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# TRANSFORMATIONS OF CAMPHOR

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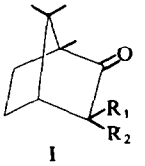
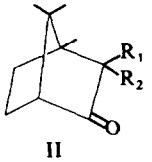
**Abstract**—The mono- and di-ethyleneketals of bornane-2,3-dione have been utilised for selective reactions in this molecule, including a new route to epicamphor. The alkylation of camphor with sodium and methyl iodide gave both C- and O-alkylation. A discrepancy in the literature concerning the synthesis of homocamphor and homoepicamphor is rectified. The reaction of 9-bromobornan-2-one with zinc and acetic acid-$d_1$ gave both the 9-deutero compound and a product of a fragmentation reaction.

IN THE course of our studies on the Clemmensen reduction of homocamphorquinone[1] and in an examination of the NMR spectra of a series of derivatives of camphor, we had occasion to investigate the reactions of camphor and some of its simple derivatives.

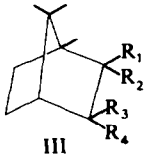
In order to introduce specific functional groups into the bornane skeleton at carbons 2 and 3 in a rational manner, we chose to use the two possible mono ethylene ketals of bornane-2,3-dione I ($R_1$, $R_2$ = —$OCH_2CH_2O$—) and II ($R_1$, $R_2$ = —$OCH_2CH_2O$—).




I




II




III

Acid catalyzed ketalization of camphor using ethylene glycol and a water separator was found to proceed comparatively slowly and under similar conditions, using one mole of ethylene glycol, (+)bonane-2,3-dione gave the 3-ketal I($R_1$, $R_2$ = —$OCH_2CH_2O$—) whose structure was established from its analysis, IR, NMR and strongly positive Cotton effect. Prolonged treatment ($2\frac{1}{2}$ days) of (+)bornane-2,3-dione with excess ethylene glycol gave the 3-ketal (70%) and the 2,3-bisketal (22%) III ($R_1$, $R_2$ = $R_3$, $R_4$ = —$OCH_2CH_2O$—). Hydrolysis of the latter with chloroacetic acid gave the 2-ketal II ($R_1$, $R_2$ = —$OCH_2CH_2O$—) which, like (+)bornan-3-one, showed a strong negative Cotton effect.

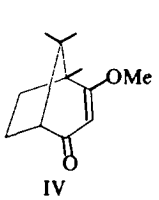
The 3-ketal provided a convenient route to bornan-3-one, in which the first step involved reduction of the free carbonyl group. Sodium borohydride or sodium-ethanol reduction of I ($R_1$, $R_2$ = —$OCH_2CH_2O$—) gave mixtures of both *endo* and *exo* epimers at $C_2$, as judged from NMR spectra, whereas lithium aluminium hydride reduction gave only the *exo* hydroxy epimer III ($R_3$, $R_4$ = —$OCH_2CH_2O$—, $R_1$ = OH, $R_2$ = H). Hydrolysis of the 2-hydroxy-3-ketal with ethanolic HCl gave the corresponding α-ketol, which was readily reduced by known methods[2] to bornan-3-one.

The mono ketals also provided convenient starting points for the synthesis of the

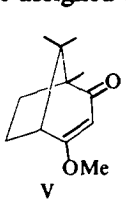
epimeric α-methyl ketones I ($R_1$, $R_2$ = H, Me) and II ($R_1$, $R_2$ = H, Me). Reaction of 3-ethylenedioxybornan-2-one I ($R_1$, $R_2$ = —$OCH_2CH_2O$—) with methylmagnesium-iodide gave only the product of *endo* attack III ($R_1$ = OH, $R_2$ = Me, $R_3$, $R_4$ = —$OCH_2CH_2O$—), in which the *exo* hydroxyl group causes a marked downfield shift of the adjacent C-8 methyl group in the NMR spectrum. Hydrolysis of the ketal group, and sodium amalgam—aqueous ethanol reduction gave 2-methylbornan-3-one II ($R_1$, $R_2$ = H, Me). In a similar manner, 2-ethylenedioxybornan-3-one was transformed into 3-*exo*hydroxy-3-methylbornan-2-one I ($R_1$ = OH, $R_2$ = Me).

Preparation of 3-methylbornan-2-one I ($R_1$, $R_2$ = H, Me) according to Glover,[3] by reaction of camphor with sodium in benzene, followed by addition of methyl iodide gave both 3-methylbornan-2-one and the methyl ethers of borneol and isoborneol, III ($R_1$ = $R_3$ = $R_4$ = H, $R_2$ = OMe) and III ($R_2$ = $R_3$ = $R_4$ = H, $R_1$ = OMe) respectively.

