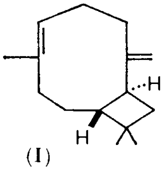
153. *Bridged Ring Systems. Part IV.* Reactions Involving Bridge Scission.*

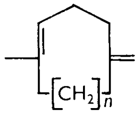
By G. L. BUCHANAN, A. MCKILLOP, and R. A. RAPHAEL.

The syntheses of 1-methyl-5-methylenecyclo-octene and of 1-methyl-5-methylenecyclononene from bridged-ring precursors are described. A number of alternative paths have been investigated and several by-products have been identified.

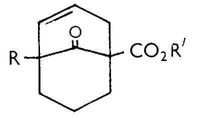
PREVIOUS publications[1,2] in this series describe the synthesis of bicyclo[3,3,1]nonane derivatives as part of a general study of bridged-ring systems, now in progress in these laboratories. Our interest in such systems includes severing the one-carbon bridge to produce medium-sized carbocycles which are otherwise inaccessible. Thus, in principle, bridge scission of a bicyclo[4,3,1]decane would give rise to a nine-membered ring, and, by choice of an appropriate starting material, the process offers a feasible route to isocaryophyllene (I). As an initial exploration of the idea this communication describes the synthesis of the related eight- and nine-membered dienes (II and III).



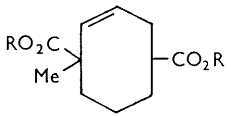
(I)



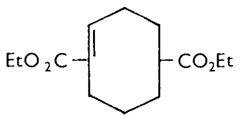
(II : $n = 3$)
(III : $n = 4$)



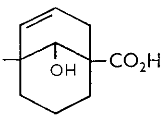
	R	R′
(IV)	Me	Et
(V)	H	Et
(VI)	Me	H
(VII)	Me	Me
(VIII)	Me	Bu^t



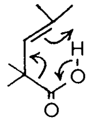
(IX : R = Et)
(X : R = H)



(XI)

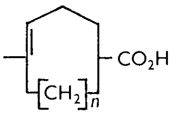


(XII)



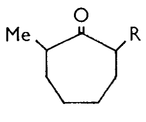
(XIII)

$CH_3\cdot CO\cdot[CH_2]_3\cdot CH(CO_2H)\cdot[CH_2]_3\cdot CO_2H$
(XVI)

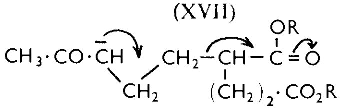


(XIV : $n = 3$)
(XV : $n = 4$)

$H\cdot C:C\cdot[CH_2]_3\cdot C(CO_2Et)_2\cdot[CH_2]_2\cdot CO_2Et$
(XVII)

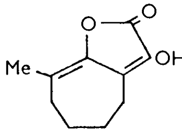


(XIX : R = CO·CO₂Et)
(XX : R = CO₂Et)

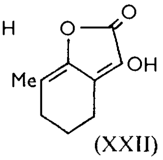


$CH_3\cdot CO\cdot CH\diagdown_{CH_2}\diagup CH_2-CH\{(CH_2)_2\cdot CO_2R\}-C(OR){=}O$

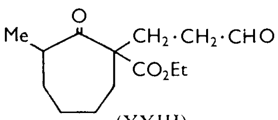
(XVIII)



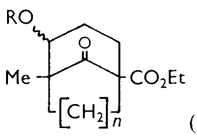
(XXI)



(XXII)



(XXIII)



	R	n
(XXIV)	H	4
(XXV)	Ts	4
(XXVI)	H	3
(XXVII)	Ts	3

The bicyclic keto-ester (IV),[2] was treated with ethanolic sodium ethoxide, in the firm expectation that it would afford the di-ester (IX), by a retro-Claisen ester reaction. However, although the analogous keto-ester (V) yields (XI) under these conditions,[3] the homologue (IV) underwent reduction in excellent yield to the hydroxy-acid (XII), or its

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* Part III, *J.*, 1964, 289.

[1] Murray, Parker, and Raphael, *Tetrahedron*, 1961, **16**, 74.

