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STUDIES IN SESQUITERPENES—LVII†‡
ISOLONGIFOLENE (PART 8): SOLVOLYSIS OF 8-BROMONEOISOLONGIFOLENE

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Abstract—Acetolysis of 8-bromoneoisolongifolene generates, besides two normal products (of elimination and S_N2 displacement), which were minor, one rearranged elimination product and a tertiary acetate. The rearranged diolefine arises from acetic acid-catalysed rearrangement of the normal elimination product, while the tertiary acetate is a Wagner substitution product arising from a *syn*-migration. In this context various factors controlling such migrations are discussed and, the possible role of energetics of the incipient carbonium ion at the migration origin highlighted.

Recently, we reported[1] that the main product of the reaction of one mole equivalent of bromine with isolongifolene (1) is 8-bromoneoisolongifolene[2] (2). Solvolysis of this compound appeared of special interest in that if a Wagner-Meerwein shift occurred, as anticipated, under solvolytic conditions, the structure of the Wagner product, which would be dictated by the various electronic/geometric/ring-strain factors, should reveal their relative importance, as in the present case, for the three possible bond migrations, some of these factors would operate in opposition to each other.

Furthermore, it has been claimed in a recent patent that acetolysis of the monochlorination product of isolongifolene yields essentially the allylic acetate 6. Inasmuch as, from previous knowledge,[1] it is known that monochlorination of isolongifolene gives none of the allylic chloride 7 and the product is essentially a mixture (1:1) of 8-chloroneoisolongifolene (3) and 5, it is difficult to see how 6 can be obtained from the acetolysis reaction, as claimed.[4] In view of these considerations, acetolysis of both 8-chloro- and 8-bromoneoisolongifolene has been investigated; solvolysis of chloride 5 has been reported earlier.[1]

Exposure of either 8-chloro- or 8-bromoneoisolongifolene to refluxing AcOH–KOAc, resulted in very similar product mixture consisting essentially (GLC) of two hydrocarbons (4–10%, 33–40%) and two acetates (40–50%), besides some minor products. Structures of these products are discussed in the sequel, however, it will be pertinent to mention at this stage that of the two acetates, one is secondary and the other, which is major (~95%), is a tertiary acetate arising from Wagner-Meerwein rearrangement. We assign to this, structure 8, *arising from a* syn-*migration.*

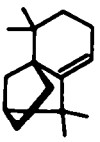
Hydrocarbons

Column chromatography of the total reaction product either before or after alkali hydrolysis, gave a mixture (GLC) of hydrocarbons, which was examined (GLC, PMR, IR) without further separation.

The major hydrocarbon (RRT = 1.5, 80–88%) was readily recognized (GLC, PMR, IR, UV) as the known[5] conjugated diene, dehydroisolongifolene (10).

Evidently, if structures 2/3 are correct, 10 cannot be the primary product of elimination. It was suspected that the anticipated initial elimination product 9 may be sufficiently labile to isomerise with refluxing acetic acid to dehydroisolongifolene (10) (Fig. 1). In view of this, dehydrohalogenation of 2/3 has been investigated. Dehydrobromination of 2 in presence of Li_2CO_3 in refluxing dimethylformamide (DMF) furnished in over 80% yield, the expected non-conjugated diene (9, dehydroneoisolongifolene): PMR, –C=CH–CH (*d*, 5.60 ppm, J = 3.0 Hz), $-CH_2-CH=CH-C$ ($d \times d \times d$, 5.86 ppm, J_1, J_2, J_3 = 2.6, 4.6, 10.0 Hz resp.), $-CH_2-CH=CH-C$ (m, 5.47–5.65 ppm). Structure 9 was further secured by its selective hydrogenation (Raney Ni) to the known[3] neoisolongifolene (11). The minor hydrocarbon component (RRT = 1.0, 8–20%) of the product from the original acetolysis reaction was found (GLC, PMR) to be identical with dehydroneoisolongifolene (9). Further, it was shown that 9 on being exposed to refluxing acetic acid slowly rearranges to 10. As a matter of fact, if dehydrobromination of 2 in refluxing DMF is carried out in the *absence* of Li_2CO_3, the product is the conjugated diene 10.

Another minor product (RRT = 3.0, 3–6%) of this hydrocarbon fraction was identified (GLC, PMR) as the known[6] tetralin 12.



