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

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The primary product of this reaction is shown to be 1β,1′-epoxy-10β-vinyl-*trans*-decalin * (II). The following evidence for the *trans*-configuration is provided. (*a*) The derived hydroxy-ketone (X) and the monoacetyl derivative of its oxime (see XII; Z = OAc) gave respectively 10-acetyl-$\Delta^{1(9)}$-octalin (XI) and the acetyl derivative of its oxime when treated with phosphorus oxychloride in pyridine. These results establish that, in (X), the hydroxyl group, and therefore the acetyl group, is *trans*-related to the 9-hydrogen atom; the corresponding substituents in the vinyl ether must be similarly related to the 9-hydrogen atom. (*b*) Desulphurisation of the thiouronium salt [V; Y = $SC(NH_2){:}NH_2^+$, $C_7H_7{\cdot}SO_3^-$], obtained by direct reaction of the vinyl ether, afforded 9-acetyl-*trans*-decalin. (*c*) The infrared spectra of derivatives (*e.g.*, XIV) conform with previous observations [2] on *trans*-decalin derivatives.

Other new derivatives of decalin are described.

In Part I,[3] the interaction of acetyl chloride–aluminium chloride and decalin in the presence of an excess of the metal halide was shown to give 9-acetyl-*trans*-decalin (VI), 10-acetyl-$\Delta^{1(9)}$-octalin (XI), and other compounds. Part II [1] described how, in the absence of an excess of the metal halide, and under the mildest conditions compatible with a convenient rate, the primary product was 1,1′-epoxy-10-vinyldecalin † (II). The present paper is concerned with those reactions of compound (II), to be called the vinyl ether, which were involved in showing that the decalin portion has the *trans*-configuration. For convenience, and without intent to beg the question, this configuration is assigned to all formulations.

Homolysis of ethers by Grignard reagents in the presence of cobalt chloride is well known [4] and analogous reactions have been effected [5] with lithium aluminium hydride–cobalt chloride. Acylic vinyl ethers have been cleaved by Grignard reagents even in the absence of cobalt chloride. The site of fission depends on the structure of the vinyl ether: thus, while those of the type $R{\cdot}CH{:}CH{\cdot}OR'$ react with $R''MgBr$ to give $R'OH$ and $R{\cdot}CH{:}CHR''$, those of the type $R{\cdot}CH{:}CR'''{\cdot}OR'$ give $R{\cdot}CH_2{\cdot}COR'''$ and $R'R''$.[6] The yields of cleavage products usually exceed 50%. All our attempts to effect reductive fission of the vinyl ether (II) were unsuccessful; the vinyl ether was recovered in almost quantitative yield.

Acid hydrolysis of the vinyl ether gave two hydroxy-ketones: the action of dilute sulphuric acid on the vinyl ether in diethyl ether gave the hydroxy-ketone (X), m. p. 62°, which is intramolecularly hydrogen-bonded,[1] while boiling dilute sulphuric acid gave the hydroxy-ketone (V; Y = OH), m. p. 57°, in which, from infrared spectra, hydrogen bonding is only intermolecular. When oxidised with chromium trioxide in pyridine, both products gave the same diketone (IX). Apparently, interaction of the vinyl ether with acid gives first the oxonium ion (III) which can be attacked by a water molecule at either of the carbon atoms attached to oxygen. Reaction in the side chain (III $\rightleftharpoons$ VII) is the

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* All the compounds discussed in this paper were racemates: α- and β- have only relative significance with respect to an arbitrarily 10β-substituent.

† Incorrectly called 10-vinyldecalin 1,1′-oxide in Part II.

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

[2] Baker, Minckler, and Hussey, *J. Amer. Chem. Soc.*, 1959, **81**, 2379.

