848. *The Interaction of Decalin and Isobutyryl Chloride–Aluminium Chloride.*

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This reaction, in the absence of an excess of the metal halide and under the mildest conditions compatible with a convenient rate, is shown to give 10β-2′-methylpropenyl-*trans*-decalin 1β,1′-oxide (I) in about 40% yield. Several novel decalin derivatives are provided by oxidation of compound (I) with peracid.

Previous investigations [1,2] having shown the primary product of interaction of decalin and acetyl chloride–aluminium chloride to be 1β,1′-epoxy-10β-vinyl-*trans*-decalin, we wished to know whether other fatty acid chlorides having at least one hydrogen atom on the α-carbon atom would react similarly. We have used propionyl and isobutyryl chloride and this paper is concerned with the product given by the latter reagent. In a typical experiment, decalin (1·8 mol.) reacted in the cold (<10°) with aluminium chloride (2·0 mol.) and isobutyryl chloride (2·2 mol.) in ethylene dichloride, to give an oil, $C_{14}H_{22}O$ (0·40 mol.), b. p. 128—130°/10 mm., which was shown, as described below, to be the oxide (I), called below the vinyl ether. In accordance with the formulation (i) of the reaction, isobutyraldehyde was another product.

The vinyl ether (I) gave a deep colour with tetranitromethane, decolorised bromine in carbon tetrachloride, reacted with 1 mol. of perbenzoic acid, and has a strong absorption band at 1695 cm.$^{-1}$ which is provided by the vinyl ether group and not by a carbonyl group since the compound is unreactive towards lithium aluminium hydride. As a vinyl ether, it is stable in alkali but not in acid, and it slowly combines with hydroxylamine in neutral and weakly acid media to give an oxime, $C_{14}H_{25}O_2N$, which, doubtless, is correctly represented by (V). Ozonolysis of the vinyl ether in ethyl acetate gave acetone and the lactone [1] (II) which, for identification, was reduced to 10β-hydroxymethyl-*trans*-1β-decalol (VI) which also has previously been described.[1] These results described suffice to

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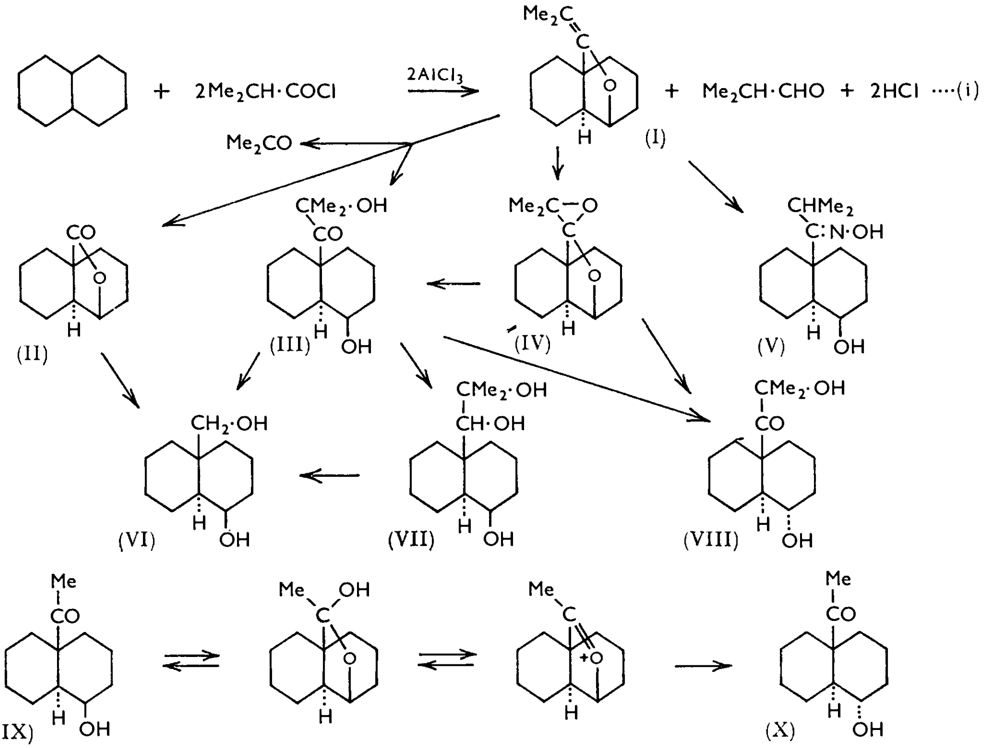
[1] Baddeley, Heaton, and Rasburn, *J.*, 1960, 4713.

