48. *Bridged Ring Systems. Part III.*[1] *Homoallylic Alcohols of the Bicyclo*[3,3,1]*nonane Series.*

By J. MARTIN, W. PARKER, and R. A. RAPHAEL.

Synthetic routes are described to 1,5-dimethylbicyclo[3,3,1]non-2-en-9-one (III) and the related epimeric homoallylic alcohols (I) and (II).

NEIGHBOURING-GROUP participation in the reactions of homoallylic alcohols has been demonstrated for a variety of systems.[2] In particular, the much faster acetolysis [3] of *anti*-7-norbornenyl toluene-*p*-sulphonate than of the 7-norbornyl ester indicated the extent to which a neighbouring double bond can provide anchimeric assistance when the geometry of the system allows maximum overlap of the π-electrons of the double bond with the developing *p*-orbital at the reacting site. Our interest in allied bridged ring systems led to a parallel investigation of the homoallylic *syn*- and *anti*-1,5-dimethylbicyclo[3,3,1]non-2-en-9-ols (I) and (II) (*syn* and *anti* relate the hydroxyl group to the double bond).

As precursor to these alcohols we chose the corresponding ketone (III) and in the first attempt to prepare it employed Cope and Synerholm's method.[4] Alkylation of 2,6-dimethylcyclohexanone with 3-chloro-1,1-diethoxypropane gave a low yield of 3-(1,3-dimethyl-2-oxocyclohexyl)propionaldehyde diethyl acetal (IV); this was treated with hydrochloric acid in dioxan, affording the bicyclic ketol as its two epimers (V; R = H) and a considerable quantity of the corresponding ethyl ether (V; R = Et). Formation of the ether is rationalised in terms of the accepted mechanism [5] for acetal hydrolysis if we assume that reaction of the positively charged intermediate (VI) follows the mechanism shown rather than the normal route to the keto-aldehyde and thence by aldolisation to the bicyclic ketol (V; R = H). Various attempts to dehydrate this ketol proved unpromising. Drastic procedures gave intractable polymers, and milder techniques [6] produced deep-seated rearrangements,[1] and only a small yield of the required ketone (III) was obtained.

In another approach, ethyl 2-ethoxy-1,3-dimethyl-2-oxocyclohexanecarboxylate was cyanoethylated,[7] and the product was hydrolysed and decarboxylated to give the keto-acid (VII), but attempted cyclisation of this product and its ester to the bicyclic diketone

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[1] Part I, Murray, Parker, and Raphael, *Tetrahedron*, 1961, **16**, 74; Part II, Murray, Parker, Raphael, and (in part) Jhaveri, *ibid.*, 1962, **18**, 55.

[2] Streitwieser, *Chem. Rev.*, 1956, **56**, 571; Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co. Inc., New York, p. 598.

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

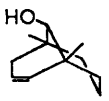
[4] Cope and Synerholm, *J. Amer. Chem. Soc.*, 1950, **72**, 5228.

[5] O'Gorman and Lucas, *J. Amer. Chem. Soc.*, 1950, **72**, 5489.

[6] O'Connor and Nace, *J. Amer. Chem. Soc.*, 1955, **77**, 1578.

[7] Woodward, Sondheimer, Taub, Heusler, and McLamore, *J. Amer. Chem. Soc.*, 1952, **74**, 4243.

(VIII) in acidic[8] or basic conditions failed. However, treatment of the keto-acid with acetic anhydride or oxalyl chloride produced the crystalline enol-lactone (IX) which, by low-temperature reduction with lithium hydridotri-t-butoxyaluminate[9] gave the required



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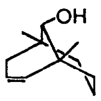

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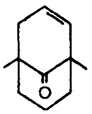

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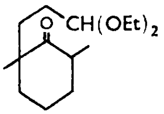

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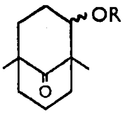

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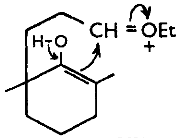

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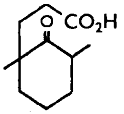

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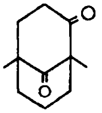

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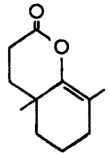

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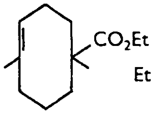