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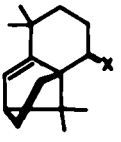
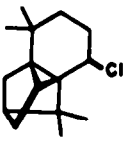


2: X = Br
3: X = Cl
4: X = OH



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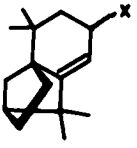

6: X = OAc
7: X = Cl

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†MRC Communication No. 14.
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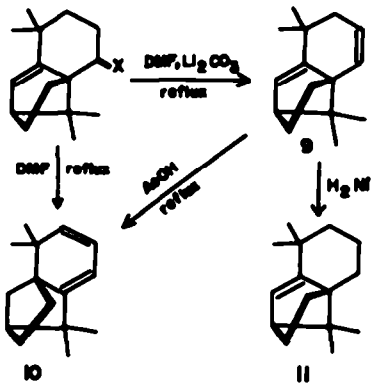
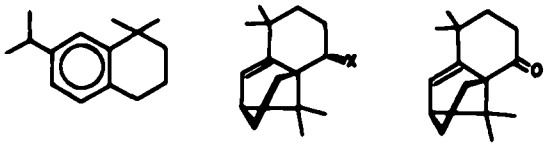


Fig. 1. Dehydrohalogenation of 8-haloneoisolongifolene.

Secondary alcohol (14)

The two acetates could not be separated as such, hence, the total acetate cut was saponified and the resulting alcohols separated by systematic column chromatography (SiO_2-gel).

The secondary alcohol (m.p. 41–43°, PMR: –CH̲OH, unresolved t, 4.14 ppm, $J \simeq 3$ Hz; –C=CH̲·CH, d, 5.73 ppm, $J = 3$ Hz) was clearly derived from the anticipated S_N2 displacement product (13). This was easily confirmed by its comparison (m.p., mixed m.p., IR, PMR) with an authentic sample obtained by LAH reduction of the known[3] ketone 15 (also see note 13).



12 13: X = OAc 14: X = OH 15

Tertiary alcohol

The second alcohol (m.p. 54.5–55.5°, IR: OH 3608, 3495, 1188, 1061 cm^{-1}), which analyses for $C_{15}H_{24}O$ (M^+, *m/e* 220) and which is by far the most predominant product of substitution reaction, is clearly tertiary (PMR) and hence, must have arisen from Wagner substitution. It is mono-olefinic (quantitative perbenzoic acid titration; PMR: C=CH̲, d, 5.30 ppm, $J = 3$ Hz) and hence the compound must still be tricyclic and conceivably could have arisen from a simple 1,2-shift.

In theory, three structures 17, 18, 19 (Fig. 2), all of which meet the gross structural requirements of the new product, come up for consideration. The olefinic proton in the tertiary alcohol appears as a doublet at 5.30 ppm ($J = 3$ Hz), the position and magnitude of coupling constant being essentially identical to those for the olefinic proton signal for neoisolongifolene (11), the parent bromide (2) or the chloride 3 or ketone 15. This suggests that the olefinic proton of the new compound is located in a ring of the same size and environment, as obtains in the above mentioned compounds. These considerations would clearly favour structure 19 (*cf* 16 and 19, Fig. 2).

Clearcut evidence against formulation 17 was forthcoming when oxidative ozonolysis of the tertiary acetate furnished a keto acid, the methyl ester of which displayed, in its IR spectrum, besides a band at 1735 cm^{-1} (COOMe, $OCOCH_3$), absorption at 1705 cm^{-1} clearly assignable to a 6-membered ketone.

From an inspection of the remaining two alternatives, 18/19, it is obvious that though both are allylic alcohols, the OH, in both cases, is located on the bridge-head and hence, under acid catalysis, the compound may be expected to preferentially rearrange[7] to a saturated ketone (*cf* 23) rather than undergo simple elimination. If this were to happen, the spectral properties of the resulting ketone should suffice to distinguish between the parent structures 18/19. In practice, exposure of the tertiary alcohol to H_2SO_4 aq.–dioxane (95°, 2 hr), gave in excellent yield a ketone, displaying in its IR spectrum carbonyl absorption at 1730 cm^{-1}, thus clearly favouring structure 19 (*cf* 22 vs 20/21, Fig. 2). Furthermore, LAH reduction of the ketone yielded the corresponding alcohol, showing in its PMR spectrum CH̲OH signal as a *sharp* singlet (at 3.40 ppm), as required by a product based on structure 22; for the alcohol derived from the alternative 20/21, one would expect splitting/broadening of the CH̲OH signal. Thus, structure 18 stands ruled out.

