114. *Photoisomerisation of Eucarvone to* 1,5,5-*Trimethylnorborn-2-en-7-one.*

By J. J. Hurst and G. H. Whitham.

Irradiation of a solution of eucarvone (I) in aqueous acetic acid has given the bridged ketone (II). Evidence for the structure of the latter is presented and some of its reactions are described.[1]

In a study of the effect of solvent on the outcome of the photochemical reactions of eucarvone (I), which will be reported later, we have encountered a photoisomerisation to 1,5,5-trimethylnorborn-2-en-7-one (II). Since this appears to be the first example of the direct conversion of a cycloheptane derivative into a norbornane derivative * we are reporting on this aspect of the work separately.

Irradiation of a solution of eucarvone in aqueous acetic acid with sunlight resulted in the formation of two photoisomers in approximately equal amounts. One of these, 1,4,4-trimethylbicyclo[3,2,0]hept-6-en-2-one (III), has already been obtained and identified by Büchi and Burgess.[3] The other photoisomer is shown in the ensuing discussion to be 1,5,5-trimethylnorborn-2-en-7-one (II).

The bridged ketone (II) had $\nu_{\max.}$ (in CCl_4) at 1782 cm.$^{-1}$ consistent with either a cyclobutanone or a highly strained cyclopentanone. Other infrared bands (in CCl_4) at 3050 and (in CS_2) at 792, 737, and 690 cm.$^{-1}$ indicated a *cis*-disubstituted double bond. The presence of one double bond, and therefore a bicyclic structure, was confirmed by the uptake of one mol. of hydrogen in the presence of palladium–carbon with formation of a saturated ketone (IV), $\nu_{\max.}$ (in CS_2) 1770 cm.$^{-1}$. Other results suggestive of the norbornan-7-one structure for (II) were (*a*) the mass spectrum, which showed the highest peak at *m*/*e* 122, *i.e.*, indicative of the loss of carbon monoxide (see below), and (*b*) failure of attempted deuteration by sodium methoxide in dioxan–deuterium oxide.

Structure (II) for this photoisomer of eucarvone was shown by the following degradation. Reduction with lithium aluminium hydride gave a single alcohol (V) (for configuration see below) which could be oxidised back to the parent ketone. The alcohol (V) with perbenzoic acid gave an epoxy-alcohol assigned structure (VI) since *exo*-attack is the normal course of reaction of perbenzoic acid with unhindered norbornenes.[4] The epoxy-alcohol (VI) was stable to lithium aluminium hydride in tetrahydrofuran under reflux, but the epoxide ring was cleaved by lithium in ethylamine giving a mixture of two crystalline glycols (VII) and (VIII) separable by chromatography. The latter were oxidised in turn to the corresponding diketones (IX) and (XII), each possessing infrared bands at 1780 and 1735 cm.$^{-1}$. Treatment of the β-diketones (IX) and (XII) with potassium hydroxide in methanol resulted in cleavage to the keto-acids (XI) and (XIV) respectively. Cleavage in this direction would be expected as a consequence of addition of hydroxide ion to the more reactive highly strained carbonyl group as shown in (X) and (XIII). The keto-acids (XI) and (XIV) had infrared bands at 1717 (ketone C=O) and 1702 cm.$^{-1}$ (CO_2H); the corresponding methyl esters absorbed at 1735 (CO_2Me) and 1715 cm.$^{-1}$ (ketone C=O). Since neither of these acids exhibited selective ultraviolet absorption the position of the ketone-carbonyl band in the infrared spectrum is only compatible with a cyclohexanone or acyclic ketone. The nuclear magnetic resonance spectra of the keto-acids (see Experimental section) indicated the absence of both olefinic protons and

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* The reverse process is known, *e.g.*, the pyrolytic conversion of norbornadiene into cycloheptatriene.[2]

[1] Preliminary communication: Hurst and Whitham, *Proc. Chem. Soc.*, 1961, 116.