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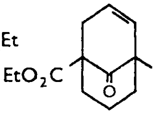
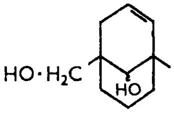


(XI)



(XII)

bicyclic ketol (V; R = H) directly in excellent yield as an epimeric mixture (the proportion of epimers produced can be controlled by adjusting the pH during working up.) Separation of the two epimers was difficult and tedious but their toluene-*p*-sulphonates were readily separated by fractional crystallisation. The lower-melting ester was quantitatively converted into the monocyclic cyclo-octane derivative (X) by reaction with sodium ethoxide,[10] but similar treatment converted the higher-melting ester smoothly into the desired 1,5-dimethylbicyclo[3,3,1]non-2-en-9-one (III).

Although this method (which is expected to be general) had produced the required ketone (III) a shorter method for large-scale preparation was developed from the easily accessible ester[1] (XI). The corresponding diol (XII), prepared from this keto-ester by reduction with lithium aluminium hydride, was selectively converted into the primary monotoluene-*p*-sulphonate. Hydrogenolysis[11] of this derivative with lithium aluminium hydride gave a mixture of the epimeric alcohols (I) and (II) which was oxidised in high yield with chromium trioxide[12] to the ketone (III).

Generalisations as to the stereochemistry of carbonyl reduction could not be applied with certainty in the case of the ketone (III); a 9-hydroxyl group in this system, which is axial or equatorial to the cyclohexane ring, is respectively pseudo-equatorial or pseudo-axial to the cyclohexene ring. In the event, reduction by lithium aluminium hydride gave a separable 1 : 3 mixture of *syn*-1,5-dimethylbicyclo[3,3,1]non-2-en-9-ol (I), m. p. 80°, and the *anti*-epimer (II), m. p. 55°, whereas sodium in moist ether gave a 1 : 0·8 proportion of the epimers. That the alcohol of m. p. 80° was the *syn*-epimer (I) was proved by its infra-red spectrum which showed intramolecular π-hydrogen bonding involving the hydroxyl grouping and the double bond; this spectral feature was absent for the isomer (II) of m. p. 55°. Catalytic hydrogenation of both epimers gave 1,5-dimethylbicyclo[3,3,1]-nonan-9-ol.

EXPERIMENTAL

M. p.s were determined on a Kofler block and are corrected. B. p.s are uncorrected. The alumina used for chromatography (Spence's type H) was acid-washed and activated by Brockmann and Schodder's method.[13] Light petroleum refers to the fraction of b. p. 40—60° unless stated otherwise. Ultraviolet absorption spectra refer to ethanol solutions and were measured with a Unicam S.P. 500 spectrophotometer. Infrared absorption spectra were

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[8] Loewenthal, *Proc. Chem. Soc.*, 1960, 355; 1962, 230.

[9] Parham and Huestis, *J. Amer. Chem. Soc.*, 1962, **84**, 813; Brown and Subba Rao, *ibid.*, 1958, **80**, 5377.

[10] Buchanan, McKillop, and Raphael, unpublished results.

[11] Rapaport and Bonner, *J. Amer. Chem. Soc.*, 1951, **73**, 2872.

[12] Bowden, Heilbron, Jones, and Weedon, *J.*, 1946, 39.

[13] Brockmann and Schodder, *Ber.*, 1941, **74**, 73.

measured on a Perkin-Elmer Infracord instrument unless stated otherwise. Nuclear magnetic resonance spectra were measured with an A.E.I. R.S.2 spectrometer operating at 60 Mc./sec. with tetramethylsilane as internal reference. Thin-layer chromatoplates were prepared [14] from Merck's "Kieselgel G." Gas-liquid chromatograms were run on the Pye-Argon Chromatograph.