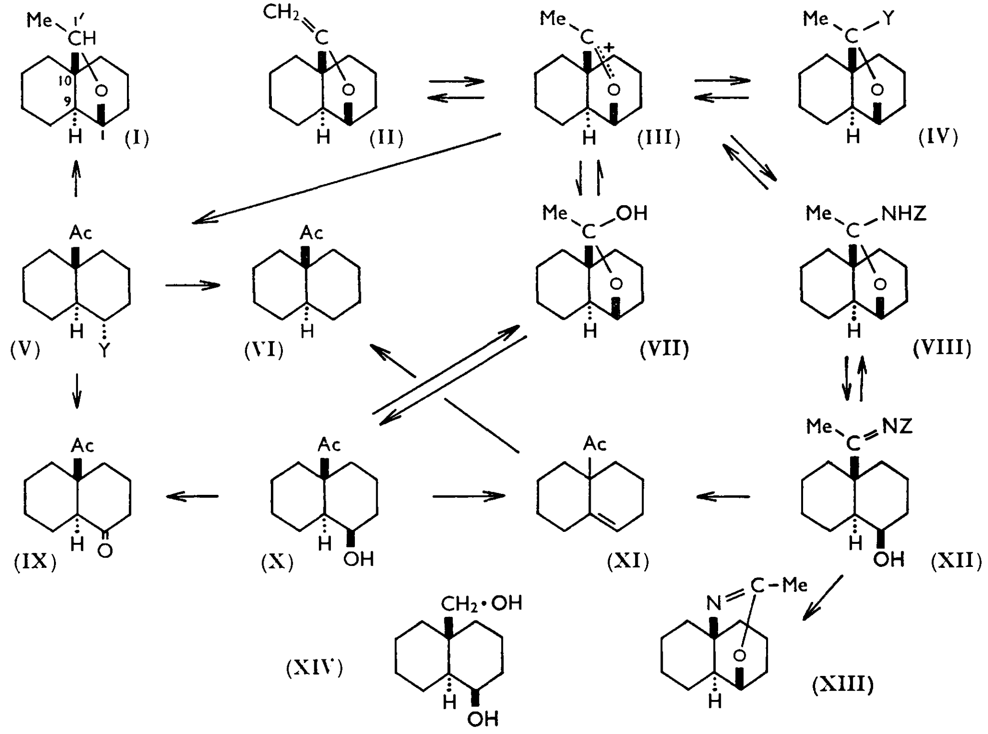
[3] Baddeley and Wrench, *J.*, 1959, 1324.

[4] Kharasch and Urry, *J. Amer. Chem. Soc.*, 1944, **66**, 1438; *J. Org. Chem.*, 1948, **13**, 101.

[5] Karrer and Ruttner, *Helv. Chim. Acta*, 1950, **33**, 812.

[6] Hill, Woodberry, Simmons, Hill, and Haynes, *J. Amer. Chem. Soc.*, 1958, **80**, 4602; Hill, Prigmore, and Moore, *ibid.*, 1955, **77**, 352.

faster and more reversible process and gives compound (X); the other, less easily reversible, process is favoured by protracted reaction and provides the product (V; Y = OH). Thus these two hydroxy-ketones were obtained respectively by kinetic and thermodynamic control of the hydrolysis. With phosphorus oxychloride in pyridine, compound (X) lost the elements of water and gave 10-acetyl-$\Delta^{1(9)}$-octalin (XI) which was described in Part I. This means of obtaining an unsaturated compound from a secondary alcohol has been used by Davy, Halsall, Jones, and Meakins,[7] and now provides evidence for a *trans*-diaxial relation between the hydroxyl group and the 9-hydrogen atom in compound (X). This configurational relation, in conjunction with the fact that the hydroxyl group and the acetyl group are on the same side of the molecule (cf. the evidence of intramolecular hydrogen bonding and the ready recombination [1] of the groups to give the vinyl ether), shows the decalin portion of compound (X), and therefore of the vinyl ether (II), to have the *trans*-configuration.



(The compounds handled were all racemates.)

The vinyl ether reacted with hydroxylamine, semicarbazide, and phenylhydrazine only in acidic media and gave addition products which are, respectively, the oxime, semicarbazone, and phenylhydrazone (XII; Z = OH, $NH{\cdot}CO{\cdot}NH_2$, and NHPh) of the hydroxy-ketone (X). These reactions did not involve preliminary hydrolysis of the vinyl ether since the oxime was obtained from the vinyl ether and hydroxylamine hydrochloride in dry pyridine and, again, in anhydrous ethanol with fused sodium acetate to liberate hydroxylamine from its hydrochloride. These reactions are, therefore, represented by the scheme (II $\rightleftharpoons$ III $\rightleftharpoons$ VIII $\rightleftharpoons$ XII). In contrast to the ready formation of the foregoing derivatives (XII), the isomeric hydroxy-ketone (V; Y = OH) was recovered almost quantitatively after prolonged heating with hydroxylamine hydrochloride (in

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[7] Davy, Halsall, Jones, and Meakins, *J.*, 1951, 2702.

excess) and sodium hydroxide in aqueous alcohol, conditions which afford the oxime (XII; Z = OH) very rapidly from the vinyl ether. When heated with dilute mineral acid, the compounds (XII) gave the vinyl ether and this was partly converted into the hydroxy-ketone (V; Y = OH). The vinyl ether was again recovered when the semicarbazone (XII; Z = $NH{\cdot}CO{\cdot}NH_2$) was heated for a short time above its melting point. The action of hot polyphosphoric acid on the oxime (XII; Z = OH) gave a compound which we believe to be the dihydro-oxazine (XIII).

