916. *The Isomerisation and Dehydration of Some Decalin Derivatives. The Formation of* 10-*Acetyl*-trans-$\Delta^{1(2)}$-*octalin*

By R. J. EMARTON and J. W. RASBURN

The acid-catalysed isomerisation of 1β,1′-epoxy-10β-vinyl-*trans*-decalin (II) is shown to produce *ca.* 12% of 10-acetyl-*trans*-$\Delta^{1(2)}$-octalin (V) in addition to the main product, 10-acetyl-$\Delta^{1(9)}$-octalin (I), reported earlier.[1] Both ketones are produced also by dehydration of the hydroxy-ketones (IV) and (VI) under acidic conditions, and by the interaction of decalin and Friedel–Crafts acetylating agent; these reactions afford (V) in excess of (I) unless the conditions allow the isomerisation of (V) to (I). Procedures to obtain (I) free from (V), and (V) free from (I), are described.

THE formation of 10-acetyl-$\Delta^{1(9)}$-octalin (I) by the acid-catalysed isomerisation of 1β,1′-epoxy-10β-vinyl-*trans*-decalin (II) and, along with 10β-acetyl-*trans*-2β-decalol (III), by the action of Friedel–Crafts acetylating agent on the vinyl ether (II), has been reported.[1] The unsaturated ketone (I) was prepared also [1] by the dehydration of 10β-acetyl-*trans*-1β-decalol (IV) with phosphorus oxychloride in pyridine. The possibility that 10-acetyl-*trans*-$\Delta^{1(2)}$-octalin (V) may also be a product of these reactions was considered, but no evidence of its formation was obtained. Re-investigation and, in particular, the application of gas–liquid chromatography (g.l.c.) to the products of these and related reactions has now shown not only that the ketone (V) is produced in many cases but that it may be the major product in certain circumstances.

Acid-catalysed isomerisation of the vinyl ether (II) was effected by heating at 160° with *ca.* 1—2% by weight of toluene-*p*-sulphonic acid monohydrate. This procedure (see Experimental section), although mentioned and employed previously,[1,2] has not been described. The isomerisation product has now been shown (g.l.c.) to contain two components in the ratio 88 : 12. This composition was essentially unchanged ($\not>$1%) after repeating the treatment with acid catalyst. Identification of the major component, which

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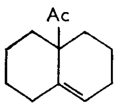
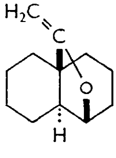
[1] G. Baddeley, B. G. Heaton, and J. W. Rasburn, *J.*, 1960, 4713; 1961, 3828, 3835.

[2] G. Baddeley, E. K. Baylis, B. G. Heaton, and J. W. Rasburn, *Proc. Chem. Soc.*, 1961, 451.

had the shorter retention time, as the $\Delta^{1(9)}$-ketone (I), *i.e.*, the product reported previously,[1,2] was as follows.

The major product of acid isomerisation of (II) was identical (g.l.c., relative retention time) with the single compound obtained by dehydration of (IV) with phosphorus oxychloride in pyridine (*ca.* 10% of a much lower boiling substance, with a much lower retention time, is here disregarded in the dehydration product). Confirmation, if required, of the identity of these two products is that each gave, in at least 80% yield, the same oxime; the latter has been described,[1] with other supporting evidence, as the oxime of the $\Delta^{1(9)}$-ketone (I). Further evidence of the structure of the product of acid isomerisation of (II) has been obtained [3] by use of unsaturated ketone purified through its semicarbazone and hence presumably free from the $\Delta^{1(2)}$-isomer (compare below).


(I)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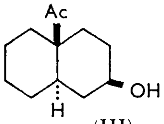
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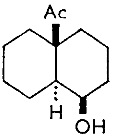
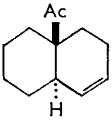
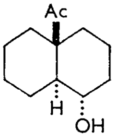
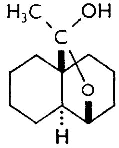

(IV)


(V)


(VI)


(VII)

Identification of the minor product of acid isomerisation of (II) as the $\Delta^{1(2)}$-ketone (V) was on the following evidence.

(1) Prolonged treatment of the total isomerisation product with hydroxylamine almost entirely removed the $\Delta^{1(9)}$-ketone (I) as its oxime, and the recovered oil was greatly enriched (84% or better) in the minor product of isomerisation of (II). Dreiding models show clearly that the approach of reagent to the carbonyl group should be more difficult with (V) than with (I) or with any other isomer with a *trans*-fused ring junction. That the ring junction in the minor product is *trans*-fused was shown by the formation of 9-acetyl-*trans*-decalin, identified as previously,[1] on catalytic hydrogenation of the oil recovered from the oximation procedure. With lithium aluminium hydride the same oil gave two stereoisomeric unsaturated alcohols, neither of which gave the 1-naphthylurethane previously reported [1] from the same procedure applied to the $\Delta^{1(9)}$-ketone.

