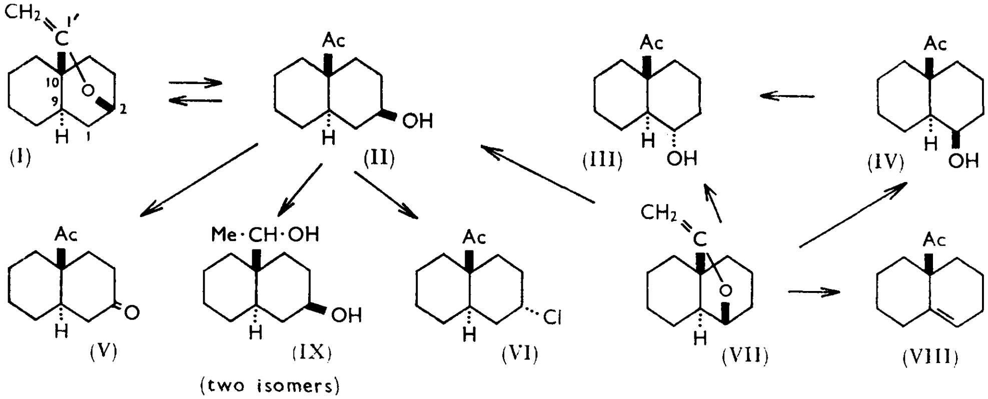
746. *The Interaction of Decalin and Friedel–Crafts Acetylating Agents. Part IV.*[1]

By G. BADDELEY, B. G. HEATON, and (in part) J. W. RASBURN.

This reaction, in the presence of an excess of aluminium chloride or an amount equimolar with that of the acetyl chloride, gives 10β-acetyl-*trans*-2β-decalol * (II) which is also obtained, together with 10-acetyl-$\Delta^{1(9)}$-octalin (VIII), when 1,1′-epoxy-10β-vinyl-*trans*-decalin (VII), the primary product of the interaction, is added to an excess of the metal halide in ethylene chloride. Several new derivatives of *trans*-decalin are described.

PART I [2] showed that decalin and acetyl chloride at 20—35° in the presence of an excess of aluminium chloride gave a mixture which included 9-acetyl-*trans*-decalin, 10-acetyl-$\Delta^{1(9)}$-octalin (VIII), 6-acetyltetralin, and a solid, $C_{12}H_{20}O_2$, m. p. 107—108°. We now report that this solid is formed, together with 1,1′-epoxy-10β-vinyl-*trans*-decalin [1,3] (VII), when the reaction mixture contains acetyl chloride and aluminium chloride (as $AlCl_3$) in equimolecular amounts, or, together with the acetyloctalin (VIII), when the 1β,1′-oxide (VII) in ethylene chloride is left for several days in contact with an excess of aluminium chloride. This solid, called here the hydroxy-ketone, was shown to be 10β-acetyl-*trans*-2β-decalol (II).



All the compounds were racemates.

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* See footnote, p. 3828.

[1] Part III, preceding paper.

[2] Baddeley and Wrench, *J.*, 1959, 1324.

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

The solid was shown in Part I to be a hydroxy-ketone giving a semicarbazone and α-naphthylurethane; an oxime and *p*-nitrobenzoate have also been prepared, but the former only in acid media.

Reduction of the hydroxy-ketone with lithium aluminium hydride, like that of 10β-acetyl-*trans*-1α-decalol (III) but unlike that of the 1β-alcohol (IV), is not stereospecific and gave a mixture of diols which was separated into its components: these are presumably the two stereoisomers of 10-1′-hydroxyethyl-*trans*-2β-decalol (IX).

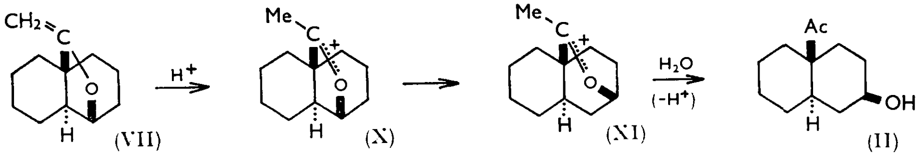
The hydroxy-ketone did not react with chromium trioxide in pyridine at room temperature but with 8N-chromic acid in acetone[4] gave a diketone (V), m. p. 42°, with carbonyl absorption bands at 1706 and 1715 cm.$^{-1}$. Dehydrogenation of this compound with sulphur gave β-naphthol. The evidence thus far indicates that the hydroxyl and the acetyl group are attached to the decalin skeleton at the 2- and 10- or 2- and 9-positions respectively.

The infrared absorption spectrum of the hydroxy-ketone has a band at 1709 cm.$^{-1}$ (C=O) and bands at 3636 and 3460 cm.$^{-1}$ which are provided by free and intermolecularly hydrogen-bonded hydroxyl groups since their intensities were increased and decreased respectively by dilution of the carbon tetrachloride solution. The fingerprint region of the spectrum is similar to that of 10β-acetyl-*trans*-1α-decalol (III), indicating an equatorial hydroxyl group and a *trans*-decalin grouping. This conformation of the hydroxyl group is further reflected by the resistance to chromium trioxide in pyridine.