[2] Murray, Parker, Raphael, and Jhaveri, *Tetrahedron*, 1962, **18**, 55.

[3] Cope, Graham, and Marshall, *J. Amer. Chem. Soc.*, 1954, **76**, 6159.

ester, according to the experimental conditions employed. The identity of the product was established by an unambiguous synthesis from the keto-ester (IV), by borohydride reduction. As isolated from either reaction the reduction product appeared as a single epimer and stereospecific reduction is probably due to hydride attack from the more exposed side of the carbonyl bridge. For this reason we assign it structure (XII). That the ethoxide reduction was in fact a hydride exchange process was corroborated by investigating the effects of different bases. Sodium methoxide reacted with the methyl ester (VII) producing, exclusively, the same acid (XII), and more surprisingly, prolonged reaction of the ethyl ester (IV), with either sodamide or potassium t-butoxide, likewise furnished reduction products in very high yield; these were, respectively, the acid (XII) and its t-butyl ester. In both cases reduction must be effected by the one mole of ethoxide generated by an interchange process; this implies unusual reactivity in the carbonyl bridge.

In order to achieve ring scission it was necessary to treat the t-butyl ester (VIII) with t-butoxide or sodamide. The product (X) showed the expected infrared absorption (1700 and 743 cm.$^{-1}$), was a dicarboxylic acid (titration), and absorbed one mole of hydrogen on reduction. The same product was obtained by the action of sodamide on the parent bicyclic keto-acid (VI), but the latter was unaffected by strong aqueous alkali.

These unexpected carbonyl reductions result directly from the presence of the methyl group at the bridgehead position. It now becomes apparent that Cope's ready conversion[3] of the lower homologue of (V) into (XI) depends critically on the incidental migration of the olefinic bond; this event removes the newly-formed ester grouping from the vicinity of the transannular reactive methine. In the homologous series this migration is impossible and, consequently, the interaction of (IV) and ethoxide produces an equilibrium mixture (IV $\rightleftharpoons$ IX) from which the bicyclic keto-ester component is slowly removed by hydride reduction.

The flexibility of the eight-membered ring in the diacid (X) allows the carboxyl group and the βγ-double bond to attain the coplanar configuration (XIII) appropriate to ready decarboxylation,[4] and, when heated with copper dust, the acid was indeed smoothly decarboxylated. The acidic product, which is assigned structure (XIV) was characterised as its amide and methyl ester, although the acid itself was difficult to purify. This was due to contaminating traces of the bicyclic acid (VI), whose presence was discernible by the infrared spectrum of the product. This bicyclic acid was the major product when (X) was pyrolysed in the absence of copper dust. The intramolecular transannular reaction may be readily rationalised by the close proximity of the carboxyl and double-bond functions in the cyclo-octene acid (X).

The structure (XIV) ascribed to the pyrolysate was consistent with titration and hydrogenation data, and with its infrared spectrum (830 cm.$^{-1}$; trisubstituted double bond), but before embarking on its elaboration to (II) rigorous confirmation of the cyclo-octene ring was obtained. Ozonolysis afforded the keto-diacid (XVI) which was identical with the authentic compound synthesised independently from the acetylenic triester (XVII) by hydration, followed by hydrolysis and decarboxylation. Attempts were made to prepare a bis-*p*-bromophenacyl ester of (XVI) but, under standard basic conditions, the product obtained was bis-*p*-bromophenacyl glutarate. This unusual transformation can be rationalised as the cyclopropane analogue of a retro-Michael reaction as shown in (XVIII) (the corresponding Michael reaction is well known[5]) to give glutaric acid and cyclopropyl methyl ketone. The latter was isolated as its 2,4-dinitrophenylhydrazone when the acid (XVI) was treated with base alone.

With the preparation of (XIV) now fully explored, the cognate synthesis of (XV) was investigated. Under appropriate conditions, diethyl oxalate condensed with 2-methylcycloheptanone, yielding the glyoxylate ester (XIX), which was readily decarbonylated

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[4] Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart, and Winston, New York, 1959, p. 544.