In a repetition of the reported preparation[4] of 5,8,8-trimethylbicyclo [3.2.1] octan-2-one (homocamphor) and the 1,8,8-derivative (homoepicamphor), bornane-2,3-dione was reacted with diazomethane to give a mixture of the two isomeric enol methyl ethers, IV and V, whose structures were assigned on the basis of their NMR

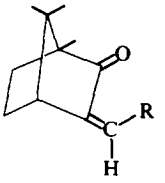


IV

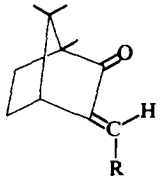


V

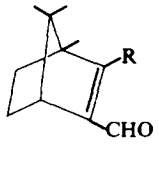
spectra and ORD curves, and by their subsequent transformations. The melting points of these two enol ethers are the reverse of those reported.[4] In related work, the enol methyl ethers of 3-hydroxymethylenebornan-2-one VI (R = OH) were



VI



VII

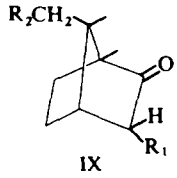


VIII

prepared by reaction with diazomethane in ether.[5] Separation of the products on alumina gave the *syn* and *anti* 3-methoxymethylenebornan-2-ones, VII (R = OMe) and VI (R = OMe), identified by their IR and NMR spectra, along with some 30% of the less stable 3-formyl-2-methoxyborn-2-ene VIII (R = OMe) although the parent aldo-enol form VIII (R = OH) is not detectable in the original compound by spectral means.[6]

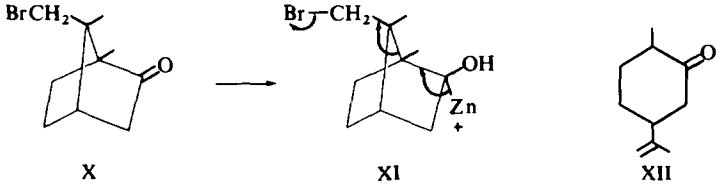
An X-ray determination of the structure of 3-bromobornan-2-one-π-sulphonic acid[7] has shown that the sulphonic acid group is attached to C-9. Thus since the sulphonic acid may be converted to 2,π-dibromobornan-2-one,[8] the position of the second bromine is shown to lie at C-9. In work designed to label and hence assign the methyl groups in the NMR spectra of camphor and its derivatives, 9-bromobornan-2-one X was prepared by reduction of 3,9-dibromobornan-2-one IX ($R_1$ = $R_2$ = Br)

with zinc in acetic acid and ether. Similarly reduction of 2,9-dibromobornan-2-one with zinc in acetic acid-$d_1$ and ether gave 9-bromo-3-deuterobornan-2-one IX ($R_1$ = D, $R_2$ = Br). In model experiments, the bromoketone X was treated with zinc and acetic acid under reflux for 9 hr. The chief product was camphor and also present was a product of a fragmentation reaction, dihydrocarvone XII. Carvenone




IX

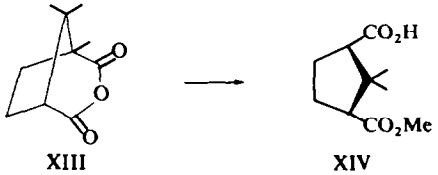
was the only other product. Similar results were obtained using zinc and acetic acid-$d_1$ to give 9-deuterobornan-2-one IX ($R_1$ = H, $R_2$ = D) and 2-deutero-2-methyl-5-isopropylidenecyclohexanone. The mechanism of this reaction is presumably that indicated (X → XI → XII);[9] attack of zinc at a carbonyl carbon atom to act as an electron source, finds analogy in fragmentation reactions accompanying the Clemmensen reduction of some 1,4-diketones.[10] The stereochemistry necessary for a concerted fragmentation reaction is provided by *exo* attack of the zinc at the carbonyl group together with the suitably placed bromine atom at C-9. Selenium dioxide oxidation[11] of 9-deuterobornan-2-one gave 9-deuterobornane-2,3-dione.




X XI XII

An unsuccessful attempt to synthesize 9-deuterobornan-2-one by formation of the Grignard compound from 9-bromo-2-ethylenedioxybornane and subsequent decomposition with $D_2O$, gave only 9,9′-bi(2-ethylenedioxybornane), characterized by its NMR and mass spectra. This dimer was converted by acid hydrolysis to 9,9′-bi(bornan-2-one) and thence by selenium dioxide oxidation[11] to 9,9′-bi(bornane-2,3-dione).

In steps designed to synthesize 7,7-dimethylbicyclo[2.2.1]heptan-2-one, apocamphoric anhydride[12] XIII, was reacted with sodium methoxide in methanol, to




XIII XIV

give the dicarboxylic acid half methyl ester XIV. Treatment of the corresponding acid chloride with diazomethane followed by silver oxide, in an Arndt–Eistert transformation gave the homologous acid, but attempts to effect a Dieckmann-type cyclization were unsuccessful.

## EXPERIMENTAL

Microanalyses were by Dr A. D. Campbell and his associates, University of Otago, New Zealand. IR spectra were measured with a Perkin–Elmer 237 instrument. ORD curves and optical rotations were determined with a Jasco ORD/UV-5 spectrophotometer at 25°. NMR spectra were measured with a Varian A-60 spectrometer using TMS as internal reference. Light petroleum was of b.p. 50–60° and alumina used for chromatography was P. Spence Type H material, deactivated with 5% of 10% acetic acid. M.ps on a Kofler block were uncorrected.