(2) Dehydration of the hydroxy-ketone (VI) with phosphorus oxychloride in pyridine gave the vinyl ether (II) (92% by g.l.c.) and the compound (8%) now under chief discussion. The formation even of such a small amount of the latter, and the complete absence of the $\Delta^{1(9)}$-ketone (I), provides strong support for the location of the 1,2-double bond, *i.e.*, that the compound is the $\Delta^{1(2)}$-ketone (V). The formation of vinyl ether (II) from (VI) further illustrates the participation of the acetyl group as with the 10-acetyl-1α-halogeno-decalins.[2]

Having failed to obtain (V) other than as a minor reaction product, we studied the acid-catalysed dehydration of (IV) and of (VI). Distillation of (VI) from toluene-*p*-sulphonic acid (*ca.* 1—2%) gave a mixture of (I) and (V) in the ratio 34 : 66. Similar treatment of (IV) gave three products, a mixture of (I), (II), and (V) in the ratio 26 : 25 : 49. The formation of vinyl ether (II) under these acidic conditions probably occurs through the hemiketal (VII) which may be expected from (IV) but not from (VI). In the reverse process, *i.e.*, the acid hydrolysis of an alkyl vinyl ether, Kiprianova and Rekasheva [4] showed, by use of $H_2{}^{18}O$, that the alkyl–oxygen bond is not broken. Since the ratio of (I) to (V) is almost identical in each case, *i.e.*, 1 : 1·94 from (VI) and 1 : 1·88 from (IV), and since (II) can be

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[3] G. Baddeley and E. K. Baylis, personal communication.

[4] L. A. Kiprianova and A. F. Rekasheva, *Doklady Akad. Nauk S.S.S.R.*, 1962, **142**, 589.

distilled without change from the acid catalyst, the formation of (I) and (V) probably occurs through a common intermediate, *e.g.*, the simple C-1 carbonium ion; neither (II) nor its protonated form is apparently involved.

Evidence that the isomerisation (V) $\rightleftharpoons$ (I) may also occur in these acid-catalysed reactions was provided by the isolation of (I) and (V) in the ratio 67 : 33 from the treatment of (VI) with acid catalyst at 160° for 1 hr. before distillation. Confirmation followed our further observation that a mixture of (I) and (V) in the ratio 46 : 54 gave, by the same treatment but including *ca.* 10% of water, a mixture in the ratio 89 : 11, *i.e.*, identical with that from acid isomerisation of (II). No isomerisation occurred, however, in the absence of the added water, thus accounting for the non-equilibration of the products of many earlier experiments.

We have also re-examined the unsaturated ketone (*ca.* 5%) which accompanies the vinyl ether (II) when the latter is prepared in the usual way.[1] Gas–liquid chromatography again established the presence of (V) and that the ratio of (I) to (V) is approximately 1 : 4. The large excess of (V) in this case again suggests that an intermediate other than (II) is involved; this may be chloro-ketone which is present (*ca.* 5%) in the undistilled reaction product. Initial experiments[5] on the dehydrohalogenation of 10β-acetyl-1α-chloro-*trans*-decalin[1] have indicated that the main product is (II), accompanied by (V) and a smaller amount of (I).

EXPERIMENTAL

Gas–liquid chromatography was performed on a Pye Argon Chromatograph using a column composed of 4% Apiezon L on Celite at *ca.* 110°. Relative retention times (r.r.t.) were calculated from that (30 min.) of the vinyl ether (II).

Isomerisation of the Vinyl Ether (II) *with Toluene*-p-*sulphonic Acid.*—The vinyl ether (II),[1] b. p. 103—106°/8 mm. (25 g.), and toluene-*p*-sulphonic acid monohydrate (0·5 g.) were heated in an oil-bath at 160° for 1 hr. The product (22 g.), b. p. 112—114°/8 mm., n_D^{23} 1·5034, was isolated by distillation from the acid catalyst; it had strong infrared bands at 3030, 2866, 2836, 1709, 1661, 1444, 1348, 1211*, 1149, 1130, 1088*, 934*, 862*, 809* cm.$^{-1}$. Those marked (*) were absent or very small in the spectrum of the $\Delta^{1(2)}$-ketone. G.l.c. showed a trace (≯1%) of the vinyl ether (retention time 30 min.) and two other components (r.r.t. 1·25 and 1·38) in the (approximate) ratio 88 : 12. The major component (r.r.t. 1·25) was identified as the $\Delta^{1(9)}$-ketone (I), and the minor component (12%) as the $\Delta^{1(2)}$-isomer (V). The vinyl ether (II) was recovered unchanged when distilled, without prior heating at 160°, from the acid catalyst (1—2% by weight).