The hydroxy-ketone with concentrated hydrochloric acid gives 10β-acetyl-2α-chloro-*trans*-decalin (VI), which has strong infrared absorption bands at 712 cm.$^{-1}$ (axial C–Cl) and 1258 cm.$^{-1}$ (cf. 3α-chlorocholestane, which has an axial chlorine and *trans*-A/B fusion). This reaction provides further evidence for the equatorial hydroxyl group.

The hydroxy-ketone has an unexpectedly high volatility: its boiling point, 120°/12 mm., is much lower than that of the isomer (III), b. p. 160°/12 mm., which also has an equatorial hydroxyl group and an infrared absorption spectrum which shows intermolecular but not intramolecular hydrogen bonding. We suggest that the high volatility is provided by intramolecular hydrogen bonding which occurs when the ring carrying the hydroxyl group assumes a boat conformation and that it is evidence for the β-configuration of both the acetyl and the hydroxyl group.

When the hydroxy-ketone was heated under reduced pressure with toluene-*p*-sulphonic acid, it lost the elements of water and gave a mobile oil, $C_{12}H_{18}O$, which has not a hydroxyl group but, as a vinyl ether (cf. I), shows strong infrared absorption at 1653 cm.$^{-1}$. Like vinyl ethers which have a terminal methylene group, it absorbs strongly also at 795 and weakly at 3106 cm.$^{-1}$. The frequency 1653 cm.$^{-1}$ is lower than that (1667 cm.$^{-1}$) of the vinyl ether (VII) and is in accordance with the formula (I) in which the double bond is exocyclic to a six-membered ring and not to a five-membered ring as in (VII). The vinyl ether (I) readily decolorises bromine in carbon tetrachloride, is readily hydrolysed to the original hydroxy-ketone, m. p. 107°, by dilute mineral acid, and with hydroxylamine in acid gives the oxime of this hydroxy-ketone. These results prove the *cis*-relation between the hydroxyl and the acetyl group, and, therefore, show that the hydroxy-ketone, m. p. 107°, is 10β-acetyl-*trans*-2β-decalol (II). The mechanism of its formation from decalin and an acetylating agent and from 1,1′-epoxy-10β-vinyl-*trans*-decalin has previously been discussed.[5] It includes the ring enlargement (X ⟶ XI) which is similar to that proposed



(VII) (X) (XI) (II)

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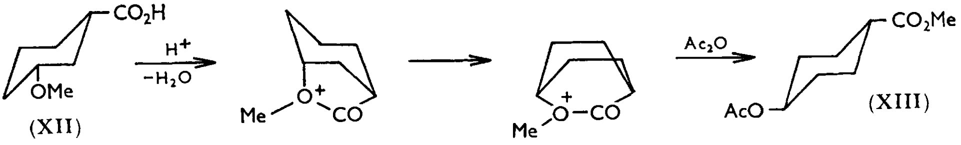
[4] Bladon, Fabian, Henbest, Koch, and Wood, *J.*, 1951, 2402.

[5] Ahmad, Baddeley, Heaton, and Rasburn, *Proc. Chem. Soc.*, 1959, 395.

by Noyce and Weingarten [6] to explain the change of *cis*-3-methoxycyclohexanecarboxylic acid (XII) into methyl *trans*-4-acetoxycyclohexanecarboxylate (XIII) through the agency of sulphuric acid in acetic anhydride.



EXPERIMENTAL

10β-*Acetyl*-trans-2β-*decalol* * (II).—(i) A solution of acetyl chloride (150 ml.) in ethylene chloride (600 ml.) was saturated with aluminium chloride (280 g.) and decanted from undissolved chloride. Decalin (170 g.) was gradually added to the stirred solution at 7°, and the mixture was held at 10—12° for 7 hr., decomposed with ice and water, and worked up in the usual way. Distillation gave 1,1′-epoxy-10β-vinyl-*trans*-decalin (VII) (63·8 g.), b. p. 107—112°/13 mm., and a fraction (29 g.), b. p. 115—125°/13 mm., from which the required [2] hydroxy-ketone (*ca.* 9 g.), m. p. 107°, slowly separated. (ii) 1,1′-Epoxy-10β-vinyl-*trans*-decalin (15 g.) was gradually added, with cooling, to aluminium chloride (22·4 g.) in ethylene chloride (40 ml.); after 2 days at room temperature, the mixture was decomposed with ice and worked up in the usual way. Distillation gave the unchanged oxide (5 g.), b. p. 110—113°/14 mm., a fraction (5 g.), b. p. 115—122°/14 mm., and a residue (5 g.) which under 14 mm. pressure did not distil below 140°. The second fraction in light petroleum at −10° gave the hydroxy-ketone (1·0 g.) as needles, m. p. and mixed,[2] m. p. 107°. The filtrate contained an oil which was placed on an alumina column and eluted with light petroleum (b. p. 60—80°). It gave a fraction (1·2 g.) which was identified as 10-acetyl-$\Delta^{1(9)}$-octalin by its infrared spectrum and its semicarbazone, m. p. and mixed m. p. 216—218°.

