 h, during which period the reaction temp rapidly rose to ~50° initially. The cooled reaction mixture was diluted with water (500 ml), filtered and the filtrate extracted with ether (100 ml × 3) and then further processed in the usual manner to give 70 g of a brownish liquid, which was distilled to get **17** (60 g), b.p. 138–142°/1 mm.

1,8-Dibromoneoisolongifolene (**17**) *from 8-bromoneoisolongifolene* (**11**)

A mixture of **11** (2.7 g), water (10 ml), dioxane (20 ml), $CaCO_3$ (1 g) and NBS (2 g) was stirred at 25–28° for 2 h and worked up as above to give after distillation **17** (3.0 g).

All these preparations of **17** slowly partly crystallised, due to separation of the racemic dibromide (*vide supra*).

Neoisolongifolene (**14**) *from 8-bromoneoisolongifolene* (**11**)

(i) *With LAH.* To a slurry of LAH (0.46 g) in diglyme (20 ml), a soln of **11** (1.2 g) in diglyme (20 ml) was added and refluxed (N_2) for 5 h. Usual work-up (water/10% H_2SO_4 aq/light petrol extraction), gave after solvent removal a liquid (0.72 g), which was purified by chromatography over 15% $AgNO_3$–SiO_2 gel column (34 × 2.4 cm) to get pure **14** (0.43 g) (eluted with light petrol, 100 ml × 3), b.p. 90–95° (bath)/1.5 mm.

(ii) *By hydrogenolysis.* 8-Bromoneoisolongifolene (**11**; 34 g) in EtOH (300 ml) containing 20 ml of 40% NaOH aq was hydrogenated at room temp. (25°) and pressure in the presence of Raney Ni (14 g). After 1 mole equivalent of H_2 had been consumed (2 h), the reaction mixture was worked up in the usual manner (filtration/dilution of filtrate with water/extraction with light petrol) to furnish, after solvent removal, a product (23.0 g) which was distilled to get pure (GLC purity, 95%) **14** (21.8 g), b.p. 78–81°/1 mm. PMR: tert. Me's, 0.73, 0.77, 1.02, 1.10 ppm; C=CH, d, 5.61 ppm, J = 4 Hz.

Reaction with chlorine (one mole equivalent)

Chlorine was passed (1 h) into a stirred mixture of isolongifolene (20.4 g, 0.1 mole) in CCl_4 (100 ml) and $Na_2CO_3.H_2O$ (18 g) in H_2O (130 ml), at $-2 \pm 1°$, so that the total increase in wt. was

†No micro analytical facilities are available to the authors in their laboratory. The poor analyses are due to the instability of the bromo derivatives. The mass spectral data should be adequate.

~5.5 g (≡7.0 g of chlorine, 0.2 g atom, minus wt. of CO_2 evolved), after displacing any excess Cl_2 with N_2. The CCl_4 layer was separated, washed neutral with water (50 ml × 2) and dried. From a small sample (2 ml), CCl_4 was cautiously removed at 10° under suction and the residue examined by PMR (see text). The main product was divided into two equal parts for separate treatment.

8-Chloroneoisolongifolene (**12**) *and dehydrocycloisolongifolene* (**21**)

The CCl_4 soln was freed of the solvent from a water-bath (~90°), when concomitant dehydrochlorination of one component (**19**) also occurred. The product (10.2 g) was fractionated to get, besides a small (1.0 g) intercut, two main fractions:

Fraction b.p. 78–80°/2 mm (3.0 g), was characterised (mixed GLC, IR, PMR) as the known[22] hydrocarbon *dehydrocycloisolongifolene* (**21**).

Fraction b.p. 90–95°/2 mm (3.5 g) was characterised as 8-chloroneoisolongifolene (**12**). IR (liq.): 1292, 1280, 1260, 1250, 1072, 936, 865, 821, 802, 780, 750, 727 cm^{-1}. (Found: C, 75.30; H, 9.74; Cl, 14.41. $C_{15}H_{23}Cl$ requires: C, 75.45; H, 9.71; Cl, 14.85%).