Both hydroxyl groups in the oxime (XII; Z = OH) were esterified by acetyl chloride, whereas only the hydroxyimino-group reacted with acetic anhydride and with toluene-*p*-sulphonyl chloride: understandably, esterification of the alcohol group is sterically hindered. However, this group is readily oxidised by chromium trioxide in pyridine and the monoacetyl derivative (XII; Z = OAc) gave the acetate of the mono-oxime of the diketone (IX). The monoacetyl derivative of the oxime (*i.e.*, XII; Z = OAc) lost the elements of water through the agency of phosphorus oxychloride in pyridine to give an oil which must have been the acetyl derivative of the oxime of 10-acetyl-$\Delta^{1(9)}$-octalin since it gave this oxime when gently hydrolysed by alkali; and this reaction with phosphorus oxychloride, like that of the hydroxy-ketone (X) with this reagent, is further evidence for the *trans*-configuration of the decalin moiety in these compounds and, therefore, in the vinyl ether from which they were prepared.

Equimolecular amounts of the vinyl ether and *p*-nitrobenzoic acid at 170° gave 10β-acetyl-*trans*-1α-decalyl *p*-nitrobenzoate * (V; Y = $O{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2$); and the 3,5-dinitrobenzoate was similarly prepared. The well-known ready addition of acids to vinyl ethers: $-O-\overset{|}{C}=CH- + HA \rightleftharpoons -O-\overset{|}{C}A-CH_2-$ makes it likely that the present interactions first gave a compound (IV; Y = $O{\cdot}COAr$) by a readily reversible process which was accompanied by substitution at position 1 (III ⟶ V; Y = $O{\cdot}COAr$), a less easily reversible process. Alkaline hydrolysis of the esters gave the hydroxy-ketone (V; Y = OH) in nearly quantitative yields. With an excess of concentrated hydrochloric acid at room temperature, the vinyl ether rapidly gave 10β-acetyl-1α-chloro-*trans*-decalin (V; Y = Cl) which has an infrared absorption band at 743 $cm.^{-1}$ as required for an equatorial C–Cl bond.[8] Reduction of this compound with lithium aluminium hydride did not give 9-1′-hydroxyethyl-*trans*-decalin, which, by comparison with an authentic sample,[3] would have provided further evidence for the *trans*-configuration of the decalin moiety; instead, 1β,1′-epoxy-10β-ethyl-*trans*-decalin (I) was obtained by intramolecular displacement of chloride ion. It is noteworthy that all our attempts to obtain this saturated ether by catalytic hydrogenation of the vinyl ether have failed. Interaction of the vinyl ether and mineral acid in methanol or ethanol gave 10β-acetyl-1α-methoxy- or 10β-acetyl-1α-ethoxy-*trans*-decalin (V; Y = OMe and OEt) respectively.

The vinyl ether in ethanol combined with thiourea in the presence of toluene-*p*-sulphonic acid to give *S*-(10β-acetyl-*trans*-1α-decalyl)thiouronium toluene-*p*-sulphonate [V; Y = $SC(NH_2){\vdots}NH_2^+$, $C_7H_7{\cdot}SO_3^-$] from which the picrate, being a less soluble salt, was obtained quantitatively. Oxalic acid and even acetic acid are able to effect this combination of the vinyl ether with thiourea. The toluene-*p*-sulphonate with Raney nickel in boiling ethanol gave a mixture of 9-acetyl-*trans*-decalin (VI) and the vinyl ether (II). The latter was the main product when less active Raney nickel was used and is probably given by reversal of the process affording the thiouronium salt. Nickel–aluminium alloy in aqueous-alcoholic sodium hydroxide provided the saturated ketone (VI) in highest yield. This compound was identified (*a*) by comparing its infrared spectrum with that of an authentic sample,[3] (*b*) by reducing it with lithium aluminium hydride to the corresponding alcohol which was identified as its α-naphthylurethane,[3] and (*c*) by oxidation to *trans*-decalin-9-carboxylic acid.[3] These observations are yet more evidence for the

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* See footnote on p. 3828.

[8] Barton, Page, and Shoppee, *J.*, 1956, 331.

trans-configuration of the decalin structure in the vinyl ether, but only if the formation of the thiouronium salt and its desulphurisation do not provide configurational rearrangement at $C_{(9)}$. We have shown that the unsaturated ketone (XI) is not an intermediate in the preparation of the thiouronium salt by demonstrating that this ketone does not react with thiourea under the experimental conditions. Previous reductive desulphurisations of thiouronium salts[9] and other sulphur compounds have shown that epimerisation does not occur when the hydrogen in question is attached to the carbon atom adjacent to that carrying the sulphur atom.

