909. *Further Reactions of* 10-*Acetyl*-$\Delta^{1(9)}$-*octalin*

By G. Baddeley and E. K. Baylis

10-Acetyl-$\Delta^{1(9)}$-octalin (II) has been oxidised with perbenzoic acid to the epoxide (III) from which the compound (II) has been regenerated by successive interaction with lithium aluminium hydride, chromium trioxide in pyridine, and formic acid. The epoxide (III) is isomerised by dilute sulphuric acid to the hydroxy-vinyl ether (VII). This isomerisation and the reaction of compound (III) with hydroxylamine [(III) ⟶ (IV)] and concentrated hydrochloric acid [(III) ⟶ (VIII)] are considered to involve the cation (IX) as an intermediate.

The vinyl ether (I) has been obtained in 40—45% yield by the interaction of decalin and Friedel–Crafts acetylating agent at $<10°$ and in the absence of an excess of aluminium chloride,[1] whereas the interaction in the presence of an excess of the metal halide, like the action of an excess of the metal halide on the vinyl ether,[2] gave 10-acetyl-$\Delta^{1(9)}$-octalin (II)

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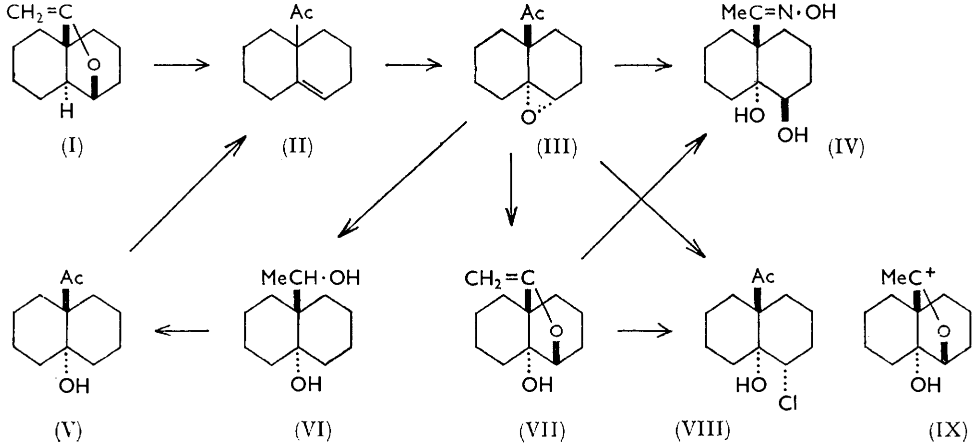
[1] G. Baddeley, B. G. Heaton, and J. W. Rasburn, *J.*, 1960, 4713.

[2] G. Baddeley, B. G. Heaton, and (in part) J. W. Rasburn, *J.*, 1961, 3835.

and other products.[3] The unsaturated ketone (II), which has also been obtained from 10β-acetyl-*trans*-1β-decalol through the agency of phosphorus oxychloride,[4] is conveniently prepared by isomerising the vinyl ether (I) with toluene-*p*-sulphonic acid monohydrate at 130°, reacting the product with semicarbazide and hydrolysing the resulting semicarbazone, m. p. 216—217°, with mineral acid. This procedure (see Experimental section), though referred to and employed by Baddeley, Heaton, and Rasburn,[1] has not previously been described. The product was identified by comparison with previously prepared samples. Its structure was confirmed by heating the semicarbazone with potassium hydroxide, a hydrocarbon $C_{12}H_{20}$ being obtained which, as expected for 10-ethyl-$\Delta^{1(9)}$-octalin, (*a*) has the infrared absorption bands of a trisubstituted olefin, (*b*) combined with hydrogen chloride in dry diethyl ether to give a chloro-compound which, in 80% aqueous ethanol at 25·0°, solvolysed five times faster than did t-butyl chloride, and (*c*) provided a ketoaldehyde when subjected to the oxidative procedure of Castells and Meakins.[5] Further investigations of the isomerisation of the vinyl ether (I) with toluene-*p*-sulphonic acid monohydrate have shown that 10-acetyl-$\Delta^{1(2)}$-octalin is also formed.[6]