[5] Bone and Perkin, *J.*, 1895, **67**, 108; Kierstead, Linstead, and Weedon, *J.*, 1952, 3616.

to the corresponding β-keto-ester (XX). A crystalline by-product, isolated from the above condensation when moisture was not rigorously excluded was formulated as (XXI) on the basis of spectroscopic evidence, derived by analogy with the authenticated lactone (XXII).[6] The β-keto-ester (XX) condensed smoothly with acrolein and the product (XXIII) was cyclised by dilute acid to the bicyclic alcohol (XXIV), but all attempts to dehydrate this alcohol to (XXVIII) yielded the tetralin acid (XXX) as the only recognisable product. An analogous aromatic acid had been isolated, as a *minor* product, in the preparation of (IV),[2] and structure (XXX) was hence predictable. It was verified by dehydrogenation to 4-methyl-1-naphthoic acid, and by conversion via the amine (XXXI) into the known naphthol (XXXII).[7] (We are indebted to Professor M. S. Newman, Ohio State University, for an authentic sample). An unambiguous synthesis of the acid has since been achieved.[8]

Because of this unwanted rearrangement it became necessary to find a new synthetic route to (XIV) and (XV) from the hydroxyketo-esters (XXIV) and (XXVI), the only bicyclic derivative available in both series. As before, exploratory work was carried out on the more plentiful bicyclo[3,3,1]nonane derivative (XXVI). This alcohol, obtained as a mixture of epimers, was rapidly decomposed by alkali, but its tosylate (XXVII) reacted smoothly and rapidly with ethoxide, giving a good yield of the cyclo-octene diester (XXXIII), showing infrared spectral bands at 1725 (ester) and 830 cm.$^{-1}$ (trisubstituted double bond). The extreme facility of this reaction suggested a concerted mechanism (XXXV), and confirmatory evidence will be detailed in a later publication. The high yield of diester is also consistent with the view that the mixture of epimeric alcohols (XXVI), formed under equilibrating conditions, must be rich in the equatorial epimer. Furthermore, a by-product from the ethoxide reaction was shown to be an unchanged tosylate (XXVII); this must be the axial epimer, since it was unaffected even by prolonged treatment with ethoxide.

Hydrolysis and concomitant decarboxylation of the cyclo-octene diester (XXXIII) proceeded easily, affording the cyclo-octene acid (XIV), previously described. Again, the product was contaminated with about 5% of the bicyclic acid (VI). An analogous transannular acylation was found to occur during the reduction of (XXXIII) with lithium aluminium hydride, when the sole product was the bicyclic diol (XXXVI) formed by reduction of the presumed intermediate (IV). An obvious rationalisation of these events is depicted in (XXXVII) and implies a particularly ready removal of an allylic proton. This may well be a consequence of the special geometry of the molecule which places the ester grouping in close proximity to the double bond.

The cyclo-octene acid (XIV) was likewise prone to transannular reactions; for example slow distillation produced large amounts of a lactone (ν_{CO} 1745 cm.$^{-1}$) which is formulated as (XXXVIII). However, when appropriate precautions were taken, this route to the acid (XIV) was preferable to that described previously. With the quantity thus available it was now possible to make a thorough investigation of the final transformation of the acid (XIV) into the diene (II).

The ester derived from (XIV) was reduced to the alcohol (XXXIX) which readily dehydrated by distillation from boric acid. This procedure, which is notoriously prone to produce rearrangements,[9] gave a mixture containing only small quantities of the required diene. Pyrolysis of the acetate of the alcohol (XXXIX) proceeded in high yield and the product showed the required absorption at 890 cm.$^{-1}$. However, the spectrum also showed vinyl absorption (910 cm.$^{-1}$) but no evidence of the presence of a trisubstituted double bond (~830 cm.$^{-1}$). The most plausible explanation of these data, for which we are indebted to Dr. J. K. Sutherland, involves a Cope rearrangement of the expected cyclo-octadiene to the

