849. *The Interaction of Decalin, Propionyl Chloride, and Aluminium Chloride.*

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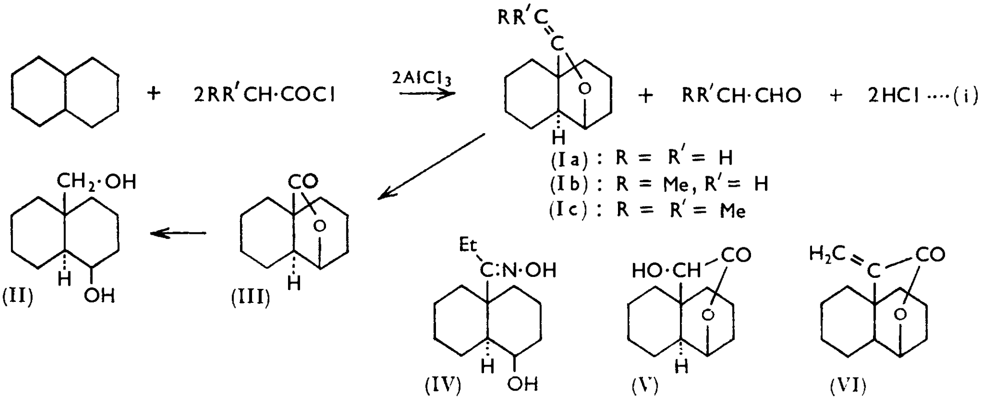
A product of this reaction gave acetaldehyde and the lactone (III) of 4β-hydroxy-*trans*-decalin-9β-carboxylic acid on ozonolysis; it is, therefore, the vinyl ether (Ib). Some of its properties are compared with those of the previously reported[1,2] vinyl ethers (Ia and c). Like them it was obtained in 40% yield.

The reaction (i) formulated below, in which the interaction of decalin and a Friedel-Crafts acylating agent gives a vinyl ether (I), was shown to occur when R = R′ = H or Me; we are now concerned to show that it occurs also when R = Me, R′ = H, and to compare several properties of the products (Ib and c) with those of (Ia). By using propionyl chloride, the ether (Ib) was obtained in about the same yield (40% based on the amount of aluminium chloride) as was reported[1,2] for (Ia and c). The structure of the product was easily determined: the product was an oil, $C_{13}H_{22}O$, which decolorised bromine in carbon tetrachloride, was not reduced with lithium aluminium hydride, was stable in alkali, combined with hydroxylamine in neutral or weakly acidic media to give an oxime, $C_{13}H_{23}O_2N$ (IV), and on ozonolysis in hexane gave acetaldehyde and the lactone (III) which was identified by its infrared spectrum and by its reduction by lithium aluminium hydride to 10β-hydroxymethyl-*trans*-1β-decalol. The vinyl ether (Ib) can be either of two geometrical isomers and we assume that out product is the less crowded one, the methyl group being *trans* to the decalin portion with respect to the ethylenic double bond.



The three vinyl ethers (Ia, b, and c) behaved differently towards an excess of perbenzoic acid: (Ic) reacted with only one mol. of the peracid to give a viscous oil which was probably the acetal;* (Ib) rapidly consumed this amount of peracid and a third more in 67 hours,

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* Cf. compound (IV) of preceding paper.

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

[2] Ahmad and Baddeley, preceding paper.

to give a mixture from which a small amount of a solid, $C_{13}H_{18}O_2$, was isolated; and (Ia) consumed about 2 mol. of the peracid in 24 hours, to give the hydroxy-lactone (V), the corresponding keto-lactone, and a little of the γ-lactone (III). The solid, $C_{13}H_{18}O_2$, rapidly decolorised bromine in carbon tetrachloride, gave a brown colour on addition to tetranitromethane, has strong absorption bands at 1733 and 917 cm.$^{-1}$ (δ-lactone), and has a vinyl group (see VI).

Towards hydroxylamine in weakly acidic media, the ether (Ic) is far less reactive, possibly as a consequence of steric hindrance, than the other two.

Infrared absorption by the vinyl ether groups in (Ia, b, and c) is at 1667, 1698, and 1695 cm.$^{-1}$, respectively. The strong band at 793 $[\cdot O\cdot C(\colon CH_2)\cdot]$ cm.$^{-1}$ in the spectrum of (Ia) is not given by compounds (Ib and c). The stretching vibration of the C–H bonds of the ethylenic groups in (Ia and b) provides weak absorption at 3110 and 3086 cm.$^{-1}$, respectively, while (Ic), understandably, does not absorb in this region.

EXPERIMENTAL

1β,1′-*Epoxy*-10β-*prop*-1′-*enyl*-trans-*decalin* (Ib).—Decalin (69 g.) was added to a homogeneous solution of propionyl chloride (102 g.) and aluminium chloride (133 g.) in ethylene chloride (300 ml.) at 10°. The mixture was kept overnight at this temperature and then slowly added to a stirred mixture of ice and water. The organic layer was separated, washed with water, dried (K_2CO_3), and distilled; it gave decalin (25 g.), b. p. 70—80°/17 mm. and the required *compound* (42 g.), b. p. 118—122°/17 mm., n_D^{25} 1·5033 (Found: C, 80·8; H, 10·4. $C_{13}H_{20}O$ requires C, 81·2; H, 10·4%), $\nu_{max.}$ at 1698, 1100, 1010, and 912 cm.$^{-1}$.

The oxime of 10β-*Propionyl*-trans-1β-*decalol* (IV).—The above vinyl ether (0·9 g.) with hydroxylamine hydrochloride (2·5 g.) and potassium hydroxide (1·0 g.) in 50% aqueous ethanol (20 ml.) was heated on the steam bath and then made homogeneous by addition of ethanol (7 ml.). After 15 min., the mixture was cooled and the required *oxime* (0·77 g.) separated as prisms, m. p. 172—174° (Found: C, 69·7; H, 10·5; N, 6·2. $C_{13}H_{23}NO_2$ requires C, 69·3; H, 10·2; N, 6·2%).

Ozonolysis of the Vinyl Ether.—This compound (10 g.) was ozonised in n-hexane at 4° and evolved acetaldehyde (2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 159—161°), when heated with water (20 ml.) on the steam bath. The residue gave an oil (1·0 g.), b. p. 143—148°/16 mm., and the lactone (III) of 4β-hydroxy-*trans*-decalin-9-carboxylic acid (5·3 g.) which was identified by its infrared absorption spectrum and by reduction of a sample (1·0 g.) with lithium aluminium hydride in ether (80 ml.) to 10β-hydroxymethyl-*trans*-1β-decalol (II) (0·8 g.,), m. p. and mixed m. p. 110°.

The Vinyl Ether and Perbenzoic Acid.—These reactants (0·31 and 0·66 g., respectively) in chloroform (40 ml.) at 0° provided a rapid reaction which consumed 1 mol. of peracid in a few minutes and a further 0·33 mol. in the following 67 hr. A mixture of the vinyl ether (10 g.) and perbenzoic acid (8·6 g.) in chloroform (380 ml.) was kept at 0° for 2·5 hr. Calcium hydroxide (20 g.) was then added, the mixture was filtered, and the filtrate was distilled at 0·55 mm., three fractions being collected: b. p. 75—102° (2·9 g.); b. p. 102—115° (2·4 g.); and b. p. 115—118° (2·0 g.). The last fraction solidified and crystallised from light petroleum in prisms, m. p. 192—194° (Found: C, 76·1; H, 8·7. Calc. for $C_{13}H_{18}O_2$: C, 75·7; H, 8·7%).

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