Reactions of the Hydroxy-ketone (II).—(i) *With hydroxylamine.* A mixture of the hydroxy-ketone (0·45 g.), hydroxylamine hydrochloride (1·25 g.), and potassium hydroxide (0·50 g.) in 50% aqueous ethanol (10 ml.) was heated at 100° for 20 min. The *oxime* separated on cooling and crystallised from light petroleum–ethanol in prisms (0·22 g.), m. p. 150·5—151·5° (Found: C, 68·2; H, 10·0; N, 6·4. $C_{12}H_{21}NO_2$ requires C, 68·2; H, 10·0; N, 6·6%). The oxime was not formed when the reaction mixture was alkaline.

(ii) *With* p-*nitrobenzoyl chloride.* The hydroxy-ketone (0·50 g.) and *p*-nitrobenzoyl chloride (0·55 g.) were heated in benzene (5 ml.) and pyridine (6 ml.) on the steam-bath for 2 hr. After cooling, the mixture was diluted with ether and washed severally with dilute sulphuric acid (30 ml.), saturated sodium hydrogen carbonate solution (10 ml.), and water (20 ml.). The ether extract was dried (Na_2SO_4) and gave the p-*nitrobenzoate* (0·67 g.) which separated from light petroleum–ethanol in straw-coloured needles, m. p. 172—173° (Found: C, 66·2; H, 6·8; N, 3·8. $C_{19}H_{23}NO_5$ requires C, 66·1; H, 6·7; N, 4·1%).

(iii) *With chromic acid.* A portion (3 ml.) of a solution of chromium trioxide (33 g.) in dilute sulphuric acid (125 ml. containing 27 ml. of the concentrated acid) was added dropwise to a solution of the hydroxy-ketone (1·2 g.) in acetone (100 ml.). After 3 min., water (350 ml.) was added and the mixture was extracted with ether. The extracts were washed with water and dried (K_2CO_3) and gave 10β-*acetyl*-trans-2-*decalone* (1·0 g.) which separated from light petroleum (b. p. <40°) in needles, m. p. 42—43·5° (Found: C, 74·4; H, 9·4. $C_{12}H_{18}O_2$ requires C, 74·2; H, 9·3%), $\nu_{max.}$ (in CCl_4) 1706 and 1715 cm.$^{-1}$ (C=O). Dehydrogenation of this diketone by sulphur gave β-naphthol, m. p. and mixed m. p. 119—121°.

(iv) *With concentrated hydrochloric acid.* After 2 days at room temperature there was no reaction between the hydroxy-ketone (0·35 g.) and concentrated hydrochloric acid (5 ml.), but when the mixture was heated at 100° for 1 hr. it gave 10β-*acetyl*-2α-*chloro*-trans-*decalin* which separated from light petroleum (b. p. 40—60°) in prisms, m. p. 75—76° (Found: C, 67·3; H, 9·0. $C_{12}H_{19}ClO$ requires C, 67·1; H, 8·9%), $\nu_{max.}$ 1701 (C=O), and 712 and 1258 cm.$^{-1}$ (axial C–Cl).

(v) *With toluene*-p-*sulphonic acid.* A mixture of the hydroxy-ketone (2·2 g.) and the acid

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* See footnote, p. 3828.

[6] Noyce and Weingarten, *J. Amer. Chem. Soc.*, 1957, **79**, 3098.

(0·04 g.) was heated at 125° for 90 min. and distilled under reduced pressure. It gave *2β,1′-epoxy-10β-vinyl-*trans*-decalin* (1·1 g.), b. p. 117°/18 mm. (Found: C, 81·3; H, 10·0. $C_{12}H_{18}O$ requires C, 80·9; H, 10·1%). This decolorised bromine in carbon tetrachloride, gave a brown colour with tetranitromethane, was readily hydrolysed by dilute mineral acid to the original hydroxy-ketone, m. p. and mixed m. p. 107°, and gave the oxime of this hydroxy-ketone when warmed with hydroxylamine in acidic aqueous ethanol. Its infrared absorption spectrum showed the absence of a hydroxyl group and had strong bands at 1653, 1441, 1227, 1143, 1038, and 795 cm.$^{-1}$.

(vi) *With lithium aluminium hydride.* Reduction of the hydroxy-ketone (0·50 g.) with the hydride (0·50 g.) in ether (50 ml.) gave a solid (0·50 g.), m. p. 105—118°, which was separated into two, apparently stereoisomeric, *diols* which severally crystallised from light petroleum (b. p. 60—80°) containing a little ethyl acetate in plates, m. p. 137—137·5° (Found: C, 72·9; H, 11·2. $C_{12}H_{22}O_2$ requires C, 72·7; H, 11·1%), and in prisms, m. p. 126—127° (Found: C, 72·7; H, 10·8%). A mixture of the two diols melted at 108—116°. These compounds were shown, by infrared analysis, to contain both free and intramolecularly hydrogen-bonded hydroxyl groups.

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MANCHESTER COLLEGE OF SCIENCE AND TECHNOLOGY,
MANCHESTER, 1.

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