In an effort to further secure structure 19, some more transformations have been carried out. In an obvious extention of the above acid-catalyzed isomerization of the tertiary alcohol to the saturated ketone 22, epoxide derived from the tertiary alcohol has been treated with $BF_3 \cdot Et_2O$. For the epoxide, one would expect the *exo*-structure 24, as the reagent (perbenzoic acid) may be expected to approach 19 from the same side as the OH group.[8] It may be noted that in structure 24, the usual isomerization[9] of an oxirane to a ketone under the influence of $BF_3 \cdot Et_2O$ is blocked, as the migration of the *endo* hydrogen from C-1 to C-6 as required by such an isomerization will result in inversion at C-6, which, in the present case, is sterically prohibitive. Hence, in analogy with the rearrangement 23 (Fig. 2) discussed earlier, one would expect this epoxy alcohol to rearrange (*cf* 26) to the keto alcohol 27. In practice, exposure of 24 to $BF_3 \cdot Et_2O$ in benzene yielded a keto alcohol, having characteristics fully consistent with the expected structure 27: $C_{15}H_{24}O_2$, tetranitromethane test negative. IR ($CHCl_3$), C=O 1730 cm^{-1}; OH 3610 cm^{-1}. PMR, CH̲OH signal occurs at 4.42 ppm as a singlet even though there is a vicinal H at C-2; however, this is understandable as the dihedral angle between these two protons is ~90°. When the epoxy acetate (25) was similarly treated with $BF_3 \cdot Et_2O$, the same rearrangement took place with concomitant transfer of acetyl moiety from oxygen at C-7 to oxygen on C-1 to furnish 28 (IR: C=O 1730, 1735 cm^{-1}. PMR: CH̲OAc, 1H, s, 5.23 ppm); base hydrolysis (10% KOH alcoholic, reflux, 2 hr) of 28 furnished the keto alcohol 27. The rearrangement of 25 to 28, which involves concomitant acyl transfer from one oxygen to another is visualised as proceeding *via* 29.

Additional support for structure 19 was forthcoming, when its product of hydroboration, 30, on oxidation with Jones reagent,[10] furnished a keto alcohol, the carbonyl frequency (1730 cm^{-1}) of which is consistent with the expected structure 31.

The data presented so far clearly suffice to establish unequivocally the structure of the tertiary alcohol as 19.

Mechanistic considerations. It is obvious that for any valid discussion, the configuration of the bromine atom in 2 must be above reproach. Earlier,[1] we assigned the configuration shown in 2(16) on the basis of known[11,12] preference for *endo* attack at the ethylene linkage in isolongifolene. To obtain further confirmation we have