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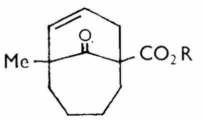
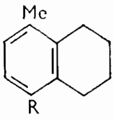
[6] Plattner and Jampolsky, *Helv. Chim. Acta*, 1943, **26**, 687.
[7] Newman and Mekler, *J. Org. Chem.*, 1961, **26**, 336.
[8] McKillop, unpublished work.
[9] Chapman and Borden, *J. Org. Chem.*, 1961, **26**, 4193.

isomeric 1-methyl-3-methylene-1-vinylcyclohexane (II ⟶ XL). The preparation of (II) was finally achieved by conversion of the acid (XIV) into its dimethylamide, reduction by lithium aluminium hydride to the tertiary amine (XLI), and pyrolysis of the corresponding *N*-oxide. The infrared spectrum of the product (II) in carbon disulphide showed bands due to the exocyclic methylene (3064, 1639, and 890 cm.$^{-1}$; ε_{890} 186; $\Delta\nu_{\frac{1}{2}}^{a}$ 7 cm.$^{-1}$) and the trisubstituted double bond (3032, 1668, and 822 cm.$^{-1}$; ε_{822} 70: $\Delta\nu_{\frac{1}{2}}^{a}$ 11 cm.$^{-1}$). In the nuclear magnetic resonance (n.m.r.) spectrum the single vinyl proton appeared as a multiplet centred at τ 4·65 and the exocyclic methylene protons as doublets at τ 5·28 and 5·31 ($J\sim2$ c./sec.). A quantitative estimation carried out on the n.m.r. spectrum by Dr. A. Melera indicated that the diolefin (II) accounted for not less than 90% of the pyrolysate.

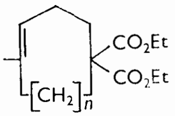
Having now mapped the route to the cyclo-octadiene (II), the synthesis of the nine-membered isocaryophyllene model (III) was undertaken. The tosylate (XXV) reacted rapidly with ethoxide affording the cyclononene *gem*-diester (XXXIV), contaminated with unchanged tosylate. The latter could be eliminated either by distillation or by chromatography, but neither process was completely satisfactory. The first was accompanied by decomposition, and furnished pure diester in low yield; the second produced a new contaminant, the hitherto elusive bicyclic keto-ester (XXVIII), but on balance it was preferable. The presence of this keto-ester was suspected on spectral evidence and confirmed by the preparation of the pyrazolone (XLII) from the crude mixture. As already described, previous attempts to prepare the keto-ester (XXVIII) had suggested that it was very readily rearranged by strong acid to the tetralin acid (XXX); this was confirmed on the pure keto-ester now available. The same mixture afforded a barbituric acid (XLIII) in high yield thus verifying that (XXXIV) was the major component. Alkaline hydrolysis of the cyclononene diester (XXIV) increased the proportion of the bicyclic keto-acid (XXIX), providing a further striking example of the



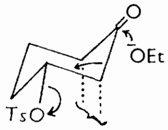
(XXVIII : R = Et)
(XXIX : R = H)



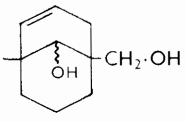
(XXX : R = CO₂H)
(XXXI : R = NH₂)
(XXXII : R = OH)



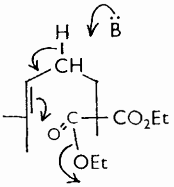
(XXXIII : n = 3)
(XXXIV : n = 4)



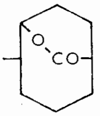
(XXXV)



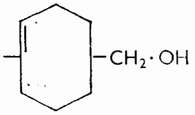
(XXXVI)



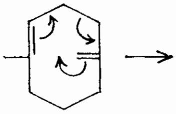
(XXXVII)

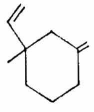


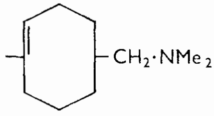
(XXXVIII)



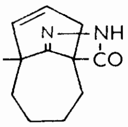
(XXXIX)


(II)

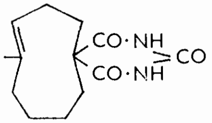

(XL)



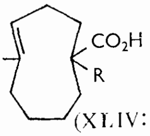
(XLI)