Peracid oxidation of compound (II) in diethyl ether gave only 10β-acetyl-1α,9-epoxy-*trans*-decalin (III). When treated successively with lithium aluminium hydride, chromium trioxide in pyridine and formic acid (>98%), the epoxide (III) gave first a diol [see compound (VI)], then a hydroxy-ketone [see compound (V)] which was not intramolecularly hydrogen-bonded, and, finally, the unsaturated ketone (II). This sequence of reactions establishes the structures of compounds (III), (VI), and (V). Dilute sulphuric acid at room temperature readily effected the quantitative isomerisation of compound (III) to compound (VII). The latter, 1β,1′-epoxy-10β-vinyl-*trans*-9α-decalol, has many of the properties of the vinyl ether (I); it has infrared absorption bands at 798, 1668, and 3077 cm.$^{-1}$, readily decolourises bromine in carbon tetrachloride, resists catalytic hydrogenation, reacts with ozone in ethyl acetate at 0° to give formic acid and a γ-lactone, adds a molecular proportion of hydroxylamine in weakly acid solution [see formulæ (VII) ⟶ (IV)], and, when shaken with concentrated hydrochloric acid, affords a chloro-ketone, probably compound (VIII), which, in 70% aqueous acetone at 50°, solvolyses three times as fast as t-butyl chloride.

The expoxide (III) reacted severally with hydroxylamine and hydrochloric acid to give the same oxime (IV) and chloro-ketone (VIII) as did the hydroxy-vinyl ether (VII). These reactions of compound (III) and its isomerisation to compound (VII) probably involve the cation (IX) as an intermediate.

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[3] G. Baddeley and E. Wrench, *J.*, 1959, 1324.
[4] G. Baddeley, B. G. Heaton, and J. W. Rasburn, *J.*, 1961, 3828.
[5] J. Castells and G. D. Meakins, *Chem. and Ind.*, 1956, 248.
[6] R. J. Emarton and J. W. Rasburn, personal communication.

EXPERIMENTAL

10-*Acetyl*-$\Delta^{1(9)}$-*octalin* (II).—A mixture of 1,1′-epoxy-10β-vinyl-*trans*-decalin (25 g.) and toluene-*p*-sulphonic acid monohydrate (1 g.) was heated at 130° for an hour or at 150° for 0·5 hr. and distilled under reduced pressure. It gave an oil (22 g.) of camphor-like odour, b. p. 114—115°/10 mm., n_D^{25} 1·5062 (Found: C, 80·9; H, 10·0. Calc. for $C_{12}H_{18}O$: C, 80·9; H, 10·1%), from which a semicarbazone, m. p. 216—217° (Found: C, 66·4; H, 8·9; N, 18·0. Calc. for $C_{13}H_{21}N_3O$: C, 66·4; H, 8·9; N, 17·9%) was obtained as fine needles (from ethanol). Hydrolysis of the semicarbazone with sulphuric acid (2N) gave 10-acetyl-$\Delta^{1(9)}$-octalin, b. p. 114—115°/10 mm., n_D^{25} 1·5062, which was identified by its infrared absorption spectrum, the m. p. and mixed m. p. 216—217° of its semicarbazone, and by reduction ($LiAlH_4$) to 10-1′-hydroxyethyl-$\Delta^{1(9)}$-octalin [4] which, in turn, was identified by its infrared absorption spectrum and its α-naphthylurethane, m. p. and mixed m. p. 143—145°.