Reaction of the Mixed Ketones (I) *and* (V) *with Hydroxylamine. Isolation of* 10-*Acetyl*-trans-$\Delta^{1(2)}$-*octalin* (V).—The product (30 g.) from the acid isomerisation of (II) was refluxed for 40 hr. with a solution of hydroxylamine hydrochloride (60 g.) and sodium hydroxide (24 g.) in ethanol (150 ml.) and water (150 ml.). After cooling, the oxime of (I) (26·35 g.), m. p. 122—124°, was collected by filtration, and the filtrate and washings were extracted with ether. The dried ether extract gave an oil (*ca.* 4 g.), b. p. 114—124°/8 mm., $n_D^{22\cdot5}$ 1·5040, which g.l.c. showed to contain the same two components as the starting material but in the ratio 16 : 84 (cf. 88 : 12 before oximation). This product was used in the reduction processes (see below), and is shown, by evidence presented here, to consist largely (84%) of the $\Delta^{1(2)}$-*ketone* (V) (Found: C, 80·2; H, 10·0. $C_{12}H_{18}O$ requires C, 80·9; H, 10·1%). The infrared spectrum showed bands at 3008, 2866, 2836, 1709, 1667, 1444, 1359*, 1348, 1233, 1190*, 1156, 1136, 1112*, 1099*, 1019*, 952*, 917*, 744*, 680*. Those marked (*) were absent or very weak in the spectrum of the $\Delta^{1(9)}$-ketone.

Although further treatment of the above product with hydroxylamine reagent gave no more oxime, the $\Delta^{1(2)}$-ketone (V) was obtained almost pure, with not more than *ca.* 1% of the $\Delta^{1(9)}$-isomer (I), by increasing the refluxing period to 120 hr. The oxime isolated after 40 hr. represents 92% of the $\Delta^{1(9)}$-ketone originally present.

Reduction of 10β-*Acetyl*-trans-$\Delta^{1(2)}$-*octalin.*—(*a*) The $\Delta^{1(2)}$-ketone (84% by g.l.c.) (3·0 g.) was smoothly hydrogenated at room temperature and pressure in absolute ethanol (40 ml.) containing Adams catalyst (0·05 g.). The product (2·5 g.), b. p. 100—110°/8 mm., n_D^{23} 1·4914,

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[5] R. J. Emarton and J. W. Rasburn, unpublished work.

had an infrared spectrum identical with that of 9-acetyl-*trans*-decalin,[1] and, on reduction with lithium aluminium hydride, gave an alcohol, b. p. 118—126°/8 mm., n_D^{22} 1·5053, which gave the 1-naphthylurethane, m. p. and mixed m. p. 162°, of 9-1′-hydroxyethyl-*trans*-decalin.[1]

(*b*) The $\Delta^{1(2)}$-ketone (3·0 g.), in ether (25 ml.), was added slowly with stirring to lithium aluminium hydride (0·6 g.) in ether (50 ml.). After refluxing (3 hr.), the excess of hydride was destroyed with ethyl acetate in ether and an excess (50 ml.) of dilute hydrochloric acid (2N) was added. The ethereal layer was separated, washed, and dried, and gave an oil (1·99 g.), b. p. 123—130°/9 mm., $n_D^{23\cdot5}$ 1·5115, $\nu_{max.}$ bands at 3571, 3000, 2866, 2836, 1449, 1362, 1269, 1190, 1139, 1124, 1044, 1019, 917. The alcohol (1 g.), with 1-naphthyl isocyanate (1 g.) at 100° for 5 min., gave a mixture of two 1-*naphthylurethanes*, m. p. 135—150°, which were separated by crystallisation from light petroleum (b. p. 40—60°) containing *ca.* 10% of ethyl acetate, into colourless crystals, m. p. 155—157° (Found: N, 4·31. $C_{23}H_{27}NO_2$ requires N, 4·01%), and colourless crystals, m. p. 135—138° (Found: N, 4·20. $C_{23}H_{27}NO_2$ requires N, 4·01%). The m. p. of each form was depressed on admixture with the other and also with the 1-naphthylurethane, m. p. 143—145°, of 10-1′-hydroxyethyl-$\Delta^{1(9)}$-octalin.[1]

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