3-(1,3-*Dimethyl*-2-*oxocyclohexylpropionaldehyde Diethyl Acetal* (IV).—A solution of 2,6-dimethylcyclohexanone (37·8 g.) in dry xylene (50 ml.) was added to a stirred suspension of sodamide (11·7 g.) in xylene (600 ml.) at 30° under nitrogen, and the mixture refluxed until no more ammonia was evolved (*ca.* 12 hr.) and a yellow gelatinous suspension had been formed. A solution of 3-chloropropionaldehyde diethyl acetal (55·0 g.) in dry xylene (100 ml.) was then added in 40 min. and the mixture refluxed for 22 hr. The brown mixture was cooled, washed with saturated brine solution, and dried ($MgSO_4$) and the solvent was removed *in vacuo*. Fractional distillation of the residual oil gave the *acetal* (IV) (9·6 g.), b. p. 90—98°/0·15 mm. A second distillation afforded an analytical sample, b. p. 92—95°/0·15 mm., n_D^{22} 1·4732, $\nu_{max.}$ 1695, 1120, and 1050 cm.$^{-1}$ (Found: C, 70·45; H, 10·1. $C_{15}H_{28}O_3$ requires C, 70·25; H, 11·0%).

The 2,4-*dinitrophenylhydrazone* of the free aldehyde crystallised from ethanol as yellow needles, m. p. 138—140° (Found: C, 56·45; H, 5·85; N, 15·6. $C_{17}H_{22}N_4O_5$ requires C, 56·35; H, 6·1; N, 15·45%).

2-*Hydroxy*-1,5-*dimethylbicyclo*[3,3,1]*nonan*-9-*one* (V; R = H) *and* 2-*Ethoxy*-1,5-*dimethylbicyclo*[3,3,1]*nonan*-9-*one* (V; R = Et).—A solution of the acetal (IV) (55·7 g.) in dioxan (200 ml.) containing 6N-hydrochloric acid (50 ml.) was heated under reflux for 4 hr., cooled, diluted with saturated brine, and evaporated under reduced pressure. The residue was extracted with ether (2 × 100 ml.), the combined extracts were washed with aqueous sodium carbonate solution and water and dried, and the solvent was removed to give a dark brown oil (51 g.). A sample of this oil (22 g.) was adsorbed on silica gel (200 g.) from benzene. Elution with this solvent gave the *ethoxy-ketone* (V; R = Et) (7·5 g.), b. p. 128—133°/15 mm., n_D^{21} 1·4758, $\nu_{max.}$ 1710, 1200, and 980 cm.$^{-1}$ (Found: C, 74·1; H, 10·3. $C_{13}H_{22}O_2$ requires C, 74·25; H, 10·55%).

Further elution with benzene-chloroform (1 : 3) gave the *hydroxy-ketone* (V; R = H) (14·5 g.) as a mixture of epimers m. p. 35—50°, $\nu_{max.}$ (in Nujol) 3500—3350, 1700, 1060—1040, and 980 cm.$^{-1}$ (Found: C, 72·25; H, 9·75. $C_{11}H_{18}O_2$ requires C, 72·50; H, 9·95%).

A solution of the mixed hydroxyketones (3·97 g.) and toluene-*p*-sulphonyl chloride (4·20 g.) in pyridine (10 ml.) was warmed on a steam-bath for 1 hr. and kept at room temperature for 15 hr., then diluted with ethyl acetate (50 ml.) and water (50 ml.). The separated organic layer was washed with dilute hydrochloric acid, saturated sodium carbonate solution, and water, and dried. Removal of solvent gave a pale yellow solid (6·5 g.), m. p. 110—130°, which was fractionally crystallised from benzene-light petroleum. The early crops (1·5 g.) crystallised from ethanol as colourless plates to give one epimeric *toluene*-p-*sulphonate*, m. p. 145—146° (decomp.), $\nu_{max.}$ (in Nujol) 1710, 1350, 1190, 1180, 923, 900, and 875 cm.$^{-1}$ (Found: C, 64·0; H, 7·4. $C_{18}H_{24}O_4S$ requires C, 64·25; H, 7·2%). Later fractions (3·0 g.) crystallised from ethanol to give the second pure epimeric *ester* as colourless plates, m. p. 114—115°, $\nu_{max.}$ (in Nujol) 1710, 1350, 1190, 1180, 943, 870, 840, and 817 cm.$^{-1}$ (Found: C, 64·15; H, 7·2%).