10-*Ethyl*-$\Delta^{1(9)}$-*octalin*[3].—A mixture of the above semicarbazone (27 g.), potassium hydroxide (19 g.), and diethylene glycol (350 ml.) was refluxed for 16 hr. Nitrogen (2170 ml.) was evolved and a mobile oil (8 g.), b. p. 100—110°/15 mm., was isolated. Chromatographic purification in light petroleum over alumina gave the required hydrocarbon (7·5 g.) (Found: C, 88·1; H, 12·0. Calc. for $C_{12}H_{20}$: C, 87·8; H, 12·2%), $\nu_{max.}$ 1645 and 808 cm.$^{-1}$ (trisubstituted olefin). It combined with the calculated amount of bromine (in CCl_4) and when treated successively with osmium tetroxide in ether, lithium aluminium hydride in tetrahydrofuran, ice-cold dilute sulphuric acid, and lead tetra-acetate in glacial acetic acid-t-butyl alcohol [5] gave an oil, $\nu_{max.}$ (in CCl_4) 1705 ($>$C=O) and 1727 ($\smallsetminus$CH=O) cm.$^{-1}$. The hydrocarbon combined with hydrogen chloride in dry ether to give a crystalline chloro-compound which is a 10-chloro-9-ethyldecalin since, in 80% aqueous ethanol at 25°, it was solvolysed faster than t-butyl chloride: k_{25} = 0·174 and 0·0345 hr.$^{-1}$, respectively.

1α,9-*Epoxy*-10β-*acetyl*-trans-*decalin* (III).—Perbenzoic acid (2 mol.) in ether (360 ml.) was gradually added to 10-acetyl-$\Delta^{1(9)}$-octalin (12·5 g.) in ether (100 ml.) at 0°. Peracid (1 mol.) was consumed in *ca.* 2 hr. The ethereal solution was thoroughly washed with sodium hydrogen carbonate solution, then with water, and dried (Na_2SO_4). Distillation gave the required *epoxide* (11·1 g.), b. p. 130—133°/10 mm., which crystallised from light petroleum (b. p. $<$40°) cooled in a mixture of cardice and methanol in plates, m. p. 51—52° (Found: C, 74·2; H, 9·3. $C_{12}H_{18}O_2$ requires C, 74·2; H, 9·3%). It has strong infrared absorption bands at 1718, 1704, 1131, and 919 cm.$^{-1}$, and gave naphthalene (picrate m. p. and mixed m. p. 148—149°) when heated with sulphur. Its structure is established by the following reactions.

10-*Acetyl*-trans-9-*decalol* (V).—The epoxide (III) (10 g.) in dry ether (200 ml.) was gradually added to lithium aluminium hydride (3 g.) in dry ether (200 ml.) and the mixture was boiled for 3 hr. After the excess of hydride had been destroyed with ethyl acetate the mixture was worked up in the usual way and gave 10-1′-hydroxyethyl-*trans*-9-decalol (VI), b. p. 155—158°/10 mm., which crystallised with difficulty from light petroleum containing diethyl ether (5%) in prisms (8·5 g.), m. p. 60—69 and 71·5° after chromatographic purification in light petroleum–chloroform over alumina. It decomposed on prolonged contact with the atmosphere and did not provide consistent data when analysed quantitatively for C and H. Its solution in carbon tetrachloride has strong absorption bands at 3636 (free OH) and 3484 cm.$^{-1}$; the intensity of the latter band varied with the concentration of the solution as required by intermolecular hydrogen bonding. It reacted with lithium aluminium hydride with the evolution of 2 molecular proportions of hydrogen, and a sample (0·50 g.), with chromium trioxide in pyridine, gave 10-*acetyl*-trans-9-*decalol* (V) (0·42 g.) which crystallised from light petroleum–ethyl ether in plates, m. p. 133·5° (Found: C, 73·5; H, 10·0. $C_{12}H_{20}O_2$ requires C, 73·5; H, 10·2%); $\nu_{max.}$ 3636 (free OH) and 1698 ($>$C=O) cm.$^{-1}$. A solution of this product in formic acid ($>$98%) was set aside at room temperature for 3 hr.; it afforded 10-acetyl-$\Delta^{1(9)}$-octalin which was identified by its camphor-like odour, its infrared absorption spectrum, and by its semicarbazone, m. p. and mixed m. p. 216—217°.