Cycloisolongifolol (**20**). The other part of the CCl_4 soln containing **12** and **19**, was stirred at room temp. (29–30°) with $Ca(OH)_2$ (10.0 g) and water (130 ml), for 16 h. The reaction mixture was filtered, the CCl_4 layer separated and aqueous phase extracted with CCl_4 (25 ml × 2). The combined extracts were washed with water till neutral and dried. The solvent was removed at ~20° under reduced pressure and the residue (11.5 g) treated as follows.

A part (1.1 g) of the above product was chromatographed over Al_2O_3/III (40 g, 27 × 1.5 cm). Light petrol (30 ml × 2), eluted **12** (483 mg). Benzene (30 ml × 4) eluted a solid (490 mg), m.p. 96–99°, which was recrystallised from light petrol to give a product m.p. 99.5–100°, identified as *cycloisolongifolol* (**20**).[22]

Another part (1.9 g) in acetone (10 ml) was treated with Jones' reagent[38] (1.5 ml) at 0° and then left aside at 10° for 3 hr. Usual work-up yielded a product (1.8 g), which was chromatographed over Al_2O_3/III (40 g, 27 × 1.5 cm). Light petrol (40 ml × 2) eluted **12** (550 mg), while benzene (40 ml × 3) furnished a liquid (470 mg), b.p. 110–115° (bath)/2 mm, identified as *cycloisolongifolone* (**25**). λ_{max}^{EtOH} 270 nm (ε 119). IR(liq.): 1667, 1285, 1275, 1108, 1058, 980 cm^{-1}. PMR: tertiary Me's, 0.98, 1.06, 1.08, 1.11 ppm. (Found: C, 82.13; H, 10.28. $C_{15}H_{22}O$ requires: C, 82.51; H, 10.16%).

Action of chlorine on 8-chloroneoisolongifolene (**12**)

A slow stream of Cl_2 was passed in a well-agitated mixture of chloride **12** (6.98 g) in CCl_4 (21 ml) and anhydrous Na_2CO_3 (2.8 g) at 28–30°, till a test sample, showed by PMR, the disappearance of olefin signal (15 min; weight increase = 1.2 g). Inorganic salts were filtered off and the filtrate freed of solvent at 20° under reduced pressure, to furnish 7.1 g of a product, showing in the PMR spectrum, signals assignable to *1,8-dichlorocycloisolongifolene* (**27**) (since the product is very labile, no attempt was made to isolate pure **27**). PMR: tert. Me's 0.96, 1.04, 1.18, 1.18 ppm; CHCl.CH, 1H, d, 4.27 ppm, J = 2 Hz; CHCl.CH_2, 1H, t, 4.56 ppm, J = 4.5 Hz.

Reaction with chlorine (*two mole equivalents*)

To a well-stirred mixture of isolongifolene (10.2 g, 0.05 mole) in CCl_4 (35 ml) and anhyd Na_2CO_3 (4.4 g), Cl_2 was slowly passed at 28–30° till a sample showed in its PMR spectrum absence of any olefin signal (30 min; weight increase = 3.5 g). To the reaction mixture, Li_2CO_3 (3 g) was added and the whole heated, with stirring at 80° for 6 h. The mixture was cooled, the inorganic salts filtered off, which when washed with CCl_4 (20 ml × 3). The combined CCl_4 soln on solvent removal offered an oil (12.0 g), a part (9.0 g) of which was fractionated to collect separately, hydrocarbon **21** (b.p. 85–90°/3 mm, 2.35 g; mixed GLC, IR, PMR) and, the chloro-olefin, *1-chloro-dehydrocycloisolongifolene* (**22**) b.p. 95–100°/2.5 mm, 4.45 g. IR (liq.): 1640, 1298, 1273, 1120, 1090, 938, 860, 820, 780, 750, 690 cm^{-1}. PMR: tert. Me's 0.93, 1.01, 1.01, 1.27 ppm; CHCl, d, 4.41 ppm, J = 2 Hz; =C=CH=CH–CH_2, 1H, d × t, 5.42 ppm, J_1 = 9.5 Hz, J_2 = 4.5 Hz; =C=CH=CH–CH_2, 1H, d × t, 5.90 ppm, J_1 = 9.5 Hz, J_2 = 1.5 Hz. (Found: C, 76.82; H, 8.65; Cl, 15.1. $C_{15}H_{21}Cl$ requires: C, 77.24; H, 8.50; Cl, 14.27).