*2-Ethylenedioxybornane* (III, $R_3 = R_4 = H$, $R_1, R_2 = OCH_2CH_2O$—)

Camphor (23·8 g), ethylene glycol (12·6 g), toluene (80 ml) and toluene-*p*-sulphonic acid (0·3 g) were heated for 20 hr using a Dean and Stark water separator. Distillation and chromatography gave camphor and 2-ethylenedioxybornane, b.p. 208°/760 mm, $n_D^{21}$ 1·4792. (Found: C, 73·6; H, 10·2; O, 16·7. $C_{12}H_{20}O_2$ requires: C, 73·4; H, 10·3, O, 16·3%.)

*3-Ethylenedioxybornan-2-one* (I, $R_1, R_2 = —OCH_2CH_2O—$)

Bornane-2,3-dione[11] (13·76 g), ethylene glycol (5·74 g), benzene (90 ml) and toluene-*p*-sulphonic acid (0·4 g) were heated for 30 hr as above. Chromatography on alumina gave *3-ethylenedioxybornan-2-one* (11·4 g, 66%) as needles from aq MeOH, m.p. 81·5–82°. (Found: C, 68·7; H, 8·6; O, 23·0. $C_{12}H_{18}O_3$ requires: C, 68·5; H, 8·6; O, 22·9%); $\nu_{max}$ 1757 $cm^{-1}$, R.D. (c 1·2, $C_6H_6$), 21°, $[\phi]_{650}$ −42, $[\phi]_{589}$ −36°, $[\phi]_{500}$ −2°, $[\phi]_{400}$ +69°, $[\phi]_{342}$ +2174°, $[\phi]_{332}$ 0°, $[\phi]_{294}$ −2946°. A small quantity (0·12 g, 0·4%) of 2-ethylenedioxybornan-2-one was identified with a sample prepared below. Benzene eluted yellow needles of bornane-2,3-dione, m.p. 194°.

*2,3-Bisethylenedioxybornane* (III, $R_1, R_2 = R_3, R_4 = —OCH_2CH_2O—$)

Bornane-2,3-dione (13·31 g) and ethylene glycol (17·2 g) were treated, as above, for 60 hr. Chromatography of the product gave 3-ethylenedioxybornan-2-one (11·7 g, 70%) identified by m.p. and IR spectrum, along with *2,3-bisethylenedioxybornane* (4·57 g, 22%) as plates from aq EtOH, m.p. 55·5–56°. (Found: C, 66·0; H, 8·8; O, 25·0. $C_{14}H_{22}O_4$ requires: C, 66·2; H, 8·7; O, 25·2%); IR no C=O absorption, R.D. (*c* 7·3, MeOH) 25°, $[\phi]_{650}$ −12°, $[\phi]_{589}$ −16°, $[\phi]_{400}$ −32°, $[\phi]_{300}$ −69°, $[\phi]_{210}$ −272°.

*2-Ethylenedioxybornan-3-one* (II, $R_1, R_2 = —OCH_2CH_2O—$)

2,3-Bisethylenedioxybornane (1·3 g) and chloracetic acid (2·5 M, 70 ml) were heated under reflux for 1½ hr, to give a product, m.p. 37–38°, which was chromatographed on alumina to give needles (from light petroleum) of *2-ethylenedioxybornan-3-one* (0·59 g, 55%), m.p. 41·5–42°. (Found: C, 68·1; H, 8·7; O, 22·9. $C_{12}H_{18}O_3$ requires: C, 68·5; H, 8·6; O, 22·8%); $\nu_{max}$ 1767 $cm^{-1}$, R.D. (*c*, 1·6, MeOH), 25°, $[\phi]_{589}$ −53°, $[\phi]_{500}$ −210°, $[\phi]_{400}$ −789°, $[\phi]_{337}$ −4576°, $[\phi]_{315}$ 0°, $[\phi]_{294}$ +4576°. Benzene eluted 2,3-bisethylenedioxybornane (0·22 g).

*3-Ethylenedioxybornan-2-ol* (III; $R_1, R_2 = H, OH$, $R_3, R_4 = —OCH_2CH_2O—$)

(a) $NaBH_4$ (0·60 g) was added to 3-ethylenedioxybornan-2-one (0·90 g) in MeOH (20 ml) and the soln stood at 20° for 36 hr. The product (0·90 g) was distilled to give the *hydroxy ketal*, b.p. 92–94°/1·2 mm, $n_D^{18}$ 1·4912. ((Found: C, 67·7; H, 8·9. $C_{12}H_{20}O_3$ requires: C, 67·7; H, 9·4%); $\nu_{max}$ 3472 $cm^{-1}$ (OH), R.D. plain negative curve (*c* 7·2, MeOH), 21°, $[\phi]_{589}$ −44°, $[\phi]_{200}$ −132°. The NMR spectrum showed the presence of *endo* and *exo* derivatives in the ratio 4:5.