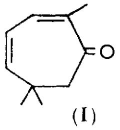
[2] Woods, *J. Org. Chem.*, 1958, **23**, 110.

[3] Büchi and Burgess, *J. Amer. Chem. Soc.*, 1960, **82**, 4333.

[4] Walborsky and Loncrini, *J. Amer. Chem. Soc.*, 1954, **76**, 5396.

methyl groups attached to a double bond. These acids must, therefore, be trimethyloxocyclohexanecarboxylic acids. Finally, acid (XIV) was identified as 1,3,3-trimethyl-5-oxocyclohexanecarboxylic acid by comparison with an authentic sample obtained on hydrolysis of the known methyl ester.[5] The structures already assigned to the bridged ketone (II) and the intermediate products then follow by working back from acid (XIV).

Further proof of structure (II) for the eucarvone photoisomer was obtained by pyrolysis at 450°. Under these conditions the carbonyl group was lost, presumably as carbon monoxide (cf. mass spectrum), with the formation of a mixture of 1,5,5- and 3,5,5-trimethylcyclohexa-1,3-diene.[6] Pines and Kozlowski [6] have shown that pyrolysis of either of these two hydrocarbons results in a mixture of the two. Norbornen-7-ones are known to be readily decarbonylated.[7]



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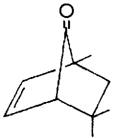

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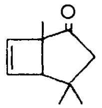

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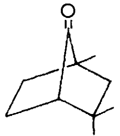

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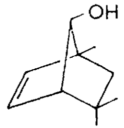

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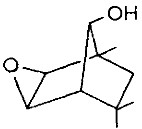

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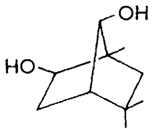

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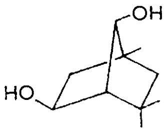

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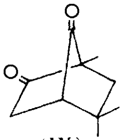

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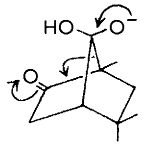

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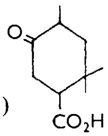

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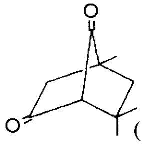

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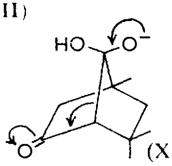

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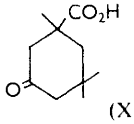

(XIV)

The ultraviolet spectrum of bridged ketone (II) is of interest. It shows $\lambda_{max.}$ (in EtOH) 270 mμ (ε 58) for the $n \longrightarrow \pi^*$ transition while at lower wavelengths it shows only ill-defined absorption rising to ε 3000 at *ca.* 200 mμ. This spectrum conflicts with statements in the literature [8] that 7-norbornenones show distinct charge-transfer bands in the region 220—230 mμ. The absence of solvent-sensitive bands in the low-wavelength region of the spectrum of bridged ketone (II) has been confirmed by Dr. R. Orloski (U.C.L.A.).[9] He has also re-examined the spectrum of pure norbornen-7-one and shown it to be very similar to that of our ketone (II), thereby removing the discrepancy. Apparently, therefore, βγ-unsaturated ketones of this structural type show *neither* charge transfer *nor* enhanced $n \longrightarrow \pi^*$ absorption.[8]

As already mentioned, reduction of the bridged ketone (II) with lithium aluminium hydride gave a single alcohol to which structure (V) was assigned. When reduction was carried out with sodium in alcohol a mixture of two alcohols was obtained. One of these, eluted first on chromatography, was identical with that obtained by means of lithium aluminium hydride; the other was shown to be the 7-epimer since it regenerated the parent ketone (II) on oxidation. Apparently attack by hydride on compound (II) occurred from the less hindered side, away from the steric influence of the 5-*exo*-methyl group, giving the *anti*-alcohol † (V) with the more highly hindered hydroxyl group. The

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† *anti* here defines the relationship of the hydroxyl group to the double bond.

[5] Whitmore and Roberts, *J. Org. Chem.*, 1948, **13**, 31.