Interaction of the thiouronium salt with potassium borohydride, and again with hydrazine hydrate and potassium hydroxide under Wolff–Kishner conditions, gave an alkali-soluble compound, $C_{12}H_{20}OS$, which, according to its infrared absorption spectrum, is 10β-acetyl-1α-mercapto-*trans*-decalin (V; Y = SH). The benzylthio-compound (V; Y = $S{\cdot}CH_2Ph$) was afforded by interaction of the vinyl ether and toluene-α-thiol in the presence of a trace of hydrochloric acid.

The infrared absorption spectra of *cis*- and *trans*-decalin are very similar and do not afford distinguishing evidence regarding the nature of the ring junctions in the compounds. However, diagnostic differences have recently been reported[2] for all the stereoisomers of 10-methyl-2-decalol and 9-hydroxymethyldecalin, and for some of the isomers of 10-hydroxymethyl-2-decalol; the derivatives of *trans*-decalin showed a single strong absorption band at 1448—1452 cm.$^{-1}$ and the *cis*-isomer derivatives showed, in addition, a second strong band of only slightly lower intensity at 1470—1475 cm.$^{-1}$. We now report that 10β-hydroxymethyl-*trans*-1β-decalol (XIV) shows only a single strong absorption band at 1450 cm.$^{-1}$; in view of the close structural similarity between the diol (XIV) and the aforementioned decalols this infrared absorption may be considered as further support for the *trans*-configuration of the decalin portion of the diol (XIV) and, therefore, of the vinyl ether (II) from which the diol has been prepared (see Part II[1]). The infrared spectrum of the vinyl ether (II) contains only a single strong absorption band (at 1451 cm.$^{-1}$) in the region 1450—1475 cm.$^{-1}$ but in this case the trigonal carbon atom (1′) of the 10-substituent provides a structural difference which may be sufficient to prejudice a close comparison with the saturated compounds.

The high-resolution nuclear magnetic resonance spectrum of the pure vinyl ether was determined by Dr. J. Lee. In the region associated with the decalin-hydrogen atoms, it has a single absorption band which is broader than, though otherwise similar to, that of *cis*-decalin and its derivatives.[10] In this respect the spectrum was remarkable since the vinyl ether, whether it has the *cis*- or *trans*-decalin structure, should, as a consequence of the rigidity imposed upon the molecule by the 1,1′-ether bridge, have the fine structure shown by *trans*-decalin, and, presumably, any decalin derivative which has axial and equatorial hydrogen atoms of non-interchangeable conformation.

Further evidence for our view that the vinyl ether (II) is the primary product of the interaction of decalin and a Friedel–Crafts acetylating agent under mild conditions, is our observation that the yield of the vinyl ether was not lowered when the crude reaction mixture, after it had been freed from aluminium chloride and dried, was treated with an excess of lithium aluminium hydride. This result excludes the possibility that the chloro-ketone (V; Y = Cl) or the hydroxy-ketone (X) is first formed and provides the vinyl ether (II) on distillation, since only the vinyl ether resists reduction with lithium aluminium hydride. It is therefore probable that the vinyl ether, in some protonated form such as (III), is present in the reaction mixture before the latter is decomposed on ice during the usual isolation procedure.[1] A reaction mechanism for the formation of the vinyl ether (II) from decalin has already been proposed;[11] it involves the addition of acetyl cation across the double bond of 9,10-octalin and ring expansion of the resulting 4-membered

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[9] Hardegger and Montavon, *Helv. Chim. Acta*, 1946, **29**, 1129.

[10] Musher and Richards, *Proc. Chem. Soc.*, 1958, 230.

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

heterocycle. It is of interest that a cyclic oxonium salt with a 4-membered ring has been proposed [12] as an intermediate in the Friedel–Crafts acylation of cyclo-octatetraene.

EXPERIMENTAL

Attempted Reaction of the Vinyl Ether (II) *with Methylmagnesium Iodide and with Lithium Aluminium Hydride–Cobalt Chloride.*—(*a*) The vinyl ether (5·0 g.) in ether (30 ml.) was added to the Grignard reagent obtained from methyl iodide (6·2 ml.) and magnesium (2·4 g.) in ether (40 ml.). The mixture was refluxed for 3 hr. and the unchanged vinyl ether (4 g.) was subsequently recovered.

(*b*) The vinyl ether (40 g.), previously purified by means of lithium aluminium hydride,[1] in ether (50 ml.) was added to lithium aluminium hydride (6·0 g.) in ether (200 ml.) containing anhydrous cobalt chloride (50 mg.). The mixture was refluxed with stirring for 20 hr. with the addition of cobalt chloride (30 mg.) at 3-hourly intervals. The vinyl ether (>35 g.) was subsequently recovered; no other definite product was isolated.