(b) Reduction of the carbonyl group with LAH gave an oil, $n_D^{20}$ 1·4898, IR spectrum identical with that obtained in (a), NMR spectrum showed the presence of the *endo* hydroxy isomer only.

(c) Sodium-ethanol reduction gave an epimeric mixture of *endo* and *exo* isomers in the ratio 3:8 (NMR).

*2-Hydroxybornan-3-one* (II, $R_1, R_2 = H, OH$)

(a) 3-Ethylenedioxybornan-2-ol (0·40 g) from $NaBH_4$ reduction of the corresponding ketone was warmed (60°) with EtOH (3 ml), and 3M HCl (25 ml) for 1½ hr, to give 2-hydroxybornan-3-one, as needles from light petroleum (0·295 g, 93%) m.p. 219–221° (sealed tube) (lit.[2] m.p. 220–221°) $\nu_{max}$ 3500, 3400 (OH) and 1755 $cm^{-1}$ (C=O).

(b) 2-*exo*hydroxybornan-3-one (II, $R_1 = OH$, $R_2 = H$): Treatment of the product from LAH reduction of the corresponding ketone, with acid gave needles (from light petroleum) of 2-*exo*hydroxybornan-3-one,

m.p. 206–207°, R.D. (*c*, 1·7, MeOH), 21°, $[\phi]_{650}$ −50°, $[\phi]_{589}$ −71°, $[\phi]_{450}$ −128°, $[\phi]_{350}$ −494°, $[\phi]_{316}$ −1224°, $[\phi]_{298}$ 0°, $[\phi]_{279}$ +1306°.

*Bornan-3-one*[2] (II, $R_1 = R_2 = H$)

Sodium amalgam-EtOH reduction of 2-*exo*hydroxybornan-3-one gave bornan-3-one, (68%) needles from hexane, m.p. 179–180° (lit.[13] m.p. 183–184°).

3-*Ethylenedioxy*-2-*methylisoborneol* (III; $R_1$ = OH, $R_2$ = Me, $R_3$,$R_4$ = —$OCH_2CH_2O$—)

3-Ethylenedioxybornan-2-one (5·61 g) in dry benzene (30 ml) was added to an ethereal soln of MeMgI (0·058 mole), the mixture heated for 2½ hr and poured into ice-cold $H_2SO_4$ to give an oil (4·6 g). Chromatography on alumina gave 3-*ethylenedioxy*-2-*methylisoborneol* (3·86 g, 64%) as needles from aq EtOH, m.p. 19–20°. (Found: C, 69·2; H, 10·0; O, 21·1. $C_{13}H_{22}O_3$ requires: C, 69·0; H, 9·7; O, 21·2%); $\nu_{max}$ 3590 $cm^{-1}$ (OH), R.D. plain positive curve (*c* 13, MeOH), 25°, $[\phi]_{589}$ +7·6°, $[\phi]_{250}$ +190°. Ether eluted 2-*exo*hydroxy-2-methylbornan-3-one (0·45 g) identified with material prepared below.

2-exo-*Hydroxy*-2-*methylbornan*-3-*one* (II; $R_1$ = OH, $R_2$ = Me)

3-Ethylenedioxy-2-methylisoborneol (1·1 g) was warmed with EtOH (10 ml) and 3M HCl (15 ml) for 1 hr, to give 2-*exo*hydroxy-2-methylbornan-3-one as needles from light petroleum (0·68 g, 91%), m.p. 190–190·5° (sealed tube) (lit.[14] m.p. 199°). (Found: C, 72·2; H, 10·0; O, 17·7. Calc. for $C_{13}H_{22}O_3$: C, 72·5; H, 9·9; O, 17·6%); $\nu_{max}$ 3560 (OH), 3480 (OH), 1760 (C=O) $cm^{-1}$, R.D. (*c* 1·5, MeOH), 21°, $[\phi]_{589}$ −75°, $[\phi]_{400}$ −400°, $[\phi]_{314}$ −2640°, $[\phi]_{291}$ 0°, $[\phi]_{271}$ +2430°.

2-*Methylbornan*-3-*one* (II, $R_1$, $R_2$ = H, Me)

Sodium amalgam-aq EtOH reduction of 2-*exo*hydroxy-2-methylbornan-3-one gave 2-*methylbornan*-3-*one* (34%) as plates from n-hexane, m.p. 112–113° (sealed tube). (Found: C, 79·0; H, 10·5. $C_{11}H_{18}O$ requires: C, 79·4; H, 10·9%); $\nu_{max}$ 1750 $cm^{-1}$, R.D. (*c* 2, MeOH), 21°, $[\phi]_{589}$ +10°, $[\phi]_{350}$ −220°, $[\phi]_{312}$ −1360°, $[\phi]_{292}$ 0°, $[\phi]_{269}$ +1833°.