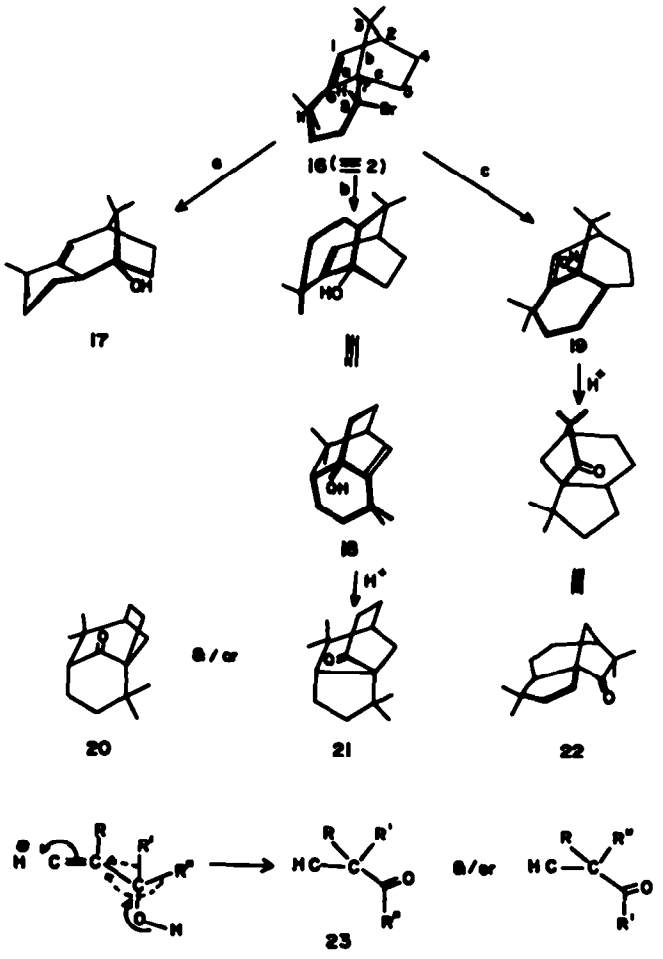
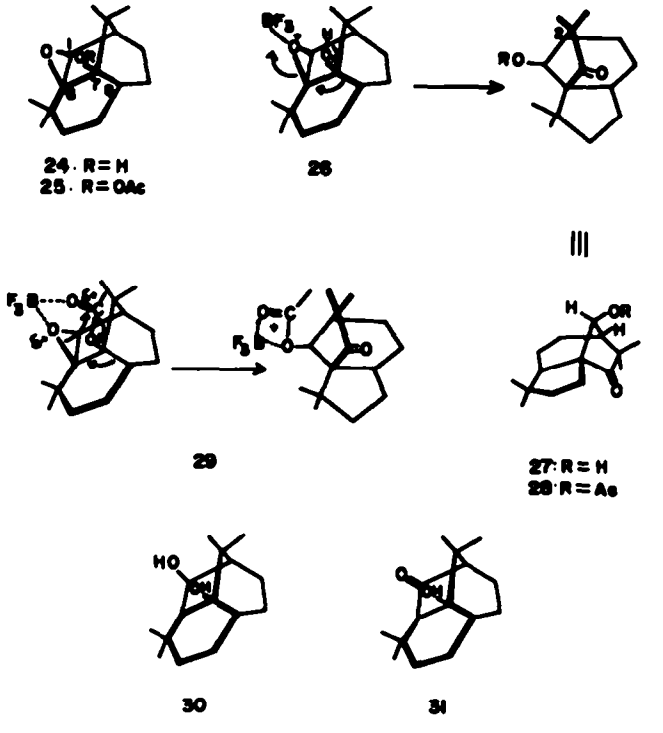


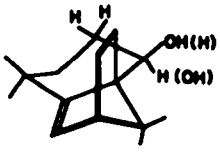
Fig. 2. Differentiation between possible formulations for the tertiary alcohol.



now compared the coupling constant of its CH_2Br signal with the *J*-values for the epimeric alcohols pair[13] 4/14. An examination of molecular models (Dreiding) would readily reveal that of the few alternatives, conformation 32 for the epimeric alcohols pair should be energetically preferable, and the *J*-values for the epimeric pair 4/14 should be quite distinct. This is borne out by the CH_2OH-CH_2 signals in the PMR spectra of the two alcohols: 4 (3.88 ppm, d × d, $J_1 = 6.5$ Hz, $J_2 = 9.5$ Hz), 14 (4.14 ppm, t, $J = 3$ Hz). Using this as a probe, it follows that 8-bromoneoisolongifolene which displays in its PMR spectrum $CHBrCH_2$ signal (4.28 ppm) essentially as a *t* with $J = 8.5$ Hz must have bromine configuration as shown in 2, in accord with our earlier reasoning.

Thus, tertiary alcohol 19 must arise from the bromide 2 by a syn-*migration*, a process, which in the absence of other compelling factors, is energetically less likely, as the preferred geometry for 1,2-migrations is anti-periplanar.[14,15] The following analysis suffices to rationalise this observed *syn*-migration. However, it may be noted that due to difficulty in evaluating quantitatively the relative importance of various factors, such an exercise carried out earlier would have failed to predict with confidence the outcome of this rearrangement.

It may be further noted that in all the three possible pathways, the strained bicyclo[2,2,1]heptene part-structure expands, thus releasing strain due to bond angle deformation[16] and this possibly constitutes the driving force for the rearrangement.



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A reference to Fig. 2 will show that bond "*a*" has more or less the correct geometry (anti-periplanar) with respect to the leaving group. However, the sp^2-sp^3 hybridization of bond "*a*" is contramigratory[17] to an electron deficit centre. Since none of 17 is produced, the latter factor would appear to be more important (also see below).