[6] Pines and Kozlowski, *J. Amer. Chem. Soc.*, 1956, **78**, 3776.

[7] Cookson, Hudec, and Williams, *Tetrahedron Letters*, 1960, **22**, 29.

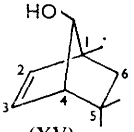
[8] Winstein, De Vries, and Orloski, *J. Amer. Chem. Soc.*, 1961, **83**, 2020; Cookson and Hudec, *J.*, 1962, 429.

[9] Orloski, personal communication.

formation of considerable quantities of the less hindered *syn*-alcohol (XV) on reduction of ketone (II) with sodium in alcohol is an example of a familiar principle.

Some preliminary results on the solvolyses of the methanesulphonates of the epimeric alcohols (V) and (XV) confirm the configurations assigned. The methanesulphonate of the *anti*-alcohol (V) underwent solvolysis in buffered aqueous acetic acid to give a mixture of the *anti*-alcohol (V) and its acetate. Solvolysis has thus proceeded by attack of water or acetic acid with retention of configuration. Unfortunately the methanesulphonate of the *anti*-alcohol (V) was not obtained sufficiently pure for a determination of the rate of solvolysis; however, under the conditions which resulted in its complete solvolysis, the methanesulphonate of the *syn*-alcohol (XV) was recovered unchanged in high yield.

There is thus an appreciable difference in the rates of these solvolyses, and the results may be compared with those obtained by Winstein *et al.*[10,11] for the epimeric 7-norbornenyl toluene-*p*-sulphonates. The rate of acetolysis of *anti*-7-norbornenyl toluene-*p*-sulphonate (XVI) is about 10^7 times faster than that of the *syn*-epimer (XVII); the enhanced rate of the former is interpreted as involving participation by the π-electrons of the double bond in the expulsion of toluene-*p*-sulphonate ion, giving a "non-classical" carbonium ion intermediate (XVIII). The latter reacts stereospecifically with the solvent, acetic acid, to form *anti*-7-norbornenyl acetate (XIX). Our results on the trimethylnorbornenyl system, though less complete, thus parallel those obtained on the parent skeleton. In particular the retention of configuration in the solvolysis of the methanesulphonate of the *anti*-alcohol (V) is noteworthy. Thus attack of solvent from the side *anti* to the double bond has occurred even though this side should be highly hindered by the 5-*exo*-methyl [cf. reduction of ketone (II) by lithium aluminium hydride]. This result clearly shows the effectiveness of the double bond as a neighbouring group.



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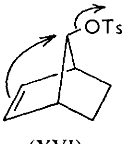

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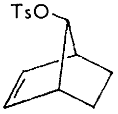

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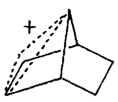

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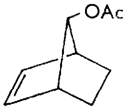

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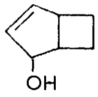

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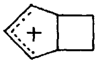

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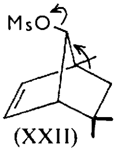
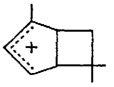


(XXII)



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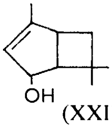

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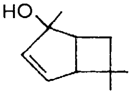

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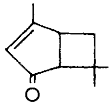

(XXVI)

Ts = p-$C_6H_4Me{\cdot}SO_2$; Ms = $Me{\cdot}SO_2$.

Winstein and Stafford[11] obtained the rearranged allylic alcohol (XX) as sole product from a preparative hydrolysis of *syn*-norbornenyl toluene-*p*-sulphonate (XVII). The allylic carbonium ion (XXI) was considered to be an intermediate in this reaction. With the methanesulphonate of our *syn*-alcohol (XV) different products should result on hydrolysis depending on whether the 1,6- or the 4,5-bond migrates. We have only investigated this hydrolysis in a preliminary fashion and have obtained a mixture of at least four alcohols. Treatment of this mixture with manganese dioxide resulted in oxidation to an unsaturated ketone, whose properties [$\nu_{max.}$ (liquid film) 1700 and 1616 cm.$^{-1}$, $\lambda_{max.}$ (in EtOH) 237 mμ (ε 8000)] indicate a conjugated cyclopentenone with at least one substituent attached to the double bond. It appears likely, therefore, that the unsaturated ketone is largely (XXVI) produced by (XXII) ⟶ (XXIII) ⟶ (XXIV) and/or (XXV) ⟶ (XXVI), though these results will require confirmation. Apparently migration of the 1,6-bond is preferred to that of the 4,5-bond, *i.e.*, the transition state