2-*Ethylenedioxy*-3-ex*ohydroxy*-3-*methylbornane* (III; $R_1$, $R_2$ = —$OCH_2CH_2O$—, $R_3$ = OH, $R_4$ = Me)

2-Ethylenedioxybornan-3-one (0·96 g) in benzene (6 ml) was added to an ethereal soln of MeMgI (0·013 mole) and the mixture refluxed for 2 hr to give an oil (0·91 g). Chromatography on alumina gave 2-*ethylenedioxy*-3-ex*ohydroxy*-3-*methylbornane* as an oil (0·81 g), $\nu_{max}$ 3521 (OH) $cm^{-1}$, R.D. plain negative curve (*c* 9·0, MeOH), 21°, $[\phi]_{589}$ −32°, $[\phi]_{300}$ −86°, $[\phi]_{250}$ −329°.

3-ex*oHydroxy*-3-*methylbornan*-2-*one* (I, $R_1$ = OH, $R_2$ = Me)

2-Ethylenedioxy-3-*exo*hydroxy-3-methylbornane (0·30 g) was warmed with EtOH (5 ml) and 6M HCl (20 ml) for 10 hr to give an oil (0·25 g). Alumina chromatography gave 3-ex*ohydroxy*-3-*methylbornan*-2-*one* as needles from $CCl_4$, m.p. 188·5–189°; $\nu_{max}$ 3546 (OH), 3452 (OH), 1754 (C=O) $cm^{-1}$, R.D. (*c* 1·2, MeOH), 21°, $[\phi]_{589}$ +60°, $[\phi]_{350}$ +633°, $[\phi]_{319}$ +2035°, $[\phi]_{300}$ 0°, $[\phi]_{276}$ −2100°.

3-*Methylbornan*-2-*one* (I, $R_1$, $R_2$ = H, Me)

Camphor (20·2 g) in benzene (60 ml) was added slowly (1 hr) to a vigorously stirred mixture of finely chopped Na-wire (3·1 g) and benzene (60 ml) at 20°, and the mixture allowed to stand for 12 hr. MeI (21·5 g) in benzene (20 ml) was then added slowly (2 hr) with warming (75°). Working up gave an oil (17·2 g) which was distilled and the fraction boiling at 80–82°/1·5 mm collected, which was separated into its components by preparative GLC.

(a) a mixture of borneol and isoborneol methyl ethers (43%) in the ratio 6:4 (NMR), b.p. 80°/1·5 mm, $n_D^{20}$ 1·4629, $\nu_{max}$ 1111, 1087 (C—O—C) $cm^{-1}$.

(b) camphor (31%).

(c) 3-methylbornan-2-one (26%), m.p. 29·5–30° (lit.[15] m.p. 38–39°); $\nu_{max}$ 1742 (C=O) $cm^{-1}$, R.D. (*c* 1·7, MeOH), 25°, $[\phi]_{589}$ +40°, $[\phi]_{360}$ +234°, $[\phi]_{308}$ +2267°, $[\phi]_{286}$ 0°, $[\phi]_{268}$ −2578°.

*Enol methyl ethers of* 1,8,8-*trimethylbicyclo*[3.2.1]*octane*-2,4-*dione* (IV, V)

10·8 g of the ethers, prepared by the treatment of bornane-2,3-dione with diazomethane according to Favre *et al.*[4] were chromatographed on alumina to give in the benzene eluate V (8·0 g, 71%), recrystallized from n-hexane as needles, m.p. 68–69° (lit.[4] m.p. 56°); $\nu_{max}$ 1670 (C=O) $cm^{-1}$, $\delta$ 0·94 (s, 6) and 0·99 (s, 3) ($C_9$, $C_{10}$ and $C_{11}$ methyls), 3·34 (s, 3, methoxyl), 5·06 (s, 1, $C_3$ vinyl), R.D. (*c* 1·3, MeOH), 21°, $[\phi]_{589}$ −113°,

$[\phi]_{350}$ −1507°, $[\phi]_{310}$ −4625°, $[\phi]_{294}$ 0°, $[\phi]_{268}$ +7430°. The ether eluate contained IV (1·32 g, 12%), recrystallized from n-hexane as needles m.p. 54–55° (lit.[4] m.p. 71°); $\nu_{max}$ 1675 (C=O) $cm^{-1}$, $\delta$ 0·93, 0·95, 1·08 (3 singlets, 9, $C_9$, $C_{10}$ and $C_{11}$ methyls), 1·78 (d, $J$ = 4 c/s, 1, $C_5$ methine proton split by $C_6$ proton), 3·71 (s, 3, methoxyl), 5·08 (s, 1, $C_3$ vinyl), R.D. (*c* 1·3, MeOH), 21°, $[\phi]_{589}$ +33°, $[\phi]_{350}$ +1857°, $[\phi]_{312}$ +7648°, $[\phi]_{295}$ 0°, $[\phi]_{270}$ −9050°.