If bond "*b*" were to migrate, the resulting compound 18 would have an ethylenic linkage at the bridgehead of a bicyclo[3,3,1]nonane system and this would be contraindicated as this is a more strained system.[18]

From the fact that compound 19 is the product of rearrangement, one may conclude that geometrically unfavourable *syn*-migration is energetically less formidable than the factors (*vide supra*) which apparently operate against the migration of bonds "*a*"/"*b*". Another factor, which may be equally or even more important in determining the outcome of this rearrangement must also be considered. It is conceivable that in a geometrically rigid system, if there is a possibility of additional stabilization of the incipient carbonium ion at the migration origin by interaction with a suitably placed compatible functional group, then that bond may be expected to migrate which will permit maximal additional stabilization. In the present context if we assume a transition state resembling the starting material[19] and apply this criterion, we find, from a study of molecular models (Dreiding) and as depicted in 33, 34 and 35, that only if bond "*c*" were to migrate (33) additional stabilization of the incipient carbonium ion becomes feasible, as the developing vacant orbital will be directed away from the π-orbitals, while in alternative 35 (migration of "*b*") it will have a diverging angle.

I

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 R32 90 MHz) NMR spectrometer; Varian Mat CH7 Mass spectrometer (70 eV, direct inlet system); Hewlett-Packarad 5712A and 7624A gas chromatographs (Al columns, 180 cm × 0.6 cm; support, 60–80 mesh chromasorb 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.

Silica gel for column chromatography (−100, +200 mesh) was washed with hot water till sulphate-free, dried, activated at 125–130° for 6–8 hr and standardised.[20] TLC was carried out on SiO_2-gel layers (0.25 mm) containing 15% gypsum and activated at 110–115° (2 hr).

Solvolysis of 8-haloneoisolongifolene[21]

(i) *8-Bromoneoisolongifolene.* A mixture of 2 (6.4 g), KOAc (4.02 g) and gl AcOH (40 ml) was refluxed till GLC showed disappearance of all bromide (~5 hr). Most of AcOH was removed under reduced pressure from a water-bath, the residue diluted with water (25 ml) and, the product taken up in light petroleum (25 ml × 3) which was then washed and dried. A test sample was distilled for GLC analysis: b.p. 100–140° (bath)/2 mm. GLC (Carbowax, 3%; 6 ft; temp, 160°): relevant components in order of increasing retention time, 9 (5%, RRT 1.0), 10 (40%, RRT 1.5), 12 (3%, RRT 3.0), 13 and 8 (50%, RRT 7.8). The rest (4.1 g) of the material was chromatographed over silica gel/IIB (2.5 cm × 55 cm):

Frac. 1. Light petroleum: 50 ml × 3; 2.0 g, mixture of 9 and 10.

Frac. 2. Light petroleum: 50 ml × 3; 200 mg.

Frac. 3. 5% C_6H_6 in light petroleum: 50 ml × 3; 1.43 g, essentially 8.

Fraction 3 was distilled to get *tertiary acetate* (8), b.p. 118–120°/1 mm. IR (liq.): CH_3COO 1740, 1240 cm^{-1}; -C=CH 1620, 870, 820 cm^{-1}. PMR: tert. Me's, singlets at 0.96, 1.13, 1.16 and 1.20 ppm; CH_3CO (s, 2.0 ppm); C=CH (1H, d, 5.36 ppm,

J = 3.0 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%). (Found: C, 78.29; H, 9.64. $C_{17}H_{26}O_2$ requires: C, 77.82; H, 9.99%).

In another experiment (9.63 g of 2), the product from acetolysis was saponified (4.0 g KOH in 15% aq MeOH, 35 ml; reflux, 36 hr) and worked up as usual to give a material (6.79 g), a part (200 mg) of which was distilled for GLC analysis: b.p. 100–140° (bath)/1 mm. GLC (Carbowax, 3%; 6 ft; temp. 150°): 9 (11.5%, RRT 1.0), 10 (38%, RRT 1.5), 12 (4.5%, RRT 3.0), tertiary alcohol 19 (40%, RRT 7.0), secondary alcohol 14 (2%, RRT 9.0). The main portion (6.5 g) was chromatographed (SiO_2 gel/IIB; 3.0 cm × 30 cm). Light petroleum (50 ml × 2) eluted 3.1 g of hydrocarbons 9, 10 (GLC). 5% benzene in light petroleum (50 ml × 4) fractions gave a solid (2.5 g, m.p. 41–48°, which was recrystallised (light petroleum) to furnish pure tertiary alcohol (19), m.p. 54.5–55.5°. IR (CCl_4): OH 3618, 3495 cm^{-1}; –C=CH 1615, 840 cm^{-1}. PMR: tert Me's, singlets at 0.92, 0.96, 1.12 and 1.27 ppm; C=CH (1H, d, 5.30 ppm, J = 3.0 Hz). 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%). (Found: C, 82.01; H, 11.05. $C_{15}H_{24}O$ requires: C, 81.76; H, 10.98%). The material (861 mg) eluted with benzene (50 ml × 3) on rechromatography, followed by crystallisation from light petroleum gave the *secondary alcohol* (14), m.p. 40–42°. IR ($CHCl_3$): OH 3620, 3460 cm^{-1}; –C=CH 1608, 835 cm^{-1}. PMR ($CDCl_3$): tert. Me's, singlets at 0.95, 1.03, 1.05 and 1.16 ppm; CHOH (1H, t, 4.14 ppm, J = 3 Hz); C=CH (1H, d, 5.73 ppm, J = 3.0 Hz). (Found: C, 82.01; H, 11.10. $C_{15}H_{24}O$ requires: C, 81.76; H, 10.98%).