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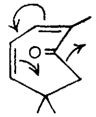
[10] Winstein, Shatavsky, Norton, and Woodward, *J. Amer. Chem. Soc.*, 1955, **77**, 4183.
[11] Winstein and Stafford, *J. Amer. Chem. Soc.*, 1957, **79**, 505.

leading to the tertiary carbonium ion (XXIII) is of lower energy than that involving migration of the more highly alkylated 4,5-bond.

It remains to consider the possible basis for the photochemical conversion of eucarvone into the bridged ketone (II) in aqueous acetic acid. First, we note that the bicyclic ketone (III) was not converted into the bridged ketone (II) on irradiation in aqueous acetic acid under conditions which lead to the formation of (II) from eucarvone. Thus ketone (III) is not an intermediate in the formation of (II), nor is it in photochemical equilibrium ‡ with eucarvone.

Formally the photoisomerisation of eucarvone into the bridged ketone (II) can be represented schematically as a bond-switching process (XXVII) $\longrightarrow$ (XXVIII); however, this gives no help in understanding the role of solvent in determining the product. Apparently it is acidity which is the important factor since 1% sulphuric acid in dioxan-water is about as effective as aqueous acetic acid in promoting the formation of ketone (II) from eucarvone.[12] It is, therefore, possible that a protonated $\pi \longrightarrow \pi^*$ excited state is involved in the reaction. A crude representation of such an intermediate (XXIX) shows how collapse could give the conjugate acid (XXX) of the bridged ketone (II). Formation of the latter might be a consequence of stabilisation of the positively charged C-7 through overlap of the vacant *p*-orbital by the π-orbital of the double bond [cf. the intermediate ion (XVIII) in the solvolyses].



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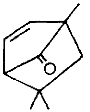

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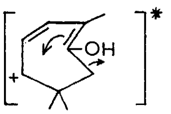

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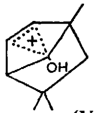

(XXX)

EXPERIMENTAL

Light petroleum refers to the fraction of b. p. 40—60°.

Irradiation of Eucarvone in Aqueous Acetic Acid.—Eucarvone (26 g.) in acetic acid–water (4 : 6; 1 l.) in a closed Pyrex tube was irradiated in sunlight for 4 weeks. The solution was poured into water and extracted with ether. After being washed with aqueous sodium carbonate and drying, the ethereal solution was evaporated and distilled through a helices-packed column to give a mixture of photo-products (12·6 g.) containing no eucarvone. The mixture in light petroleum was chromatographed on a column of alumina (activity I; 500 g.), giving fractions: (i) eluted with light petroleum–ether (99·5 : 0·5), 1,5,5-*trimethylnorborn*-2-*en*-7-*one* (II) (1·73 g.), b. p. 68—70°/12 mm., $\nu_{\text{max.}}$ (in CCl_4) 3050, 2950, 2860, 1782, 1455, 1385, 1372, 1122, 792 (CS_2), 737 (CS_2), 690 (CS_2) cm.$^{-1}$ (Found: C, 80·0; H, 9·75. $C_{10}H_{14}O$ requires C, 79·95; H, 9·4%); (ii) eluted with light petroleum–ether (99 : 1), slightly impure ketone (II) (0·7 g.); (iii) eluted with light petroleum–ether (99 : 1 to 80 : 20), a mixture of ketone (II) and ketone (III) (6·55 g.); (iv) eluted with ether, 1,4,4-trimethylbicyclo[3,2,0]hept-6-en-2-one (III) (1·81 g.), b. p. 65—67·5°/7 mm., n_D^{13} 1·4642 (Found: C, 80·0; H, 9·6. Calc. for $C_{10}H_{14}O$: C, 79·95; H, 9·4%) [2,4-dinitrophenylhydrazone, m. p. 163—165° (decomp.); *semicarbazone* m. p. 215—218° (from ethanol) (Found: C, 63·6; H, 8·05. $C_{11}H_{17}N_3O$ requires C, 63·75; H, 8·25%)]. Büchi and Burgess [3] give b. p. 95—96°/45 mm., n_D^{25} 1·4562, and 2,4-dinitrophenylhydrazone, m. p. 161·5—162·5°.