10β-*Acetyl*-trans-1α-*decalol* * (V; Y = OH).—A mixture of the vinyl ether (4·7 g.) and 2N-sulphuric acid (90 ml.) was refluxed for 30 min., cooled, and extracted with ether. The ether extract was dried (K_2CO_3) and distilled and gave, together with lower-boiling material (2·4 g.), the required *compound* (1·4 g.), b. p. 150—158°/17 mm., which crystallised from light petroleum in needles, m. p. 56—57° (Found: C, 73·3; H, 10·3. $C_{12}H_{20}O_2$ requires C, 73·5; H, 10·2%). Its infrared absorption spectrum (CCl_4 solution) showed, apart from an intense band at 1704 cm.$^{-1}$ (C=O), two weak bands at 3636 and 3484 cm.$^{-1}$; of these weak bands the former increased and the latter decreased in intensity with dilution and they are therefore ascribed to free and intermolecularly hydrogen-bonded hydroxyl groups respectively. The compound gave a p-*nitrobenzoate*, prisms (from ethanol), m. p. 122—124° (Found: C, 66·3; H, 7·0; N, 4·6. $C_{19}H_{23}NO_5$ requires C, 66·1; H, 6·7; N, 4·1%), and a 3,5-*dinitrobenzoate*, needles (from methanol), m. p. 171—172° (Found: C, 58·0; H, 5·8; N, 7·2. $C_{19}H_{22}N_2O_7$ requires C, 58·4; H, 5·6; N, 7·2%), and with chromium trioxide in pyridine gave 10-acetyl-1-decalone,[1] m. p. and mixed m. p. 67—69°.

Dehydration of 10β-*Acetyl*-trans-1β-*decalol* [1] *with Phosphorus Oxychloride in Pyridine.*—These compounds (10·0 g., 25 ml., and 100 ml. respectively) were heated together at 115° for 1 hr. and gave 10-acetyl-$\Delta^{1(9)}$-octalin [3] (6·6 g.), b. p. 114—116°/8 mm. (Found: C, 81·2; H, 10·0. Calc. for $C_{12}H_{18}O$: C, 80·9; H, 10·1%), which was identified (*a*) by its infrared absorption spectrum, (*b*) by its semicarbazone, m. p. and mixed m. p. 216°: (in Part I the m. p. was wrongly reported as 254°), and (*c*) by reduction to 10-1′-hydroxyethyl-$\Delta^{1(9)}$-octalin [3] (Found: C, 80·0; H, 11·1. Calc. for $C_{12}H_{20}O$: C, 80·0; H, 11·1%) which was identified by its infrared absorption spectrum and its α-naphthylurethane, m. p. and mixed m. p. 143—145° (reported in Part I as 136°).

Derivatives of 10β-*Acetyl*-trans-1β-*decalol.*—(*a*) A solution of the vinyl ether (0·95 g.), hydroxylamine hydrochloride (2·5 g.) and potassium hydroxide (1·0 g.) in ethanol (15 ml.) and water (10 ml.) was heated on the steam-bath for 15 min. and provided the required *oxime* as plates (1·1 g.), m. p. 198—199° (Found: C, 68·2; H, 9·9; N, 6·4. $C_{12}H_{21}NO_2$ requires C, 68·2; H, 10·0; N, 6·6%). This oxime (0·75 g.) was also obtained from the vinyl ether (0·95 g.) and anhydrous hydroxylamine hydrochloride (2·3 g.) in dry pyridine (5 ml.), and from the vinyl ether (0·95 g.), hydroxylamine hydrochloride (2·5 g.), and fused sodium acetate (2·9 g.) in absolute ethanol (20 ml.).

(*b*) The *semicarbazone* (9·5 g.) was obtained from a mixture of the vinyl ether (9·0 g.), semicarbazide hydrochloride (10·0 g.) and sodium acetate (15 g.) in ethanol (50 ml.) and water (50 ml.) on the steam-bath (30 min.). It recrystallised from ethanol in needles, m. p. 232—233° (Found: C, 62·2; H, 8·9; N, 16·4. $C_{13}H_{23}N_3O_2$ requires C, 61·7; H, 9·1; N, 16·6%).

(*c*) The *phenylhydrazone* was obtained from the vinyl ether and phenylhydrazine in glacial acetic acid and separated from light petroleum–methanol in needles, m. p. 186—188° (Found: C, 75·4; H, 9·2; N, 10·2. $C_{18}H_{26}N_2O$ requires C, 75·5; H, 9·2; N, 9·8%).

When heated at 240° for 10 min. the semicarbazone (0·50 g.) gave the vinyl ether (0·22 g.). Hydrolysis of the semicarbazone (20 g.) with 0·1N-sulphuric acid gave the vinyl ether (6·0 g.).