(ii) *8-Chloroneoisolongifolene.* A mixture of 3 (2.5 g), NaOAc (2.5 g) and AcOH (15 ml) was refluxed for 36 hr and then worked up as under (i) to furnish a product essentially similar (GLC) to that obtained by acetolysis of 2.

8-Dehydroneoisolongifolene (9)

A mixture of 2 (4.5 g) and Li_2CO_3 (7.6 g) in DMF (25 ml) was refluxed for 1 hr, and then most of the solvent removed under reduced pressure from a water bath. The residue was diluted with water (20 ml) and the product taken up in light petroleum (20 ml × 3), washed with water (20 ml × 2) and dried. The residue (3.2 g), obtained after solvent removal, was distilled to get 9: b.p. 80–85°/3 mm, 2.64 g (GLC purity, 98%). IR (liq.): 1645, 1635, 1610, 1285, 1025, 972, 888, 820, 775, 730 and 710 cm^{-1}. PMR: tert. Me's singlets at 0.73, 0.82, 1.01 and 1.11 ppm; for other signals, see text. (Found: C, 89.00; H, 11.18. $C_{15}H_{22}$ requires: C, 89.04; H, 10.96%).

Action of acetic acid on 8-dehydroneoisolongifolene

A soln of 9 (1.87 g) in gl AcOH (15 ml) was refluxed for 8 hr. Most of the solvent was removed under reduced pressure (water bath) and the residue worked up in the usual manner to furnish a product, which was chromatographed (SiO_2 gel/IIB, 2.3 cm × 55 cm). Light petroleum (25 ml × 3) eluted a hydrocarbon (1.39 g) identified (GLC, IR, PMR) as essentially the conjugated diene 10.

8-Hydroxyneoisolongifolene (14)

A soln of 8-oxoneoisolongifolene[3] (4.02 g) in ether (30 ml) was added dropwise to a stirred suspension of LAH (1.24 g) in ether (30 ml), at ~25°, during 1/2 hr. After stirring for an additional one hr, the mixture was worked up as usual (water; 15% NaOH aq). The product (4.0 g, m.p. 95–115°) was chromatographed over silica gel (IIB, 2.5 cm × 50 cm):

Frac. 1. Light petroleum: 50 ml × 4.

Frac. 2. 20% C_6H_6 in light petroleum: 40 ml × 7; 1.02 g, m.p. 41–43°.

Frac. 3. 20% C_6H_6 in light petroleum: 40 ml × 3; 0.223 g, mixture.

Frac. 4. C_6H_6: 40 ml × 6; 1.98 g, m.p. 132–136°.

Fraction 2 on recrystallization from light petroleum gave 14, m.p. 49.5–50.5° (*vide supra*).

Fraction 4 on recrystallization from the same solvent furnished the epimer 4, m.p. 141.5–142.5° (lit.,[3] m.p. 144–145°).

Reactions of tertiary acetate/alcohol (8/19)

(i) *Ozonolysis.* The tert acetate 8 (1.105 g) in MeOH (40 ml) was treated with ozonised O_2 at $-7 \pm 2°$ till it passed freely (15 min). The solvent was carefully removed at room temp (~30°) under reduced pressure, the residue taken up in acetone (10 ml) and treated[22] with Jones' reagent (1 ml) dropwise, at 0°. The mixture was diluted with water (30 ml), the product taken up in ether (25 ml × 3), and extracted with 10% KOH aq (15 ml × 3). The alkaline extract was acidified (50% H_3PO_4 aq) and extracted with ether (20 ml × 3), to afford, after solvent removal a solid (250 mg), m.p. 180–190°. Recrystallization from CH_3CN furnished pure *keto acid* (200 mg), m.p. 205–208°. IR (Nujol): C=O 1700, 1730 cm^{-1}. PMR ($CDCl_3$): tert. Me's, singlets at 1.15, 1.15, 1.20 and 1.26 ppm; CH_3CO (3H, s, 2.03 ppm). (Found: C, 65.76; H, 8.45. $C_{17}H_{26}O_3$ requires: C, 65.78; H, 8.44%).