Attempted Deuterium Exchange on 1,5,5-*Trimethyl*-2-*norbornen*-7-*one*.—Dry sodium methoxide (0·48 g.), deuterium oxide (2 ml.), dry dioxan (10 ml.), and the ketone (260 mg.) were heated under reflux for 2 hr. After addition of dry light petroleum, the organic layer was separated and evaporated and the residue was distilled. The mass spectrum and infrared spectrum of the distillate were identical with that of starting material.

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‡ Such an equilibrium would strongly favour the bicyclic ketone (III) with the weakly absorbing chromophore.

[12] Hurst and Whitham, unpublished work.

1,5,5-*Trimethylnorbornan*-7-*one*.—1,5,5-Trimethylnorborn-2-en-7-one (0·538 g.) was hydrogenated over prereduced palladised charcoal (10 mg.) in ethanol. Hydrogen (1·05 mol.) was absorbed. After filtration and evaporation the residue was distilled, giving the *ketone*, b. p. 80–81°/15 mm., $\lambda_{max.}$ (in EtOH) 282 mμ (ε 34), $\nu_{max.}$ (in CS_2) 2960, 2860, 1770, 1380, 1368, 1103, 1048 cm.$^{-1}$ (Found: C, 78·3; H, 10·6. $C_{10}H_{16}O$ requires C, 78·90; H, 10·60%). The 2,4-dinitrophenylhydrazone had m. p. 169—171° (from ethanol).

anti-1,5,5-*Trimethylnorborn*-2-*en*-7-*ol*.—1,5,5-Trimethylnorborn-2-en-7-one (0·8 g.) was reduced with lithium aluminium hydride (0·4 g.) in dry ether (20 ml.). After addition of water and dilute sulphuric acid the product was isolated with ether. Distillation gave the *alcohol* (0·6 g.), b. p. 88—90°/15 mm., $\nu_{max.}$ (in CS_2) 3610, 3050, 2930, 2860, 1375, 1362, 1086, 1067, 1054, 718 cm.$^{-1}$ (Found: C, 79·0; H, 11·05. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%). The 3,5-dinitrobenzoate had m. p. 132—134·5° (from ethanol).

exo-2,3-*Epoxy*-anti-1,5,5-*trimethylnorbornan*-7-*ol* (VI).—*anti*-1,5,5-Trimethylnorborn-2-en-7-ol (3 g.) was treated with ethereal perbenzoic acid (1·5 mol.) for 16 hr. The ether layer was washed with aqueous sodium carbonate, dried, and evaporated, giving the epoxide (VI), m. p. 69—71°, $\nu_{max.}$ (in CS_2) 3590, 3030, 2990, 2930, 2840, 1377, 1363, 1125, 1090, 977, 864, 850 cm.$^{-1}$.

Lithium–Ethylamine Reduction of the Epoxide (VI).—The epoxide (VI) (3·2 g.) in dry ethylamine (50 ml.) was treated with small pieces of lithium (1 g.), and the mixture was shaken until the blue colour persisted for 15 min. The excess of lithium was filtered off and water was added to the filtrate. After ether-extraction the upper layer was washed with aqueous hydrochloric acid and water. Evaporation of the dried extract gave a viscous liquid (2·56 g.) which solidified. A further 0·36 g. was obtained by continuous extraction of the aqueous layer with ether.