1,8,8-*Trimethylbicyclo*[3.2.1]*oct-3-en-2-one*

Compound IV (0·95 g) was reduced with LAH in ether (2 hr), to give a yellow oil which was warmed (½ hr), with EtOH (5 ml) and 3M $H_2SO_4$ (20 ml). The crystalline 1,8,8-trimethylbicyclo[3.2.1]oct-3-en-2-one (0·43 g, 54%) was filtered from the cooled mixture and recrystallized from n-hexane as plates m.p. 166–167° (sealed tube) (lit.[4] m.p. 169°); $\nu_{max}$ 1710 (C=O), 1685 (C=C) $cm^{-1}$, $\delta$ 0·91, 0·95, 1·01 (3 singlets, $C_9$, $C_{10}$ and $C_{11}$ methyls), 5·89 (d, $J$ = 9 c/s, 1, $C_3$ vinyl), 7·03 (*q*, 1, $C_4$ vinyl split by $C_3$ vinyl, $J$ = 9 c/s and split by $C_5$ methine, $J$ = 7 c/s), R.D. (*c* 1·4, MeOH), 21°, $[\phi]_{589}$ −214°, $[\phi]_{400}$ −1182°, $[\phi]_{344}$ −3894, $[\phi]_{321}$ 0°, $[\phi]_{296}$ +4177°.

1,8,8-*Trimethylbicyclo*[3.2.1]*octan-2-one* (*Homocamphor*)

Hydrogenation of 1,8,8-trimethylbicyclo[3.2.1]oct-3-en-2-one (0·19 g) in EtOH (30 ml) gave homocamphor (0·12 g, 63%) which was sublimed as needles m.p. 187–188·5° (sealed tube), (lit.[4] m.p. 196–197°). The oxime had m.p. 169·5–170° (lit.[16] m.p. 167–168°); $\nu_{max}$ 1712 (C=O) $cm^{-1}$. R.D. (*c* 1·5, MeOH), 21° $[\phi]_{589}$ −131°, $[\phi]_{400}$ −558°, $[\phi]_{298}$ −2615°, $[\phi]_{278}$ 0°, $[\phi]_{263}$ +1552°.

5,8,8-*Trimethylbicyclo*[3.2.1]*oct-3-en-2-one*

Compound V (1·06 g) was treated as for the isomeric enol ether IV to give 5,8,8-trimethylbicyclo[3.2.1]-oct-3-en-2-one, recrystallized from light petroleum as needles m.p. 164–166° (sealed tube) (lit.[4] m.p. 174–176°) $\nu_{max}$ 1700 (C=O), 1675 (C=C) $cm^{-1}$, $\delta$ 0·92 (s, 6), 1·13 (s, 3) ($C_9$, $C_{10}$ and $C_{11}$ methyls), 5·84 (d, $J$ = 9·5 c/s, 1, $C_3$ vinyl split by $C_4$ vinyl with homoallylic coupling, $J$ = 1·5 c/s, with $C_1$ methine), 6·68 (d, $J$ = 9·5 c/s, 1, $C_4$ vinyl).

5,8,8-*Trimethylbicyclo*[3.2.1]*octan-2-one*

5,8,8-Trimethylbicyclo[3.2.1]oct-3-en-2-one was hydrogenated as before to give 5,8,8-trimethylbicyclo-[3.2.1]octan-2-one (57%), recrystallized from $CCl_4$ as plates, m.p. 179–180° (sealed tube) (lit.[4] m.p. 197–199°); $\nu_{max}$ 1720 (C=O) $cm^{-1}$, R.D. (*c* 1·5, MeOH), 21°, $[\phi]_{589}$ +100°, $[\phi]_{350}$ +244°, $[\phi]_{297}$ +621°, $[\phi]_{274}$ 0°, $[\phi]_{260}$ −133°.

*Reaction of diazomethane with 3-hydroxymethylenebornan-2-one*

Diazomethane was added to excess 3-hydroxymethylenebornan-2-one in ether at 0°. Working up gave after extraction with 2M NaOH, a yellow oil (0·42 g) which was chromatographed on alumina:

(a) Light petroleum–benzene (6:4) gave *syn* VII (R = OMe) as a yellow oil (0·18 g, 42%) identical (IR and NMR) with the *syn* material prepared according to Bishop *et al.*,[17] $\nu_{max}$ 1730 (C=O), 1660 (C=C) $cm^{-1}$, $\delta$ 0·81, 0·87, 0·93 ($C_8$, $C_9$, $C_{10}$ methyls), 2·82 (d, $J$ = 3·2 c/s, $C_4$ methine), 3·81 (s, 3, methoxyl), 6·90 (s, 1, $C_{11}$ vinyl).

(b) Benzene gave the unstable VIII (R = OMe) recrystallized from light petroleum as needles m.p. 66–68°, decomposing rapidly in air, $\nu_{max}$ 1645 (C=O), 1592 (C=C) $cm^{-1}$, $\delta$ 0·82, 0·86, 0·96 ($C_8$, $C_9$, $C_{10}$ methyls), 2·93 (d, $J$ = 2·8 c/s, 1, $C_4$ methine), 4·11 (s, 3, methoxyl).