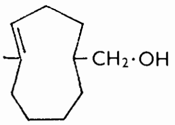
(XLII)



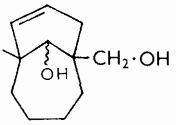
(XLIII)



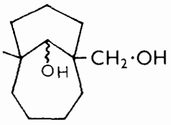
(XLIV : R = CO₂H)
(XLV : R = H)



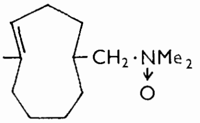
(XLVI)



(XLVII)



(XLVIII)



(XLIX)

transannular mechanism (XXXVII). Since purification was not easy at this stage the mixture of acids (XLV) and (XXIX) was decarboxylated and reduced with lithium aluminium hydride to a separable mixture of the monohydric and dihydric alcohols (XLVI) and (XLVII). The diol was catalytically reduced to the saturated diol (XLVIII) which was also produced by exhaustive lithium aluminium hydride reduction of the bicyclic tosylate (XXV). This comparison established the bicyclic nature of (XLVII) and hence of (XXVIII). The monohydric alcohol (XLVI) was now converted *via* its tosylate into the dimethylamine *N*-oxide (XLIX) which underwent smooth pyrolysis to the desired diene (III).

This product, whose purity was estimated as $\nless 90\%$ (g.l.c.) showed i.r. spectral absorption due to *exo*-methylene (3068, 1637, and 886 cm.$^{-1}$; ε_{886} 160; $\Delta\nu_{\frac{1}{2}}{}^{a}$ 7 cm.$^{-1}$) and trisubstituted (3040, 1664, and 832 cm.$^{-1}$; ε_{832} 45: $\Delta\nu_{\frac{1}{2}}{}^{a}$ 9 cm.$^{-1}$) double bonds, and an equally compatible n.m.r. spectrum. The methyl group appeared as a singlet (τ 8·36), the isolated vinyl proton as a triplet (τ 4·55; *J* 7·7 c./sec.) and the exocyclic methylene protons as doublets at τ 5·1 and 5·27 (*J* 1 c./sec.).

EXPERIMENTAL

t-*Butyl* 5-*Methyl*-9-*oxobicyclo*[3,3,1]*non*-3-*en*-1-*carboxylate* (VIII).—A 500-ml. pressure bottle was charged with ether (10 ml.), concentrated sulphuric acid (0·5 ml.), and the keto-acid [2] (VI) (6 g.), and cooled to 0°; after the addition of isobutene (8 ml.) it was closed and kept in the dark for 3 days. Thereafter the bottle was cooled to $-10°$, and the contents poured on a mixture of ice (25 g.), water (25 ml.), and sodium hydroxide (7 g.). The ethereal layer was separated, the aqueous layer was extracted with ether (2 × 10 ml.), and the combined extracts dried (K_2CO_3) and evaporated. The resulting oil was distilled, yielding the t-*butyl ester* (6·2 g.), b. p. 86°/0·005 mm., n_D^{20} 1·4779 (Found: C, 71·6; H, 8·7. $C_{15}H_{22}O_3$ requires C, 72·0; H, 8·9%). The ester slowly solidified and crystallised from methanol in needles, m. p. 47—49°.

9-*Hydroxy*-5-*methylbicyclo*[3,3,1]*non*-3-*en*-1-*carboxylic Acid* (XII) *and Derivatives* [With Dr. D. B. Jhaveri].—(*a*) The keto-ester [2] (IV) (2 g.) was boiled under reflux with a solution of sodium ethoxide [from sodium (0·172 g.) in ethanol (25 ml.)] and thereafter poured into water. The aqueous phase was made faintly acid with dilute hydrochloric acid and the precipitated oil was taken up in ether, washed successively with water and with aqueous sodium hydrogen carbonate, and dried. On evaporation the ethereal solution afforded the *ethyl ester* of (XII), b. p. 80°/0·05 mm. (Found: C, 69·4; H, 8·8. $C_{13}H_{20}O_3$ requires C, 69·6; H, 8·9%), showing ν_{OH} at 3450 cm.$^{-1}$ and ν_{CO} at 1725 cm.$^{-1}$ (film). It formed a 3,5-*dinitrobenzoate*, m. p. 114—115° (ethanol) (Found: C, 57·35; H, 5·4; N, 7·0. $C_{20}H_{22}O_8N_2$ requires C, 57·4; H, 5·3; N, 6·7%). The sodium hydrogen carbonate extract yielded on acidification the corresponding *acid* (XII) m. p. 168—169° (benzene–light petroleum) (Found: C, 67·3; H, 7·9. $C_{11}H_{16}O_3$ requires C, 67·3; H, 8·2%). The same acid was obtained by alkaline hydrolysis of the above ethyl ester.