The above glycol mixture (2·45 g.) in light petroleum–ether (1 : 3) was chromatographed on alumina (activity III; 120 g.). Elution with the same solvent gave the fractions: (i) (0·38 g.) oil, probably glycols derived from a small amount of *endo*-epoxide; (ii) (1·25 g.) m. p. 60—80°; (iii) (0·22 g.) m. p. 130—135° after softening at 80°; (iv) (0·53 g.) m. p. 138—139°. Fractions (ii) and (iii) were combined and rechromatographed, giving two fractions (v) 1·18 g., m. p. 60—80°, and (vi) 0·25 g., m. p. 132—136°. Recrystallisation of fraction (v) from light petroleum–ether gave 1,5,5-*trimethylnorbornane*-2(exo),7(anti)-*diol* (VII), (0·75 g.), m. p. 64—66° (Found: C, 67·05; H, 10·65. $C_{10}H_{18}O_2,\frac{1}{2}H_2O$ requires C, 67·0; H, 10·7%). Recrystallisation of fractions (iv) and (vi) from light petroleum–ether gave 1,5,5-*trimethylnorbornane*-3(exo),7-(anti)-*diol* (VIII) (0·47 g.), m. p. 139—140° (Found: C, 70·30; H, 10·70. $C_{10}H_{18}O_2$ requires C, 70·55; H, 10·65%).

1,5,5-*Trimethylnorbornane*-2,7-*dione*.—The glycol (VII) (0·75 g.) in "AnalaR" acetone (25 ml.) was treated with 6N-chromic acid [13] (4 ml., 1·3 mol.) with cooling and stirring. After a further 30 min., water was added and the neutral fraction was isolated with ether as a yellow oil (0·53 g.). Distillation gave the *diketone*, b. p. 110—115°/12 mm., $\nu_{max.}$ (in CCl_4) 2920, 2830, 1780, 1732, 1445, 1407, 1387, 1380, 1368, 1340, 1290, 1195, 1155, 1100, 1057, 1025, 925, 875 cm.$^{-1}$ (Found: C, 72·05; H, 8·55. $C_{10}H_{14}O_2$ requires C, 72·25; H, 8·5%).

1,5,5-*Trimethylnorbornane*-3,7-*dione*.—The glycol (VIII) (0·47 g.) was oxidised as for the glycol (VII), giving a yellow oil (0·33 g.) which solidified. Recrystallisation from light petroleum gave the *diketone*, m. p. 74—75·5°, $\nu_{max.}$ (in CCl_4) 2960, 2870, 1785, 1740, 1460, 1408, 1395, 1387, 1377, 1262, 1227, 1220, 1195, 1162, 1145, 1117, 1080, 1025, 895 cm.$^{-1}$ (Found: C, 71·9; H, 8·35%).

2,2,4-*Trimethyl*-5-*oxocyclohexanecarboxylic Acid*.—1,5,5-Trimethylnorbornane-2,7-dione (0·38 g.) was refluxed with 5% methanolic potassium hydroxide (10 ml.) for 1 hr. After evaporation of most of the methanol, water was added and the acid fraction was isolated with ether as an oil (0·37 g.). Trituration with light petroleum followed by recrystallisation from light petroleum–ether gave the *acid*, m. p. 101—104° (ε 300 at 200 mμ) (Found: C, 65·2; H, 8·5. $C_{10}H_{16}O_3$ requires C, 65·2; H, 8·75%). The nuclear magnetic resonance spectrum (in CCl_4) was complex and showed five peaks in the $CH_3{\cdot}C$ region (8·64—9·06 p.p.m.) which may be due to the presence of two geometrical isomers.

1,3,3-*Trimethyl*-5-*oxocyclohexanecarboxylic Acid*.—(*a*) 1,5,5-Trimethylnorbornane-3,7-dione (169 mg.) was treated with 10% methanolic potassium hydroxide (2 ml.) at 20° for 1 hr. Water was added and the neutral fraction (88 mg.) was isolated with ether. The acid fraction

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[13] Heilbron, Jones, and Sondheimer, *J.*, 1949, 604.