Dehydration of Hydroxy-ketone (V; R = H).—(*a*) *By sulphuric acid.* Ice-cold concentrated sulphuric acid (2 ml.) was added with shaking to the hydroxy-ketone (1·04 g.) and the mixture was kept for 20 hr. at room temperature, then poured on ice, neutralised with aqueous sodium hydrogen carbonate solution, and extracted with ether. The ethereal extracts were washed with water, dried, and evaporated, to give a red glass (0·75 g.).

(*b*) *By boric acid.*[6] The hydroxy-ketone (5·0 g.) and crystalline boric acid (2·5 g.) were heated under reflux at 300—320° for 90 min. The cooled mixture was extracted with ether, and the extract washed with saturated sodium hydrogen carbonate solution, then dried and evaporated to a brown mobile liquid (3·33 g.). This was adsorbed on alumina (300 g.) from light petroleum; elution with the same solvent gave a liquid mixture of aromatic hydrocarbons (0·61 g.), b. p. 85—96°/9 mm., n_D^{22} 1·5230, $\lambda_{max.}$ (in "iso-octane") 251 (ε 1300) and 273 mμ (ε 580), whose infrared spectrum ($\nu_{max.}$ 1600, 850, 800—750, 717 cm.$^{-1}$) was very similar to that of 4-methylindane.[15]

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[14] Heftmann, "Chromatography," Reinhold Publ. Corp., New York, 1961, p. 87.

[15] Entel, Ruof, and Howard, *Analyt. Chem.*, 1953, **25**, 1303.

Further elution with light petroleum gave 1,5-*dimethylbicyclo*[3,3,1]*non-2-en-9-one* (III) (1·05 g.) b. p. 86—87°/9 mm., n_D^{20} 1·4900, a volatile colourless liquid with a strong camphor-like odour. It solidified and crystallised from light petroleum at −70° as prisms, m. p. 25—26°, $\nu_{max.}$ 2930, 1700, 1640, 720, and 695 cm.$^{-1}$, τ 8·96, 8·92, 7·52 (centre of multiplet), and 4·46 (centre of 4 triplets at 4·1, 4·2, 4·64, and 4·8) (Found: C, 80·5; H, 9·8. $C_{11}H_{16}O$ requires C, 80·45; H, 9·85%). The ultraviolet absorption spectrum, $\lambda_{max.}$ (in EtOH) 291 mμ (ε 42), did not exhibit a high extinction coefficient of $n \longrightarrow \pi^*$ absorption[16] characteristic of many ketones with neighbouring double bonds and, in addition, showed no evidence of $\pi \longrightarrow \pi^*$ absorption. The 2,4-dinitrophenylhydrazone could not be prepared under the usual conditions, presumably owing to steric hindrance.

Elution of the column with benzene gave a yellow ketonic product (0·48 g.), b. p. 40—44°/0·06 mm., n_D^{23} 1·4875, $\nu_{max.}$ 1740, 1710, and 1650 cm.$^{-1}$ slightly contaminated with the hydroxy ketone (V; R = H). The 2,4-*dinitrophenylhydrazone* crystallised from ethyl acetate–methanol as orange needles, m. p. 145—146° (Found: C, 59·45; H, 5·95; N, 16·35. $C_{17}H_{20}N_4O_4$ requires C, 59·3; H, 5·85; N, 16·25%).

Elution of the column with chloroform gave a pale yellow oil (0·06 g.), b. p. 54—55°/0·7 mm., n_D^{21} 1·5070 whose 2,4-*dinitrophenylhydrazone* crystallised from ethanol as dark red needles, m. p. 172—174° (Found: C, 59·0; H, 5·75; N, 16·3. $C_{17}H_{20}N_4O_4$ requires C, 59·3; H, 5·85; N, 16·25%). The *semicarbazone* crystallised from ethanol as needles, m. p. 209—211° (decomp.) (Found: C, 65·15; H, 8·5; N, 18·9. $C_{12}H_{19}N_3O$ requires C, 65·1; H, 8·65; N, 19·0%). The manner of formation of this compound, and its physical and chemical properties, are in agreement with its tentative formulation as 2-acetyl-5-methylbicyclo[3,3,0]-oct-1(2)-ene.[1]