[2] Baddeley, Heaton, and Rasburn, *J.*, 1961, 3828.

show the vinyl ether (I) to be a major product of the interaction with which this paper is concerned. Below we describe other products of oxidation of the vinyl ether.

The ozonolysis described above gave also a solid, $C_{14}H_{24}O_3$, which was obtained again when the vinyl ether reacted with peracids. As shown below, it is the dihydroxy-ketone (III). (*a*) Its infrared absorption spectrum has bands at 3623 and 3448 (OH) cm.$^{-1}$ and another at 1678 (C=O) cm.$^{-1}$ which disappears when the compound is reduced with lithium aluminium hydride to a triol, $C_{14}H_{26}O_3$ (VII). (*b*) Although it does not react with periodic acid, it is oxidised by lead tetra-acetate to acetone and a compound, probably the lactone (II), which with lithium aluminium hydride gave the known diol (VI). With lead tetra-acetate, the triol (VII) gave acetone and an oil, probably 10β-formyl-*trans*-1β-decalol, which was reduced to the diol (VI). Compound (III) was most readily obtained by careful hydrolysis of the acetal (IV) produced by interaction of the vinyl ether and perbenzoic acid. Less careful hydrolysis of the acetal gave an isomer of (III), namely, the 1α-alcohol (VIII). This has infrared absorption bands at 1678 (C=O), 3460, and 3311 (OH) cm.$^{-1}$, gave acetone when oxidised with lead tetra-acetate, and was reduced with lithium aluminium hydride to a triol, m. p. 130—131°. The isomerisation (III ⟶ VIII) is readily effected by dilute acid and is analogous to the previously reported isomerisation of (IX) to (X).[2] After five hours at room temperature, a mixture of the vinyl ether and peracetic acid gave compound (III), whereas after two days and in the presence of added glacial acetic acid compound (VIII) (mainly as a monoacetyl derivative) was obtained.



Experimental

1β,1′-*Epoxy*-10β-2′-*methylpropenyl*-trans-*decalin* (I).—Decalin (55 g.) was added to a homogeneous solution of aluminium chloride (107 g.) and isobutyryl chloride (94 g.) in ethylene chloride (300 ml.) at 0°. After being kept overnight at 0°, the mixture was poured slowly on a stirred mixture of ice and dilute hydrochloric acid, and the organic layer was separated, washed with water, dried (K_2CO_3), and distilled. Decalin (24 g.), b. p. <90°/10 mm., was recovered and the required *compound* (37 g.), was obtained as an oil, b. p. 128—130°/10 mm. (Found: C, 81·2; H, 10·6. $C_{14}H_{22}O$ requires C, 81·5; H, 10·7%). A portion of the aqueous layer was heated and evolved isobutyraldehyde (2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 187°).

Oxime (V) *of* 10β-*Isobutyryl*-trans-1β-*decalol.*—The above vinyl ether reacted slowly (20 hr. on the steam bath) with hydroxylamine in neutral or weakly acidic aqueous ethanol to give the required *oxime* which separated as needles, m. p. 171—172° (Found: C, 70·4; H, 10·5; N, 6·0. $C_{14}H_{25}NO_2$ requires C, 70·3; H, 10·4; N, 5·9%).

Ozonolysis of the Vinyl Ether.—This compound (10·0 g.) in ethyl acetate (80 ml.) gave, with ozone, a greenish-yellow solution which was heated with water (10 ml.) on the steam bath. Acetone (2,4-dinitrophenylhydrozone, m. p. and mixed m. p. 125—126°) was evolved and the residue was extracted with ether. The ether extract was washed with sodium hydrogen carbonate solution and dried (K_2CO_3) and gave a solid (1·5 g.), m. p. and mixed m. p. 145—146°, shown below to be 10β-(2-hydroxy-2-methylpropionyl)-*trans*-1β-decalol (III), and an oil (6·2 g.), b. p. 145—150°/15 mm. This oil was shown to be the lactone (II) of 1β-hydroxy-*trans*-decalin-1β-carboxylic acid by (*a*) its infrared absorption spectrum which was compared with that of an authentic sample [1] and (*b*) its reduction with lithium aluminium hydride to 10β-hydroxymethyl-*trans*-1β-decalol [1] (VI), m. p. and mixed m. p. 110°.