(89 mg.) solidified. The neutral material was recycled to give a further quantity of acid (59 mg.; in all, 148 mg.). After recrystallisation from light petroleum–ether the *acid* had m. p. 121—122·5° (ε 282 at 200 mμ) (Found: C, 65·3; H, 8·75. $C_{10}H_{16}O_3$ requires C, 65·2; H, 8·75%). The methyl ester prepared by using diazomethane had infrared carbonyl bands at 1735 (CO_2Me) and 1715 (C=O of ketone) cm.$^{-1}$. The nuclear magnetic resonance spectrum (in benzene) showed the following peaks: 9·25 and 9·22, doublet (*gem*-dimethyl), 8·97 (1-Me), 8·66 and 8·12, intensity ratio 1 : 2 (protons on C-2, C-4, and C-6, respectively), 0·97 p.p.m. (CO_2H proton). The signals due to the methylene groups are sharp so there must be a rapid interconversion between the two chair conformations.

(*b*) Addition of cyanide to isophorone and methanolysis of the resulting nitrile to methyl 1,3,3-trimethyl-5-oxocyclohexanecarboxylate was carried out essentially as described by Whitmore and Roberts.[5] The infrared spectrum was identical with that obtained as under (*a*). The methyl ester (0·49 g.) was hydrolysed by a 10% solution of potassium hydroxide in boiling butan-1-ol (10 ml.). The acid fraction solidified and after two recrystallisations from light petroleum–ether had m. p. 121·5—124° undepressed on admixture with the acid obtained as under (*a*). The infrared and nuclear magnetic resonance spectra of the two samples were identical.

Pyrolysis of 1,5,5-*Trimethylnorborn*-2-*en*-7-*one.*—The ketone (II) (500 mg.) was added dropwise to the top of a column of silica chips heated to 460° in a stream of nitrogen. The pyrolysate was collected in a trap cooled in solid carbon dioxide–acetone. Distillation of the pyrolysate gave a mixture of 1,5,5- and 3,5,5-trimethylcyclohexa-1,3-diene, b. p. 132—135°/750 mm., $\lambda_{max.}$ (in EtOH) 261 mμ (ε 3870), $\nu_{max.}$ (liquid) 1660, 1590, 1470, 1445, 1400, 1375, 1360, 875, 820, 808, 727 cm.$^{-1}$. The infrared and ultraviolet spectra were identical with those reported by Pines and Kozlowski[6] for a mixture of 1,5,5- and 3,5,5-trimethylcyclohexa-1,3-diene.

Reduction of 1,5,5-*Trimethylnorborn*-2-*en*-7-*one with Sodium in Ethanol.*—The ketone (1·35 g.) in absolute ethanol (25 ml.) was heated under reflux and small pieces of sodium (3·0 g.) were added to the solution. After a further 20 minutes' refluxing the product was isolated by dilution with water and extraction with ether. The resulting alcohol mixture (1·28 g.) in light petroleum (5 ml.) was chromatographed on alumina (activity III; 60 g.). Elution with light petroleum–ether (99 : 1 to 98 : 2) gave *anti*-1,5,5-trimethylnorborn-2-en-7-ol (0·4 g.) identical with that obtained previously. After an intermediate fraction (0·17 g.), containing mixed isomers, further elution with light petroleum–ether (95 : 5 to 4 : 1) gave syn-1,5,5-*trimethylnorborn*-2-*en*-7-*ol* (0·68 g.), b. p. 66—68°/12 mm., $\nu_{max.}$ (in CS_2) 3550, 3050, 2940, 2850, 1377, 1365, 1345, 1277, 1210, 1145, 1116, 1065, 1058, 820, 724 cm.$^{-1}$ (Found: C, 79·05; H, 10·7. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%). The 3,5-*dinitrobenzoate*, plates (from ethanol), had m. p. 154—156° (Found: N, 7·95. $C_{17}H_{18}N_2O_6$ requires N, 8·1%).