Ethyl 3-2′-*Cyanoethyl*-1,3-*dimethyl*-2-*oxocyclohexanecarboxylate*.—Acrylonitrile (8·0 g.) in t-butyl alcohol (20 ml.) was added in 30 min. to a stirred solution of ethyl 1,3-dimethyl-2-oxo-cyclohexanecarboxylate[17] (9·38 g.) and 40% aqueous Triton B (6 g.) in t-butyl alcohol (50 ml.) under nitrogen, and the mixture was warmed at 50—60° for 6 hr. The solution was acidified with dilute hydrochloric acid, the solvent removed under reduced pressure, and the residue extracted with ether (3 × 50 ml.). The combined extracts were washed with saturated sodium carbonate solution and water, then dried, and evaporated to give a brown oil; fractional distillation gave the *keto-nitrile*, b. p. 116—130°/0·2 mm. (8·65 g.). Redistillation afforded a sample, b. p. 129°/0·2 mm., n_D^{21} 1·4730, $\nu_{max.}$ 2210, 1730, and 1700 cm.$^{-1}$ (Found: C, 66·85; H, 8·2; N, 5·55. $C_{14}H_{21}NO_3$ requires C, 66·9; H, 8·4; N, 5·55%).

β-(1,3-*Dimethyl*-2-*oxocyclohexyl*)*propionic Acid* (VII).—The preceding nitrile (1·00 g.) was heated under reflux for 24 hr. in 30% methanolic potassium hydroxide (25 ml.), cooled, and diluted with saturated brine, and an ethereal extract (50 ml.) was rejected. The aqueous alkaline layer was acidified with dilute hydrochloric acid and extracted with ether (2 × 50 ml.), and the combined ethereal extracts were washed with saturated brine solution and dried, and the solvent was removed, to give the *keto-acid* (VII) (0·72 g.) which crystallised from ethyl acetate–light petroleum as an epimeric mixture in colourless prisms, m. p. 84—88°, $\nu_{max.}$ (in Nujol) 1700—1695, (superimposed C=O), 1300, 1210, 1000, 950—930, 860, 770, 745 cm.$^{-1}$ (Found: C, 66·85; H, 9·05. $C_{11}H_{18}O_3$ requires C, 66·65; H, 9·15%). Repeated recrystallisation from light petroleum (b. p. 60—80°) gave what appeared to be a single epimer, m. p. 93—94°. Treatment of the keto-acid with diazomethane in ether gave the *methyl ester*, b. p. 100°/0·06 mm., n_D^{24} 1·4625, $\nu_{max.}$ 1735, 1700, 1200, 1170, 1005, and 860 cm.$^{-1}$ (Found: C, 67·65; H, 9·3. $C_{12}H_{20}O_3$ requires C, 67·9; H, 9·5%).

Attempted Cyclisation of the Acid (VII).—(*a*) Boron trifluoride–ether complex (0·2 ml.) was heated with the acid (VII) (0·5 g.) in acetic acid (2 ml.) containing acetic anhydride (0·05 ml.) at 100° for 3 hr., set aside at room temperature for 12 hr., and poured into an excess of sodium hydrogen carbonate solution. The neutral ether extract contained no product; acidification of the alkaline aqueous solution and extraction furnished only starting material.

(*b*) A solution of the methyl ester of acid (VII) (0·87 g.) in anhydrous ethanol (20 ml.) was added in 30 min. to a stirred solution of sodium (0·09 g.) in ethanol (30 ml.) at room temperature under nitrogen. The mixture was heated under reflux for 18 hr., cooled, neutralised with dilute hydrochloric acid, and evaporated under reduced pressure. The residue was extracted

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[16] McKenzie, Saila, and Shappy, *J. Org. Chem.*, 1963, **28**, 548, and references cited therein.
[17] Haworth and Barker, *J.*, 1939, 1301.

with ether, the extract washed with brine, and the solvent removed, leaving unchanged starting material.

The Enol-lactone (IX).—(*a*) The acid (VII) (0·28 g.) and acetic anhydride (2·0 ml.) were heated under reflux for 2 hr., anhydrous sodium acetate was added (10 mg.), and heating continued for an additional 2 hr. Acetic anhydride was removed under reduced pressure and the residue diluted with saturated brine solution and extracted with ether (2 × 10 ml.). The combined ethereal extracts were washed with saturated sodium hydrogen carbonate solution and brine and dried. Removal of the solvent gave the *enol-lactone* (IX) (0·26 g.) which recrystallised from light petroleum as hexagonal prisms, m. p. 47—48°, $\nu_{max.}$ 1740, 1680, 1250, 1190, 1165, 1150, 1120—1100, and 1010 cm.$^{-1}$ (Found: C, 73·55; H, 8·75. $C_{11}H_{16}O_2$ requires C, 73·3; H, 8·95%).