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* See footnote on p. 3828.

[12] Cope, Liss, and Smith, *J. Amer. Chem. Soc.*, 1957, **79**, 240.

Hydrolysis of the oxime with 2N-sulphuric acid gave the vinyl ether and 10β-acetyl-*trans*-1α-decalol. The oxime (12·5 g.) in polyphosphoric acid (300 g.) at 110° (15 min.) gave the *oxazine* (XIII) (5·1 g.), b. p. 113—116°/16 mm., n_D^{20} 1·5022 (Found: C, 74·0; H, 10·0; N, 7·2. $C_{12}H_{19}NO$ requires C, 74·6; H, 9·8; N, 7·2%), soluble in 2N-hydrochloric acid from which it was liberated by an excess of ammonia; it did not combine with toluene-*p*-sulphonyl chloride in pyridine; it gave a weak carbylamine reaction; in carbon tetrachloride it absorbed strongly at 1664 and 1377 cm.$^{-1}$ and gave no evidence for the presence of an OH or NH group; it contained 0·4 methyl group (Kuhn–Roth); its *hydrochloride* was precipitated from diethyl ether as a white powder, m. p. 232° (Found: C, 63·2; H, 8·9; N, 6·4; Cl, 15·7. $C_{12}H_{20}ClNO$ requires C, 62·8; H, 8·7; N, 6·1; Cl, 15·5%); and its *picrate* separated from ethanol in yellow needles, m. p. 158—159° (Found: C, 51·2; H, 5·2; N, 13·5. $C_{18}H_{22}N_4O_8$ requires C, 51·2; H, 5·2 N, 13·3%).

The oxime in an excess of acetyl chloride on the steam-bath gave a *diacetyl derivative*, rectangular prisms (from light petroleum), m. p. 75° (Found: C, 64·5; H, 8·4; N, 4·5. $C_{16}H_{25}NO_4$ requires C, 65·1; H, 8·5; N, 4·7%).

With excess of toluene-*p*-sulphonyl chloride in acetone over potassium carbonate, the oxime gave only a *monotoluene*-p-*sulphonate*, needles (from acetone), m. p. 169—171° (Found: C, 62·7; H, 7·8; S, 7·7. $C_{19}H_{27}NO_4S$ requires C, 62·5; H, 7·4; S, 8·8%). The oxime (2·4 g.) and acetic anhydride (3 ml.) in pyridine (3 ml.) gave a *monoacetyl derivative* (2·0 g.), needles (from light petroleum), m. p. 116—118° (Found: C, 66·4; H, 9·2; N, 5·3. $C_{14}H_{23}NO_3$ requires C, 66·4; H, 9·1; N, 5·5%). After several days at room temperature, a mixture of the monoacetate (1·01 g.) and chromium trioxide (1·2 g.) in pyridine (15 ml.) gave the *keto-oxime acetate* (0·45 g.) which separated from light petroleum in plates, m. p. 94—96° (Found: C, 67·1; H, 8·2; N, 5·8. $C_{14}H_{21}NO_3$ requires C, 66·9; H, 8·4; N, 5·6%). The monoacetate (0·6 g.) with phosphorus oxychloride (6 ml.) in pyridine (24 ml.) at 100° (3 hr.) gave an oil which, with ethanolic sodium hydroxide, gave *10-acetyl-*$\Delta^{1(9)}$*-octalin oxime*, m. p. and mixed m. p. 122—124° (0·4 g.) (Found: C, 74·4; H, 9·9; N, 7·2. $C_{12}H_{19}NO$ requires C, 74·6; H, 9·8; N, 7·2%); 10-acetyl-$\Delta^{1(9)}$-octalin does not readily give the oxime.

A mixture of the vinyl ether (10·0 g.) and *p*-nitrobenzoic acid (10·0 g.) was slowly heated to 170° and kept at this temperature for 25 min. The acid slowly dissolved to give a green solution which gradually became brown. On cooling, the mixture solidified and was shaken with diethyl ether (500 ml.) and saturated sodium hydrogen carbonate solution. The organic layer was separated, washed with water, and dried ($MgSO_4$). Volatilisation of the solvent gave a solid which was washed with light petroleum and recrystallised from ethanol (charcoal). 10β-Acetyl-*trans*-1α-decalyl *p*-nitrobenzoate (11·0 g.) was obtained as prisms, m. p. 117—118°. The 3,5-dinitrobenzoate, similarly prepared, formed needles, m. p. 171—172°, from methanol. Hydrolysis of these esters with sodium hydroxide in 50% aqueous ethanol gave 10β-acetyl-*trans*-1α-decalol, m. p. and mixed m. p. 56—57°.