(c) Ether gave the *anti* VI (R = OMe) as a yellow oil (0·08 g, 19%), $\nu_{max}$ 1728 (C=O), 1650 (C=C) $cm^{-1}$, $\delta$ 0·83, 0·87, 0·90 (s, $C_8$, $C_9$, $C_{10}$ methyls), 2·30 (d, $J$ = 1·3 c/s, $C_4$ methine), 3·81 (s, 3, methoxyl), 6·06 (s, 1, $C_{11}$ vinyl).

9-*Bromobornan-2-one* (X)

Zinc powder (50 g) was added slowly to a warmed (30°) mixture of 3,9-dibromobornan-2-one (100 g), HOAc (200 ml) and ether (260 ml) and the mixture then refluxed for 10 min. Working up gave 9-bromobornan-2-one (60 g, 80%) recrystallized from $CCl_4$-EtOH as needles m.p. 90–91° (lit.[18] m.p. 93–95°), $\nu_{max}$ 1753 $cm^{-1}$.

9-*Bromo-2-ethylenedioxybornane*

9-Bromobornan-2-one (60 g), ethylene glycol (80·5 g), benzene (200 ml) and toluene-*p*-sulphonic acid

(1·2 g) were heated together for 96 hr using a Dean and Stark water separator. Chromatography of the product (65·5 g) gave 9-*bromo*-2-*ethylenedioxybornane* (38 g, 53%) as an unstable oil. (Found: C, 52·4; H, 7·0; Br, 28·7. $C_{12}H_{19}O_2Br$ requires: C, 52·4; H, 7·0; Br, 29·0%), IR showed no C=O. The ether eluate contained 9-bromobornan-2-one.

9,9′-*Bi*(2-*ethylenedioxybornane*)

9-Bromo-2-ethylenedioxybornane (15·3 g), Mg powder (2·0 g) and ether (120 ml) were refluxed for 4 hr to give 9,9′-*bi*(2-*ethylenedioxybornane* (10·7 g, 97%), recrystallized from ether as needles m.p. 208–210°. (Found: C, 74·1; H, 9·8. $C_{24}H_{38}O_4$ requires: C, 73·8; H, 9·8%); M.W. (mass. spec.) 390.

9,9′-*Bi*(*bornan*-2-*one*)

9,9′-Bi(2-ethylenedioxybornane) (7·3 g), 3N HCl (70 ml) and EtOH (50 ml) were warmed (70°) for 1½ hr. Working up gave 9,9′-*bi*(*bornan*-2-*one*) (5·1 g, 82%) recrystallized from light petroleum as needles, m.p. 265–266°. (Found: C, 79·5; H, 10·3. $C_{20}H_{30}O_2$ requires: C, 79·4; H, 10·0%), $\nu_{max}$ 1754 $cm^{-1}$.

9,9′-*Bi*(*bornane*-2,3-*dione*)

9,9′-Bi(bornan-2-one) (0·95 g), $SeO_2$ (2·46 g) and $Ac_2O$ (3 ml) were heated to 150° for 3½ hr. After dilution with $Ac_2O$ and filtration of the Se metal, alumina chromatography of the yellow solid (1·02 g) gave in the MeOH eluate 9,9′-*bi*(*bornane*-2,3-*dione*) (0·63 g, 60%), recrystallized from MeOH as needles m.p. > 340°. (Found: C, 73·2; H, 8·1. $C_{20}H_{26}O_4$ requires: C, 72·7; H, 7·9%), $\nu_{max}$ 1780 and 1765 $cm^{-1}$.

9-*Bromo*-3-*deuterobornan*-2-*one* (IX, $R_1$ = D, $R_2$ = Br)

Zinc powder (2·0 g) was added slowly to a warmed (30°) mixture of 2,9-dibromobornan-2-one (4·0 g), ether (20 ml) and HOAc-$d_1$ (12 ml), and the mixture refluxed for 30 min. Working up gave 9-*bromo*-3-*deuterobornan*-2-*one* recrystallized from light petroleum as needles m.p. 92–93°. (Found: C, 51·6; H and D, 6·6. $C_{10}H_{14}BrDO$ requires: C, 51·7; H and D, 6·9%), $\nu_{max}$ 1755 $cm^{-1}$.

*Zinc*-HOAc *reduction of* 9-*bromobornan*-2-*one*

9-Bromobornan-2-one (1·01 g), HOAc (25 ml) and Zn powder (2·0 g) were refluxed for 9 hr. Ether extraction gave a pasty crystalline solid (0·54 g) which was separated by preparative GLC.

1. Camphor (71%).

2. Dihydrocarvone (14%) identified (IR and NMR) with a sample prepared according to Wallach and Schrader.[19]

3. Carvenone (15%) identified by IR and NMR spectra; $\nu_{max}$ 1675 (C=O), 1632 (C=C) $cm^{-1}$; $\delta$ 1·08 (d, $J$ = 6·2 c/s, 3, $C_2$ methyl split by $C_2$ methine), 1·11 (d, $J$ = 7 c/s, 6, isopropyl), 5·77 (m, 1, $C_6$ vinyl).