(*b*) Oxalyl chloride (25 g.) was added to a solution of the keto-acid (VII) (18·0 g.) in dry benzene (250 ml.), and the mixture kept at 0° for 10 hr. The solvent and excess of reagent were removed under reduced pressure at room temperature, and the residue distilled to give a colourless liquid (10 g.), b. p. 98—100°/0·2 mm., which solidified and crystallised as in (*a*) to give prisms, m. p. 47—48° undepressed on admixture with the product from (*a*).

Reduction of the Enol-lactone (IX).—A suspension of lithium hydridotri-t-butoxyaluminate was prepared by adding dry t-butyl alcohol (16·6 g.) in dry tetrahydrofuran (50 ml.) to a suspension of lithium aluminium hydride (2·58 g.) in tetrahydrofuran (50 ml.). It was added in 30 min. to a stirred solution of the enol-lactone (IX) (9·0 g.) in tetrahydrofuran (30 ml.) at −70°. The mixture was allowed to reach room temperature (1 hr.), then poured into ice-cold saturated brine (100 ml.). The inorganic insoluble matter was removed by filtration through Celite 535, and the filtrate extracted with ether (5 × 30 ml.). The combined ethereal extracts were washed with saturated brine and dried and the solvent was removed to give a colourless, viscous oil (8·3 g.) showing absorption in the infrared identical with that of the hydroxy-ketone (V; R = H) obtained as described above. Thin-layer chromatograms of this product and the hydroxy-ketone (V; R = H) were identical, both showing separation of two epimers. A specimen of the crude product was heated with toluene-*p*-sulphonyl chloride in pyridine, as described for the hydroxy-ketone (V; R = H). Two crystalline esters, m. p. 145—146° and 114—115°, respectively, were separated by fractional crystallisation, and these were identical with the epimeric toluene-*p*-sulphonates obtained from (V; R = H) (m. p., mixed m. p., infrared spectra).

When the reduction mixture was worked up with dilute hydrochloric acid, crystals were obtained which seemed to consist substantially of one epimer of the hydroxy-ketone (V; R = H) as it gave only the toluene-*p*-sulphonate of m. p. 145—146°, in high yield. Crystallisation of this product from benzene–light petroleum gave a pure *epimer* (V; R = H) as prisms m. p. 73—75°, τ = 9·1, 9·01, 8·15, 6·65, and 6·02 (Found: C, 72·25; H, 9·75. $C_{11}H_{18}O_2$ requires C, 72·5; H, 9·95%).

1,5-*Dimethylbicyclo*[3,3,1]*non-2-en-9-one* (III).—A solution from sodium (1·06 g.) and dry ethanol (30 ml.) was added in 5 min. to a stirred suspension of the toluene-*p*-sulphonate of m. p. 145—146° (12·9 g.) in dry ethanol (100 ml.), and the mixture was refluxed for 20 hr., then cooled, neutralised with acetic acid, diluted with water (200 ml.), and extracted with light petroleum (3 × 100 ml.). The combined petroleum extracts were washed with saturated sodium hydrogen carbonate solution and saturated brine, and dried. Removal of solvent gave a yellow oil (5·93 g.) which was adsorbed on neutral Woelm alumina (100 g.) from light petroleum. Elution with light petroleum–ether (20 : 1) gave the ketone (III) (5·6 g.), m. p. 25—26° identical with the compound obtained as described above.