10β-*Acetyl*-1α-*chloro*-trans-*decalin* (V; Y = Cl).—The vinyl ether (10 ml.) was vigorously shaken with concentrated hydrochloric acid (75 ml.) for 15 min. The organic layer was separated with light petroleum, washed with iced water, and dried ($MgSO_4$). Distillation gave fractions, (i) b. p. 126—140°/12 mm. (2·0 g.) and (ii) b. p. 140—150°/12 mm. (7·0 g.), n_D^{24} 1·5055 (Found: C, 68·4; H, 9·0; Cl, 15·0. Calc. for $C_{12}H_{19}ClO$: C, 67·1; H, 8·9; Cl, 16·6%). The latter product is the required chloro-ketone containing 10% of the vinyl ether. Its infrared absorption spectrum has strong absorption bands at 1704 (C=O), 743 (equatorial C–Cl),[8] and 1667, 1000, and 790 cm.$^{-1}$ (vinyl ether).

1,1′-*Epoxy*-10β-*ethyl*-trans-*decalin* (I).—The above chloro-ketone (9·0 g.) in tetrahydrofuran (50 ml.) was gradually added to lithium aluminium hydride (3·0 g.) in tetrahydrofuran (100 ml.); after the initial vigorous reaction, the mixture was refluxed with stirring for 10 hr. The excess of hydride was destroyed by ethyl acetate (25 ml.), and ice-cold 2N-sulphuric acid (150 ml.) was added to the cooled mixture. The ether extracts were washed with water and dried (K_2CO_3). Distillation gave an oil (6·0 g.), b. p. 116—122°/10 mm., n_D^{25} 1·4940, which was heated with sodium (0·5 g.) at 140° for 3 hr. Redistillation gave the *oxide* (I) (4·5 g.), b. p. 114—115°/10 mm., $n_D^{23·5}$ 1·4944, as an oil of camphor-like odour (Found: C, 79·8; H, 11·1. $C_{12}H_{20}O$ requires C, 80·0; H, 11·1%). It did not decolorise bromine in carbon tetrachloride and has strong infrared absorption bands at 1110, 1087, 1063, and 1000 cm.$^{-1}$.

10β-*Acetyl*-1α-*bromo*-trans-*decalin* (V; Y = Br).—The vinyl ether (9·5 g.) was gradually added to 60% hydrobromic acid (30 ml.) at 0° and the mixture was shaken. A solid separated which was collected in light petroleum, washed with water, and dried (Na_2SO_4). The *bromo-ketone* (13·5 g.) separated from light petroleum (b. p. <40°; 20 ml.) in prisms, m. p. 39—41° (Found: C, 55·5; H, 7·4; Br, 30·8. $C_{12}H_{19}BrO$ requires C, 55·6; H, 7·3; Br, 30·9%); it has strong infrared absorption bands at 1709 (C=O) and 699 cm.$^{-1}$ (C–Br).

10β-*Acetyl*-1α-*methoxy*-trans-*decalin* (V; Y = OMe).—The vinyl ether (5·0 g.) was refluxed in methanol (50 ml.) containing concentrated sulphuric acid (1 drop) for 90 min., then potassium carbonate (1 g.) was added. Filtration, evaporation, and addition of water gave the required *methoxy-ketone* (6·0 g.), m. p. 51—56°, which separated from light petroleum in plates, m. p. 58·5—60° (Found: C, 74·7; H, 10·8. $C_{13}H_{22}O_2$ requires C, 74·3; H, 10·5%), $\nu_{max.}$ 1706 (C=O), 1127, and 1093 cm.$^{-1}$.

The corresponding *ethoxy-ketone* (V; Y = OEt) was similarly obtained as an oil, b. p. 136—138°/6 mm. (Found: C, 75·2; H, 10·8. $C_{14}H_{24}O_2$ requires C, 75·0; H, 10·7%), $\nu_{max.}$ 1706 (C=O), 1110, and 1087 cm.$^{-1}$.

10β-*Acetyl*-1α-*benzylthio*-trans-*decalin* (V; Y = S·CH$_2$Ph).—The vinyl ether (9 g.), toluene-α-thiol (7 g.), and ZeoKarb 225 (acid-exchange resin) (0·5 g.) were heated together for 1·5 hr. at 100°. There was no apparent reaction and concentrated hydrochloric acid (0·1 ml.) was added. After several weeks at room temperature, the mixture was shaken with ether (250 ml.) and 2N-sodium hydroxide (150 ml.). The ether layer gave the required *sulphide* (11 g.), b. p. 245—250°/15 mm. (Found: C, 75·7; H, 8·6; S, 10·9. $C_{19}H_{26}OS$ requires C, 75·5; H, 8·6; S, 10·6%). When the vinyl ether (9 g.) and toluene-α-thiol (7 g.) in ethanol (25 ml.) containing concentrated sulphuric acid (4 drops) were heated on the steam-bath for 2 hr., 10β-acetyl-1α-ethoxy-*trans*-decalin (V; Y = OEt) was the major product.