Reduction of **22** *to dehydrocycloisolongifolene* (**21**)

A mixture of LAH (300 mg) and chloride **22** (250 mg) in tetrahydrofuran (15 ml) was refluxed (12 h, N_2). The mixture was cooled (5°), treated successively with H_2O (0.3 ml), 15% NaOH aq (0.3 ml) and H_2O (1 ml). The salts were removed by filtration, washed with light petrol and the soln freed of solvents to furnish a liquid (225 mg), which was distilled, b.p. 90–95° (bath)/1 mm, to get the hydrocarbon **21** (*vide supra*).

Hydrolysis of **22** *to 1-hydroxy-dehydrocycloisolongifolene* (**23**)

A mixture of **22** (1.2 g), $Ca(OH)_2$ (0.5 g) and water (20 ml) was stirred at 85–90° (16 h). The product was worked up with light petrol in the usual manner to get an oil (1.1 g), which was filtered through a column of SiO_2/IIA (40 g, 40 × 2 cm), using light petrol, to remove less polar material. The main fraction was distilled to furnish *1-hydroxy-dehydrocycloisolongifolene* (**23**), b.p. 110–120° (bath)/2 mm, 850 mg. IR (liq): 3400, 1630, 1295, 1270, 1180, 1115, 1048, 1030, 938, 745, 705 cm^{-1}. PMR: tert. Me's, 0.89, 0.96, 1.01, 1.20 ppm; CHOH, 1H, d, 4.30 ppm, J = 1.5 Hz; =C=CH=CH–CH_2, 1H, d × t, 5.40 ppm, J_1 = 9.5 Hz, J_2 = 4.5 Hz; =C=CH=CH–CH_2, 1H, d × t, 5.91 ppm, J_1 = 9.5 Hz, J_2 = 1.5 Hz. (Found: C, 82.28; H, 9.40. $C_{15}H_{22}O$ requires: C, 82.51; H, 10.16%).

1-Oxo-dehydrocycloisolongifolene (**28**)

Oxidation of the above alcohol (390 mg) in acetone (2 ml) with Jones' reagent (0.5 ml) at 0° (4 h) in the usual manner gave *1-oxo-dehydrocycloisolongifolene* (**28**), b.p. 120–125° (bath/1 mm, 305 mg. IR (liq.): 1745, 1665, 1300, 1290, 1078, 1042, 945, 862, 830, 700 cm^{-1}. PMR: tert. Me's, 1.00, 1.06, 1.08, 1.19 ppm; =C=CH=CH–CH_2, 1H, d × q, 5.52 ppm, J_1 = 10 Hz, J_2 = 4.5 Hz, J_3 = 6 Hz; =C=CH=CH–CH_2, 1H, d × q, 6.04 ppm, J_1 = 10 Hz, J_2 = J_3 ≃ 1.5 Hz. (Found: C, 83.45; H, 10.53. $C_{15}H_{20}O$ requires: C, 83.30; H, 9.85%).

Acetolysis of 1,8-dichlorocycloisolongifolene (**27**)

Crude **27** (2.0 g), described above, was mixed with AcOH (25 ml) and NaOAc (1.0 g) and the mixture heated and stirred at 80 ± 2° for 24 h. Usual work-up gave a product (2.4 g), showing on TLC (solvent: C_6H_6) at least five components of R_f 0.88, 0.50 (major), 0.37 (minor), 0.19 (trace), 0.11 (trace). The major product (R_f 0.50) was isolated by column chromatography over SiO_2/IIA (40 g, 50 × 1.5 cm) and identified as *1-acetoxy-dehydrocycloisolongifolene* (**24**); 450 mg (eluted with light petrol–C_6H_6, 1:1, 50 ml × 2), b.p. 120–125° (bath)/1 mm. IR (liq.): 1730, 1632, 1240, 1230, 1028 cm^{-1}. PMR: tert. Me's, 0.98, 0.98, 0.98, 1.04 ppm; CH_3CO, s, 1.28 ppm; CHOAc, 1H, d, 5.24 ppm, J = 2 Hz; =C=CH=CH.CH_2, 1H, d × t, 5.42 ppm, J_1 = 9.5 Hz, J_2 = 4.5 Hz; =C=CH=CH.CH_2, 1H, d × t, 5.93 ppm, J_1 = 9.5 Hz, J_2 = 1.5 Hz. (Found: C, 78.20; H, 9.44. $C_{17}H_{24}O_2$ requires: C, 78.41; H, 9.29%).