Ethyl 1,5-*Dimethylcyclo-oct-4-ene-1-carboxylate* (X).—A solution from sodium (0·19 g.) and ethanol (5 ml.) was added to a solution of the toluene-*p*-sulphonate, m. p. 114—115° (1·97 g.), in ethanol (5 ml.) at 60°. Immediate precipitation of sodium toluene-*p*-sulphonate occurred. The mixture was heated under reflux for 5 min., diluted with saturated brine solution (50 ml.), and extracted with ether (2 × 50 ml.). The combined extracts were washed with saturated brine, dried, and evaporated to a colourless, sweet-smelling oil (1·1 g.). Fractional distillation gave a pure sample of the *ester* (X) b. p. 136°/20 mm., n_D^{20} 1·4703, $\nu_{max.}$ 1720, 1255, 1200, 1150, 1100, 1025, and 820 cm.$^{-1}$ (Found: C, 74·5; H, 10·35. $C_{13}H_{22}O_2$ requires C, 74·25; H, 10·55%).

1-(*Hydroxymethyl*)-4-*methylbicyclo*[3,3,1]*non-3-en-9-ol* (XII).—The ester (XI) (138 g.) was added in dry ether (500 ml.) in 1 hr. to a refluxing solution of lithium aluminium hydride (30 g.) in ether (1 l.) and heated under reflux for 16 hr. The excess of hydride was destroyed by ethyl acetate, followed by dilute sulphuric acid. The separated ether layer was combined with two further extracts of the aqueous layer, washed with saturated brine solution, and dried. Crystallisation of the residue after removal of solvent gave the diol (XII) (104 g.), m. p. 100—125°. Recrystallisation from benzene–light petroleum gave the epimeric mixture, m. p. 127—133°, as white plates, $\nu_{max.}$ 3400—3300, 1060—1030, 1650, and 710 cm.$^{-1}$ (Found: C, 72·7; H, 9·65. Calc. for $C_{11}H_{18}O_2$: C, 72·5; H, 9·95%).

The diols (XII) (91 g.) and toluene-*p*-sulphonyl chloride (96 g.) in pyridine (250 ml.) were set aside for 20 hr. at 0°, and the solvent was then removed under reduced pressure. The residue was diluted with saturated brine and extracted with ether (2 × 300 ml.) and the combined ethereal extracts were washed with dilute hydrochloric acid and saturated sodium carbonate solution, and dried. Removal of solvent gave an oil which solidified on trituration with ether. Recrystallisation from ethyl acetate–light petroleum gave prisms of the primary *monotoluene-*p*-sulphonate* (152 g.), m. p. 65—67°, $\nu_{max.}$ 3475, 1070, 910, 860, 840, 712, and 705 cm.$^{-1}$, of (XII) (Found: C, 64·6; H, 7·1. $C_{18}H_{24}O_4S$ requires C, 64·25; H, 7·2%).

1,5-*Dimethylbicyclo*[3,3,1]*non*-2-*en*-9-*one* (III).—A solution of the last-mentioned monoester (55·4 g.) in dry ether (200 ml.) was added in 1 hr. to a stirred solution of lithium aluminium hydride (10 g.) in ether (250 ml.), and the mixture was heated under reflux with stirring for 25 hr. The mixture was worked up as above, giving a semi-solid epimeric mixture (27·0 g.) of the alcohols (I and II). This was dissolved in acetone (250 ml.) and cooled in ice. Jones's reagent (46 ml.; 8N-CrO_3 in dilute sulphuric acid) was added with cooling and shaking, and the mixture was diluted with water (1 l.) and extracted with light petroleum (2 × 250 ml.). The extracts were washed with saturated sodium hydrogen carbonate and water, dried, and evaporated. The volatile oily residue (26·0 g.) was adsorbed on alumina (250 g.) from light petroleum. Elution with the same solvent, and with benzene–light petroleum (1 : 1) gave the ketone (III) (23 g.) (mixed m. p., infrared spectra, thin-layer chromatography).