1β,1′-*Epoxy*-10β-*vinyl*-trans-9α-*decalol* (VII).—This compound was obtained quantitatively by the isomerisation of 1α,9-epoxy-10β-acetyl-*trans*-decalin, in solution in chloroform, diethyl ether or aqueous ethanol, with dilute sulphuric acid. It was formed together with the 1,9-epoxide when the peracid oxidation of 10-acetyl-$\Delta^{1(9)}$-octalin was effected in chloroform. It crystallised from light petroleum in rhombs, m. p. 107—108° (Found: C, 74·2; H, 9·3. $C_{12}H_{18}O_2$ requires C, 74·2; H, 9·3%); $\nu_{max.}$ 3597 (free OH), 798, 1668, and 3077 cm.$^{-1}$. The last three absorption bands are also features of the absorption spectrum of the vinyl ether (I). Like compound (I), compound (VII) rapidly decolorised bromine in carbon tetrachloride, was recovered after addition to lithium aluminium hydride, could not be catalytically hydrogenated, and gave naphthalene [picrate, m. p. and mixed m. p. 148—149], when refluxed with sulphur for 4 hr. The procedure previously described,[1] for the separation of the products of ozonolysis of compound (I), was applied to a preliminary investigation of the products of ozonolysis of compound (VI) in ethyl acetate at 0°. As before, formic acid, an oil [$\nu_{max.}$ 3636, 3434, and 1773 (γ-lactone) cm.$^{-1}$] and two crystalline compounds [m. p. 132°, $\nu_{max.}$ at 3571, 3436, and 1712 cm.$^{-1}$; and m. p. 177—180°, $\nu_{max.}$ at 3534, 3205, and 1736 cm.$^{-1}$] were obtained. The last product was afforded also by the oxidation of compound (VII) with perbenzoic acid in chloroform.

The hydroxy-vinyl ether (VII) (1 g.) in ethanol (5 ml.) was added to a solution of hydroxylamine and its hydrochloride in water at pH 6 and the mixture was boiled for a few minutes. A solid separated which crystallised from 70% aqueous ethanol in plates, m. p. 233—234° (Found: C, 63·5; H, 9·4; N, 6·15. $C_{12}H_{21}NO_3$ requires C, 63·4; H, 9·3; N, 6·2%). This oxime [see compound (IV)] was obtained also when the epoxide (III) was similarly treated. With acetyl chloride (1 mol.) in light petroleum, the oxime gave a *monoacetate* which crystallised from light petroleum (b. p. 80—100°) in cubes, m. p. 175—176° (Found: C, 62·8; H, 8·4; N, 5·5. $C_{14}H_{23}NO_4$ requires C, 62·5; H, 8·5; N, 5·2%); $\nu_{max.}$ 3497, 3390 (OH), and 1756 (acetate) cm.$^{-1}$. With an excess of boiling acetyl chloride, the oxime gave a diacetate which crystallised from light petroleum in cubes, m. p. 145—146° (Found: C, 61·7; H, 7·9; N, 4·5. $C_{16}H_{25}NO_5$ requires C, 61·7; H, 8·0; N, 4·5%); $\nu_{max.}$ at 3636 (free OH), 1721, and 1756 (acetate) cm.$^{-1}$.

When shaken with concentrated hydrochloric acid, the epoxides (III) and (VII) gave oils which were extracted with light petroleum and dried ($CaCl_2$). The two oils have identical infrared absorption spectra, which include bands at 3636 (OH), 1704 (CO), and 743 (equatorial Cl) cm.$^{-1}$, and hydrolysed in 70% aqueous acetone at 50° at rates ($k_{50} = 1·32 \times 10^{-3}$ and $1·28 \times 10^{-3}$ sec.$^{-1}$, respectively) which were within experimental error of one another.

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THE MANCHESTER COLLEGE OF SCIENCE AND TECHNOLOGY,
MANCHESTER 1.

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