Preparation and Solvolysis of the Methanesulphonate of anti-1,5,5-*Trimethylnorborn*-2-*en*-7-*ol.*—The alcohol (100 mg.) in dry pyridine (2 ml.) was treated with methanesulphonyl chloride (0·4 g., 5 mol.), and the mixture was set aside at 20° for 3 days. The mixture darkened and solid separated. Ice was added and the mixture set aside for 30 min. then poured into cold dilute hydrochloric acid, and the product was isolated with ether as a yellow oil (40 mg.), $\nu_{max.}$ (in CS_2) 3080, 2960, 2870, 1368, 1340, 1284, 1180, 952, 868, 816, 780, 702 cm.$^{-1}$. The crude methanesulphonate was heated under reflux with water (1·5 ml.), acetic acid (1·5 ml.), and sodium dihydrogen phosphate (1 g.) during 1 hr. The product, isolated with ether, had infrared bands characteristic of *anti*-1,5,5-trimethylnorborn-2-en-7-ol, together with bands ascribable to its acetate (notably $\nu_{max.}$ 1740 and 1240 cm.$^{-1}$). To confirm this, the solvolysis product was hydrolysed with 10% methanolic potassium hydroxide. Isolation with ether gave material (20 mg.) which had an infrared spectrum identical with that of *anti*-1,5,5-trimethyl-2-nornornen-7-ol.

Methanesulphonate of syn-1,5,5-*Trimethylnorborn*-2-*en*-7-*ol.*—The alcohol (220 mg.) in dry pyridine (4 ml.) and methanesulphonyl chloride (0·86 g.) was set aside at 20° for 16 hr. The solution was worked up as before, giving an oil (0·35 g.) which solidified; recrystallisation from light petroleum gave the *methanesulphonate*, m. p. 57—60°, $\nu_{max.}$ (in CS_2) 3050, 2930, 2840, 1365, 1345, 1178, 957, 887, 830, 713 cm.$^{-1}$ (Found: C, 57·1; H, 7·85. $C_{11}H_{18}O_3S$ requires C, 57·4; H, 7·9%).

The methanesulphonate remained unchanged under the conditions which resulted in complete solvolysis of its epimer.

Hydrolysis of the Methanesulphonate of syn-*Alcohol* (XV).—The methanesulphonate (0·22 g.) in 0·2N-aqueous sodium hydrogen carbonate (20 ml.) was heated under reflux for 4 hr. Isolation with ether gave an oil (0·12 g.) which showed hydroxyl bands in the infrared spectrum and gave one main spot together with three minor spots on thin-layer chromatography. Oxidation in light petroleum (30 ml.) by shaking the oil with manganese dioxide (10 g.) for 1 hr. gave an oil which showed $\nu_{max.}$ (liquid) 1700 and 1620 cm.$^{-1}$ and had $\lambda_{max.}$ (in EtOH) 237 mμ (ε 7500).

Irradiation of Bicyclic Ketone (III) *in Aqueous Acetic Acid.*—The ketone (100 mg.) in aqueous acetic acid was irradiated in a Pyrex tube in sunlight for a week. The product, isolated with ether, showed no band at 1780 cm.$^{-1}$ typical of the bridged ketone (II). A control experiment carried out simultaneously with eucarvone showed the formation of bridged ketone (II) and bicyclic ketone (III) in approximately equal amounts.

Nuclear Magnetic Resonance.—Spectra were measured on a Mullard instrument at 32 megacycles/sec. with tetramethylsilane as internal reference. Peak positions are quoted as τ values.

We thank Professor M. Stacey, F.R.S., for encouragement, Dr. L. F. Thomas for nuclear magnetic resonance data, and Dr. R. Orloski (Los Angeles) for communicating his results to us before their publication. One of us (J. J. H.) thanks the University of Birmingham for a Research Scholarship.

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[*Received, August 22nd*, 1962.]