Reaction with pseudohalogens

Iodine chloride. To a stirred and cooled (5°) mixture of isolongifolene (3.0 g) in CH_3CN (30 ml) and anhyd Na_2CO_3, ICl (3.2 g) was added (2 min) and the temp. allowed to rise to 15°, at which temp. it was stirred for 2.5 h. The reaction mixture was diluted with 10% $Na_2S_2O_3$ aq (20 ml) and the product taken up in light petrol (20 ml × 2). After usual work up the product (3.3 g) was distilled to get what was essentially *8-iodoisolongifolene* (**16**): b.p. 135–140° (bath)/1 mm, 2.8 g. IR (liq.): 1635, 1220, 1178, 1090, 890, 785, 720 cm^{-1}. PMR: tert. Me's, 0.93, 0.93, 1.19, 1.29 ppm; C=CI–CH_2, 2H, m, 2.58 ppm.

Iodine azide.[39] To sodium azide (2.6 g, 0.04 mole) in CH_3CN (26 ml), contained in a 100 ml 3-necked flask protected from light and cooled to 0°, ICl (4.8 g, 0.03 mole) was slowly introduced (10 min) with stirring. After stirring for an additional 0.5 h, isolongifolene (3.5 g, 0.017 mole) was added and the temp. taken to 15° over 1 h and stirred at that temp. for additional 6 h. Most of CH_3CN was distilled off (reduced pressure), the residue diluted with 10% $Na_2S_2O_3$ aq (30 ml) and the product taken up in CCl_4 (20 ml × 3). The solvent was flashed off at ~35° under suction and

the residue (4.6 g) distilled to give a liquid (3.7 g), b.p. 140–145° (bath)/1 mm, and analysed by GLC (SE-30, 3%; temp., 180°) and PMR to consist of 8-iodoneoisolongifolene (**13**) (60%; *RRT*, 1.0. PMR: tert. Me's, 0.71, 0.86, 0.95, 0.99 ppm; CHI, 1H, d × d, 4.35 ppm, $J_1 = 8$ Hz, $J_2 = 9$ Hz; C=CH, 1H, d, 5.48 ppm, J = 3.5 Hz), 8-*iodoisolongifolene* (**16**) (30%; *RRT*, 1.16), and minor products (*RRT*, < 1).

Chlorine azide[40] *and bromine azide*[41] in CH_2Cl_2 were reacted with isolongifolene (2.04 g) in CH_2Cl_2 at 0° for 15 min, in presence of Na_2CO_3 (1 g). The product was worked up in the usual manner and analysed by PMR (Table 1).

Nitrosyl chloride. To a mixture of isolongifolene (1.0 g), isoamyl nitrite (1 ml) and gl. AcOH (1 ml), at ~0°, conc. HCl aq (0.5 ml) was added and the mixture stirred at same temp. for 2 h. It was, then, diluted with water (10 ml), extracted with CH_2Cl_2 (10 ml × 3), the extract washed with water till neutral and dried. Removal of solvent furnished a brown pasty solid, which was crystallised for CH_3CN to get *Oxime* of 8-oxo-neoisolongifolene[22] (Table 1), 560 mg, m.p. 141–143°. IR (Nujol): OH 3250 cm^{-1}; C=N[42] 1655 cm^{-1}; C=C 1610 cm^{-1}; =N–O[42] 940, 920 cm^{-1}. PMR: tert. Me's, 0.88, 1.01, 1.05, 1.11 ppm; C=CH, 1H, d, 5.64 ppm, J = 4 Hz. (Found: C, 77.57; H, 9.52; N, 6.22. $C_{15}H_{23}ON$ requires: C, 77.25; H, 9.87; N, 6.01%).

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