Methyl ester. (CH_2N_2 method), m.p. 80–82°. IR (CCl_4): C=O 1705, 1730 cm^{-1}. PMR: tert. Me's, singlets at 1.07, 1.07, 1.09 and 1.20 ppm; CH_3CO (3H, s, 1.98 ppm), COOMe (3H, s, 3.58 ppm). (Found: C, 67.18; H, 9.11. $C_{18}H_{28}O_3$ requires: C, 66.64; H, 8.70%).

(ii) *Action of acid on tertiary alcohol.* Alcohol 19 (0.815 g) and 50% (v/v) aq. H_2SO_4 (1 ml) in dioxane (10 ml) were heated (N_2) at ~95° for 2 hr, when alcohol 19 had completely isomerised (TLC). Bulk of dioxane was removed under suction from a water-bath, the residue diluted with water (10 ml) and, the product taken up in light petroleum (15 ml × 3), which was washed with water and dried. The solvent was flashed off and the residue (805 mg) filtered through a small column of silica gel (IIB) using light petroleum. The material then obtained after solvent removal was distilled to get pure ketone 22, b.p. 120–130° (bath)/2 mm, 710 mg. IR (liq.): 1730, 1240, 1218, 1090, 1060, 975, 890 cm^{-1}. PMR: tert. Me's, singlets at 0.92, 0.99, 1.04 and 1.20 ppm. Mass: M^+, *m/e* 220. (Found: C, 81.17; H, 10.47. $C_{15}H_{24}O$ requires: C, 81.76; H, 10.98%).

This ketone (125 mg) in ether (10 ml) was reduced with LAH in the usual manner to get the corresponding *alcohol* (120 mg), m.p. 41–49°, which was crystallized from light petroleum, m.p. 69–70°, for examining its PMR spectrum (*vide* text).

(iii) *Epoxidation of tertiary acetate/alcohol and rearrangement of products.* A soln of tert acetate 8 (792 mg, 3.02 mmol) in benzene (2 ml) was treated with a soln of perbenzoic acid in benzene (25 ml; 510 mg of per acid, 3.6 mmol) at 10° for 8 days, when the starting material had been completely consumed (TLC). The mixture was washed with 10% Na_2CO_3 aq (10 ml × 4), water (10 ml × 2) and, after drying, freed of solvent to give a product (855 mg), which was distilled to get 25 (710 mg), b.p. 110–120° (bath)/0.5 mm. IR (liq.): 1735, 1240, 1185, 1090, 1042, 1010, 895, 878 cm^{-1}. PMR: tert. Me's, singlets at 0.78, 1.05, 1.10 and 1.20 ppm; CH_3CO (3H, s, 2.03 ppm); CHOC (1H, s, 3.07 ppm); C-8 H (?) (1H, br m, 3.42 ppm). (Found: C, 73.06; H, 9.39. $C_{17}H_{28}O_3$ requires: C, 73.34; H, 9.41%).

Epoxidation of tert. alcohol 19 (600 mg) as above, furnished 24 (580 mg), m.p. 101.5–102.5°. IR (CCl_4): 3510, 3400, 1250, 1062, 925, 910, 860 cm^{-1}. PMR: tert. Me's, singlets at 0.76, 0.83, 1.13 and 1.30 ppm; CHOC (1H, s, 3.11 ppm). (Found: C, 76.72; H, 9.66. $C_{15}H_{24}O_2$ requires: C, 76.22; H, 10.24%).

$BF_3 \cdot Et_2O$ *Catalyzed rearrangements.* $BF_3 \cdot Et_2O$ (0.1 ml) was added to a cooled (10°) soln of tert acetate epoxide 25 (410 mg) in benzene (5 ml). After keeping the mixture at that temp for 1 hr, it was worked up by washing with 5% Na_2CO_3 aq (5 ml × 3), followed by water (5 ml × 2). The residue (500 mg) obtained, after solvent removal was filtered through a small column of Al_2O_3 (neutral/III; 1 cm × 13 cm) using light petroleum and the product recrystallized from light petroleum to get the *keto acetate* 28 (350 mg), m.p. 111.5–112.5°. IR ($CHCl_3$): 1735, 1730, 1250, 1240, 1105, 1033, 881 cm^{-1}. PMR: tert. Me's singlets at 0.90, 1.09, 1.11 and 1.28 ppm; CH_3CO (3H, s, 2.0 ppm), CHOAc (1H, s, 5.23 ppm). (Found: C, 73.51; H, 9.56. $C_{17}H_{28}O_3$ requires: C, 73.34; H, 9.41%).