syn- (I) *and* anti-1,5-*Dimethylbicyclo*[3,3,1]*non*-2-*en*-9-*ol* (II),—(*a*) A suspension of lithium aluminium hydride (0·026 g.) in ether (10 ml.) was refluxed for 30 min.; to the cooled solution was added dropwise a solution of the ketone (III) (0·295 g.) in ether (100 ml.) and the whole was refluxed for 3 hr. Working up in the usual manner gave an epimeric mixture (0·29 g.) of (I) and (II) which was adsorbed on silica (12 g.) from light petroleum. Elution with light petroleum–benzene (3 : 7) separated two volatile crystalline solids with sharp camphoraceous odours. The first fractions were combined and recrystallised from light petroleum, to give stout prisms, m. p. 55°. Sublimation gave the *anti*-alcohol (II), m. p. 55° (Found: C, 79·3; H, 10·65. $C_{11}H_{18}O$ requires C, 79·45; H, 10·9%), τ 9·04, 8·97, 8·6, 8·38, 8·0, 6·72, and 4·6 (centre of 4 triplets at 5·0, 4·75, 4·5, and 4·2). The high-resolution infrared spectrum (CCl_4 solution) of this isomer exhibited a main band at 3640 cm.$^{-1}$, with a shoulder at 3625 cm.$^{-1}$, when measured with a Unicam S.P. 100 spectrophotometer equipped with an S.P. 130 sodium chloride prism grating monochromator operated under a vacuum. This pattern is consistent with the configuration assigned to this alcohol, there being no possibility of intramolecular hydrogen bonding. Such bands have been attributed to two conformations of the O–H bond in many monohydric alcohols.[18]

Later fractions from the column were combined and recrystallised from light petroleum, to give stout needles m. p. 79—80°. Sublimation afforded the syn-*alcohol* (I), m. p. 79—80° (Found: C, 79·25; H, 10·7%). The high-resolution infrared spectrum (CCl_4 solution) included a weak band at 3640 cm.$^{-1}$ (free OH); the main band at 3584 cm.$^{-1}$ persisted even at high dilution, and the shift of 56 cm.$^{-1}$ is consistent with intramolecular bonding.[18,19] In the predominant conformation the hydroxyl-proton lies above the double bond; in the other, it is directed upwards and away from it. Spectra determined for CCl_4 solutions at various temperatures and in ether–CCl_4 show intensity variations consistent with these assignments.

(*b*) Sodium (0·14 g.) was added in pieces, with shaking, to a mixture of the ketone (III) (0·338 g.), water (0·16 g.), and ether (30 ml.) at 0°, during 30 min. Water (0·16 g.), followed by sodium (0·14 g.) and water (0·7 g.), were added, and the mixture was shaken for a further 2 hr. This sequence of additions was repeated, and lastly water (3 g.) was added to destroy the excess of sodium. The ether layer was separated and washed with saturated brine solution

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[18] Dalton, Meakins, Robinson, and Zaharia, *J.*, 1962, 1566.

[19] von Schleyer, Trifan, and Backsai, *J. Amer. Chem. Soc.*, 1958, **80**, 6691.

and dried. Removal of solvent and chromatography of the product on silica, as in (*a*), afforded the *syn*- and *anti*-epimers (I) and (II).

The proportion of *syn*- and *anti*-epimers formed in the reduction of the ketone (III) could be conveniently followed by gas-liquid chromatography with a 5% poly(ethylene glycol) Embacel column at 125° (flow rate 27 ml./min.), the retention times of the *syn*- and *anti*-epimers being 9·7 and 14·3 min., respectively. By this means the *syn* : *anti* ratio in the products formed by various reduction procedures were found to be: lithium aluminium hydride–ether 1 : 3, lithium aluminium hydride–tetrahydrofuran 1 : 1·25, lithium hydridotri-t-butoxyaluminate–tetrahydrofuran 1 : 3, sodium borohydride–aqueous methanol 1 : 2, and sodium-moist ether 1 : 0·8.

1,5-*Dimethylbicyclo*[3,3,1]*nonan*-9-*ol*.—The *syn*-alcohol (I) (0·03 g.) in ethyl acetate (5 ml.) was hydrogenated on 10% palladium–charcoal for 50 min. at room temperature (uptake 1 mol.). The mixture was filtered through Celite 535, and the solvent removed to give a volatile colourless solid (100%), m. p. 54—57°. Sublimation afforded the saturated *alcohol*, m. p. 58—59°, $\nu_{max.}$ 3450, 1060, 1030, and 905 cm.$^{-1}$, τ 9·13, 6·98 (CH·OH) (Found: C, 78·3; H, 11·9. $C_{11}H_{20}O$ required C, 78·5; H, 12·0%). The *anti*-alcohol (II) gave the same saturated alcohol (m. p., mixed m. p., infrared spectrum).

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