The Vinyl Ether and Perbenzoic Acid.—A solution of these reactants (2·0 and 1·40 g., respectively) in chloroform (40 ml.) was kept at room temperature for 2 hr. and worked up in the usual way to give a syrup, presumably the acetal (IV), which was devided into two equal samples. A solution of one sample in aqueous acetone (12 ml.) was acidified with two drops of glacial acetic acid and stored at room temperature for 3 days. It gave the *dihydroxy-ketone* (III) which separated from light petroleum–ethyl acetate in needles (0·48 g.), m. p. 145—146° (Found: C, 70·2; H, 9·8. $C_{14}H_{24}O_3$ requires C, 70·0; H, 10·0%). A solution of the other sample in aqueous acetone (20 ml.) was acidified by glacial acetic acid (5 drops) and heated for 6 hr. on the steam bath. It gave the isomer 10β-(2-*hydroxy*-2-*methylpropionyl*)-trans-1α-*decalol* (VIII), which separated from light petroleum–ethyl acetate in needles (0·40 g.), m. p. 165—166° (Found: C, 69·8; H, 9·8%). In another experiment, a solution of the vinyl ether (1·0 g.) and perbenzoic acid (1·0 g., 1·5 mol.) in chloroform (26 ml.) was kept for a day: only one mol. of the oxidant was consumed. The resulting acetal (0·8 g.) was isolated as a viscous oil and was heated with several drops of 2N-sulphuric acid in dioxan (15 ml.) and water (2 ml.) at 100° for 2 hr.; it gave compound (VIII), m. p. and mixed m. p. 165—166°.

A solution of compound (III) (0·10 g.) and lead tetra-acetate (0·30 g.) in benzene (15 ml.) was kept for 2 days at room temperature and gave acetone (2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 125—126°), and an oil which with lithium aluminium hydride gave the diol (VI), m. p. and mixed m. p. 109—110°. Similar oxidation of compound (VIII) also gave acetone. Reduction of compound (III) (0·40 g.) with lithium aluminium hydride (0·250 g.) in ether (100 ml.) gave the 10β-1,2-*dihydroxy*-2-*methylpropyl*)-trans-1β-*decalol* (VII) (0·33 g.) as needles, m. p. 136—137°, from light petroleum–ethyl acetate (Found: C, 69·3; H, 10·8. $C_{14}H_{26}O_3$ requires C, 69·4; H, 10·7%). When oxidised with lead tetra-acetate in benzene it gave acetone and an oil which with lithium aluminium hydride gave the diol (VI). Reduction of compound (VIII) (0·07 g.) with lithium aluminium hydride (0·15 g.) in ether (50 ml.) gave the 1α-*triol*, m. p. 130—131° (55 mg.) (Found: C, 69·4; H, 10·8%), which separated from light petroleum–ethyl acetate in minute prisms which depressed the m. p. of its isomer (VII) on admixture.

The Epimerisation (III ⟶ VIII).—Compound (III) (100 mg.) in a little ethyl acetate was shaken with water (10 ml.) to which glacial acetic acid (5 drops) had been added. After 5 hr. at 100°, the mixture was cooled and the solid was separated and recrystallised from light petroleum–ethyl acetate; compound (VIII), m. p. and mixed m. p. 165—166°, was obtained.

The Vinyl Ether and Peracetic Acid.—A homogeneous mixture of the vinyl ether (2·0 g.), chloroform (10 ml.), glacial acetic acid (0·5 ml.), and 40% peracetic acid (7 ml.) was kept at 0° for 5 hr. It gave compound (III) (0·9 g.), m. p. and mixed m. p. 145—146°. A mixture of the vinyl ether (1·0 g.), chloroform (5 ml.), glacial acetic acid (5 ml.), and 40% peracetic acid (2·5 ml.) was kept at room temperature for 2 days and gave a product from which compound (VIII) (0·15 g.), m. p. and mixed m. p. 165—166°, and its *monoacetate* (0·40 g.), m. p. 122—123°

(from light petroleum–ethyl acetate) (Found: C, 68·1; H, 9·6. $C_{16}H_{26}O_4$ requires C, 68·1; H, 9·2%), were isolated. Compound (VIII) and its monoacetate gave the same triol, $C_{14}H_{26}O_3$, m. p. 130—131°, when reduced with lithium aluminium hydride.

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