S-(10β-*Acetyl*-trans-1α-*decalyl*)*thiouronium Toluene*-p-*sulphonate* [V; Y = $S{\cdot}C(NH_2){:}NH_2^+C_7H_7{\cdot}SO_3^-$].—Toluene-*p*-sulphonic acid monohydrate (9·5 g.) was gradually added to a hot solution of the vinyl ether (8·9 g.) and thiourea (3·8 g.) in ethanol (50 ml.). Each addition of the acid gave a greenish-yellow colour which was allowed to disappear before a further addition was made. A pale yellow colour persisted at the end of the addition and the solution was heated for a further hour on the steam-bath. The required *thiouronium salt* (13·0 g.) slowly separated from the cold mixture and concentration of the mother-liquor gave a further 6·1 g. as colourless prisms, m. p. 192—193° (Found: C, 56·3; H, 7·2; N, 6·8. $C_{20}H_{30}N_2O_4S_2$ requires C, 56·3; H, 7·0; N, 6·6%). With *S*-benzylthiouronium chloride in aqueous ethanol it readily gave *S*-benzylthiouronium toluene-*p*-sulphonate, m. p. and mixed m. p. 181—182°. With an alcoholic solution of picric acid it gave the *picrate* as yellow needles, m. p. 182—183° (Found: N, 14·2. $C_{19}H_{25}N_5O_8S$ requires N, 14·5%). The picrate was obtained in lower yield when picric acid in ethanol was added to a mixture of the vinyl ether, thiourea, and oxalic or acetic acid in ethanol which had been heated on the steam-bath for 3 hr.

10-Acetyl-$\Delta^{1(9)}$-octalin (1·0 g.) and thiourea (0·45 g.) in boiling ethanol (12 ml.) gave no colour on addition of toluene-*p*-sulphonic acid monohydrate (1·0 g.). A yellow colour slowly developed and deepened as heating was continued for 1 hr. but the decalylthiouronium picrate was not isolated on addition of picric acid.

Desulphurisation. (*a*) A solution of the thiouronium toluene-*p*-sulphonate (4·0 g.) in ethanol (160 ml.) was refluxed with Raney nickel (*ca.* 10 g.) for 3—4 hr. The mixture was filtered and ethanol was removed under reduced pressure. The residue was dissolved in ether, dried ($MgSO_4$), and distilled. An oil, b. p. 128—132°/19 mm., n_D^{24} 1·4980, was obtained which, like 9-acetyl-*trans*-decalin, did not form a semicarbazone and was reduced by lithium aluminium hydride to 9-1′-hydroxyethyl-*trans*-decalin [3] (α-naphthylurethane, m. p. and mixed m. p. 162° [3]). (*b*) The toluene-*p*-sulphonate (6·0 g.), ethanol (50 ml.), and 5N-sodium hydroxide (300 ml.) were stirred together while powdered 1 : 1 nickel–aluminium alloy (25 g.) was added during 2 hr. An oil of camphor-like odour tended to separate from solution and coat the powdered alloy; it was kept in solution by further additions of ethanol. The mixture was stirred for a further 2 hr. and worked up in the conventional way; it gave 9-acetyl-*trans*-decalin (2·0 g.), b. p. 110°/9 mm., n_D^{22} 1·4916, which was identified as described above and by its infrared absorption spectrum.

The toluene-*p*-sulphonate (43 g.) with 100% hydrazine hydrate (14 ml.) and sodium hydroxide (6 g.) in diethylene glycol (50 ml.) was heated for 1·5 hr. at 100° and then for 6 hr. as the temperature was raised to 210°. When the evolution of ammonia was complete, the mixture was cooled, acidified with concentrated hydrochloric acid, and extracted with ether.

Distillation of the dried extract gave an oil (1·5 g.), b. p. 158°/10 mm., which is probably 10β-*acetyl*-1α-*mercapto*-trans-*decalin* (V; Y = SH) (Found: C, 67·9; H, 9·7; S, 14·9. $C_{12}H_{20}OS$ requires C, 67·9; H, 9·4; S, 15·1%). It is soluble in alkali and has a strong infrared absorption band at 1706 cm.$^{-1}$ (C=O) and bands of medium intensity at 2680 and 2570 cm.$^{-1}$ (S–H). The same compound (1·5 g.) was obtained when the toluene-*p*-sulphonate (4·1 g.) was treated with potassium borohydride (0·5 g.) in water (5 ml.) containing 2N-sodium hydroxide (2 drops).

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