A similar treatment of epoxy alcohol 19 (200 mg) furnished, after recrystallization from light petroleum–methylene chloride, the *keto alcohol* 27, m.p. 178–180°. IR ($CHCl_3$): 3610, 3490, 1730, 1095, 1055, 1023, 972, 850 cm^{-1}. PMR ($CDCl_3$): tert. Me's, singlets at 1.13, 1.14, 1.26 and 1.36 ppm; CHOH (1H, s, 4.42

ppm). (Found: C, 75.84; H, 9.76. $C_{15}H_{24}O_2$ requires: C, 76.22; H, 10.24%).

(iv) *Hydroboration of tertiary alcohol and oxidation of resulting diol.* Diborane (from 1.5 g $NaBH_4$) was introduced into a cold (0–5°) soln of the tert alcohol 19 (1.8 g) in THF (30 ml) during 2.5 hr. After stirring for an additional one hr at room temp (~30°), the excess diborane was destroyed by cautious addition of water (5 ml). Then, 3N NaOH aq (5 ml), followed by H_2O_2 aq (30%, 4 ml) were introduced to oxidise the boronane ester. After stirring the mixture at room temp for 10 hr, it was saturated with NaCl and the product extracted with ether (30 ml × 3). The extract was washed, dried and freed of solvent to furnish a gum (1.9 g) which was chromatographed over silica gel (IIA, 2 cm × 42 cm). The column was eluted successively with light petroleum (20 ml × 2), 1:1 light petroleum–benzene (20 ml × 2), benzene (20 ml × 2), 5% EtOAc in benzene (20 ml × 3), 20% EtOAc in benzene (20 ml × 4). The material (1.48 g, m.p. 85–90°) eluted with 20% EtOAc in benzene was recrystallized from CH_3CN to furnish the *diol* 30, m.p. 90–92°. IR ($CHCl_3$): 3610, 3480, 1125, 1070, 1020, 975, 890 cm^{-1}. PMR ($CDCl_3$): tert. Me's singlets at 0.90, 1.05, 1.13 and 1.17 ppm; CHOH (1H, d, 3.81 ppm, $J = 6$ Hz). (Found: C, 75.22; H, 10.97. $C_{15}H_{26}O_2$ requires: C, 75.58; H, 11.00%).

The above diol (180 mg) in acetone (2 ml) was oxidised with Jones' reagent[10] (0.2 ml) at 5° (30 min) in the usual manner and then worked up to furnish a solid which was recrystallized from light petroleum to yield the *keto alcohol* 31 (175 mg), m.p. 135–137°. IR ($CHCl_3$): 3605, 3480, 1730, 1190, 1140, 1058, 973 cm^{-1}. PMR: tert. Me's, singlets at 1.02, 1.07, 1.11, 1.26 ppm. (Found: C, 76.08; H, 10.13. $C_{15}H_{24}O_2$ requires: C, 76.22; H, 10.24%).

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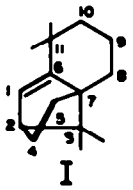
[2]For sake of convenience we have designated hydrocarbon(I),[3] neoisolongifolene.



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[13]Alcohol 4 has been described earlier.[3] However, it may be noted that the configuration of OH given in Ref. 3 is opposite to that shown in 4. The latter represents the corrected configuration arising from the revised[11] stereochemistry for isolongifolene epoxide. The other epimer (14) is best obtained from LAH reduction product of ketone 15, which consists of both epimers in the approximate ratio 1(14):2(4).

[14]See e.g.: R. Hirschmann, C. S. Snoddy, C. F. Hiskey and N. L. Wendler, *J. Am. Chem. Soc.* 76, 4013 (1954); D. J. Cram, in *Steric Effects in Organic Chemistry* (Edited by M. S. Newman), pp. 253, 270. Wiley, New York (1956); S. I. Miller, *Advances in Physical Org. Chem.* 6, 296 (1968).

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