9-*Deuterobornan*-2-*one* (IX, $R_1$ = H, $R_2$ = D)

9-Bromobornan-2-one (2·1 g) in HOAc-$d_1$ (30 ml) and Zn powder (4·0 g) was treated as above to give an oil (1·08 g), separated by preparative GLC.

1. 9-*Deuterobornan*-2-*one* (68%), m.p. 179·5–180°. (Found: C, 77·9; H and D, 10·7. $C_{10}H_{15}DO$ requires: C, 78·4, H and D 11·2%), $\nu_{max}$ 1754 $cm^{-1}$.

2. 2-*Deutero*-2-*methyl*-5-*isopropylidenecyclohexanone* (14%), $\nu_{max}$ 1720 (C=O), 1647 (C=$CH_2$), 898 (C=$CH_2$) $cm^{-1}$, $\delta$ 0·95 (m, 3, $C_2$ methyl), 1·73 (t, $J$ = 1·1 c/s, 3, isopropylidene methyl), 4·75 (d, $J$ = 1·1 c/s, 2, isopropylidene methylene).

3. *Deuterocarvenone* (18%) $\nu_{max}$ 1675 (C=O), 1618 (C=C), $\delta$ 1·10 (m, 9, methyl and isopropyl groups), no vinyl proton.

9-*Deuterobornane*-2,3-*dione*

2·43 g of the crude product from the Zn–HOAc-$d_1$ reduction of 9-bromobornan-2-one was heated to 150° with $SeO_2$ (5·0 g) and $Ac_2O$ (4 ml) for 3½ hr. Working up as before gave an oily solid (1·08 g) which on alumina chromatography gave 9-*deuterobornane*-2,3-*dione* (0·15 g), recrystallized from light petroleum as needles m.p. 198–198·5°, $\nu_{max}$ 1778 and 1764 $cm^{-1}$.

3-*Carbomethoxy*-2,2-*dimethylcyclopentanecarboxylic acid* (XIV)

Treatment of XIII[12] (4·0 g) with NaOMe (1·46 g) in anhyd MeOH (12·2 g) at 0° for ½ hr gave 3-*carbomethoxy*-2,2-*dimethylcyclopentanecarboxylic acid* (4·72 g, 98%), recrystallized from light petroleum as prisms, m.p. 93–93·5°. (Found: C, 60·1; H, 7·8. $C_{10}H_{16}O_4$ requires: C, 60·0; H, 8·0%); $\nu_{max}$ 1735, 1710 $cm^{-1}$.

*3-Carbomethoxy-2,2-dimethylcyclopentanecarbonyl chloride*

3-Carbomethoxy-2,2-dimethylcyclopentanecarboxylic acid (4·70 g) and $SOCl_2$ (5·80 g) were warmed (80°) for 1½ hr and after removal of excess $SOCl_2$ *in vacuo* gave 3-carbomethoxy-2,2-dimethylcyclopentanecarbonyl chloride as an unstable yellow oil (5·1 g) $\nu_{max}$ 1800, 1745, 1170 $cm^{-1}$.

*1-Diazoacetyl-3-carbomethoxy-2,2-dimethylcyclopentane*

Diazomethane (from 12·5 g of nitrosomethylurea) in 200 ml ether was added to 3-carbomethoxy-2,2-dimethylcyclopentanecarbonyl chloride (5·04 g) in ether (100 ml) and the mixture allowed to stand at 20° for 12 hr. Removal of solvent *in vacuo* gave a yellow crystalline deposit of 1-diazoacetyl-3-carbomethoxy-2,2-dimethylcyclopentane (4·9 g) recrystallized from light petroleum as pale yellow unstable needles, m.p. 122–123° d, $\nu_{max}$ 3520, 3420, 2120, 1740 $cm^{-1}$

*3-Carbomethoxy-2,2-dimethylcyclopentaneacetic acid*

1-Diazoacetyl-3-carbomethoxy-2,2-dimethylcyclopentane (4·80 g) in warm dioxan (85 ml) was added slowly to a suspension of freshly prepared $Ag_2O$ (5·9 g) in a mixture of water (210 ml) and $Na_2S_2O_3$ (9·4 g). After 2 hr at 75°, the mixture was filtered and the filtrate acidified with dil $HNO_3$, saturated with $(NH_4)_2SO_4$ and ether extracted to give *3-carbomethoxy-2,2-dimethylcyclopentaneacetic acid* as an orange solid (4·1 g) which was recrystallized from light petroleum as needles, m.p. 115–118°; $\nu_{max}$ 1720, 1170 $cm^{-1}$ $\delta$ 0·70, 1·15 ($CMe_2$), 3·73 (COOMe). (Found: C, 61·2; H, 8·3. $C_{11}H_{18}O_4$ requires: C, 61·6; H, 8·5%.)

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