(*b*) Sodium borohydride (0·5 g.) was added to a solution of the keto-ester (IV) (5 g.) in aqueous methanol (25 ml., 40%) and the mixture kept overnight at room temperature. Dilution with water followed by ether extraction afforded the ethyl ester of (XII) (4 g.), b. p. 83°/0·04 mm. (Found: C, 69·1; H, 8·8. Calc. for $C_{13}H_{20}O_3$: C, 69·6; H, 8·9%), which was identical (infrared spectrum) with the product described in (*a*).

(*c*) A solution of the methyl ester [2] (VII) (1 g.) in methanolic sodium methoxide, prepared from sodium (0·5 g.) and methanol (30 ml.), was boiled under reflux for 20 hr. The solvent was then removed *in vacuo* and the residual oil was diluted with water, acidified, and extracted with ether (2 × 30 ml.). The ethereal solution was washed with water, dried, and evaporated affording a mixture of acid and ester (i.r. spectrum). Total hydrolysis was effected by boiling methanolic potassium hydroxide, giving the hydroxy-acid (XII) (0·6 g.), m. p. and mixed m. p. 168—170°.

(*d*) A mixture of the ethyl ester (IV) (5 g.) and freshly prepared sodamide (3·9 g.) in xylene (150 ml.) was heated under reflux for 5 days, after which solvent was removed under vacuum, water was added, and the mixture was acidified with hydrochloric acid (6N) and extracted with ether. The extract was washed with water, dried ($MgSO_4$), and evaporated to a viscous oil, showing i.r. spectral bands appropriate to hydroxyl (3400 cm.$^{-1}$) carboxyl (3400–2700 and

1735 cm.$^{-1}$), and ketone (1705 cm.$^{-1}$) groups. A benzene solution slowly deposited crystals of the hydroxy-acid (XII) (m. p. 160—167°) whose i.r. spectrum was identical with that recorded from an authentic specimen.

(*e*) A solution of the ethyl ester (IV) (2 g.) and potassium t-butoxide (from 0·3 g. of potassium) in dry t-butyl alcohol (25 ml.) was boiled under reflux for 20 hr. and worked up as above. The t-*butyl ester* of the hydroxy-acid (XII) crystallised from aqueous methanol; it had m. p. 68—70° (Found: C, 71·9; H, 9·3. $C_{15}H_{24}O_3$ requires C, 71·4; H, 9·6%).

1-*Methylcyclo-oct*-2-*ene*-1,5-*dicarboxylic acid* (X).—A mixture of the keto-ester (VIII) (2·5 g.) and fresh sodamide (2 g.) in xylene (100 ml.) was boiled under reflux for 3 days and concentrated *in vacuo* to a brown solid which was dissolved in water. The alkaline solution was then washed with ether, acidified with mineral acid, and extracted (3 × 30 ml.) with ether. The combined extract was dried and concentrated, affording a semisolid which was washed free of coloured impurities with ether. The *di-acid* had m. p. 143—144° (from benzene–light petroleum) [Found: C, 62·8; H, 8·3%; Equiv. (by titration), 98. $C_9H_{14}(CO_2H)_2$ requires C, 62·25; H, 7·6%; Equiv. 106]. Microhydrogenation led to the absorption of 0·86 molecular equivalents of hydrogen.

By using potassium (1·5 g.) in dry t-butyl alcohol (100 ml.) the same keto-ester (VIII) (3 g.) was converted, after 30 hours' refluxing, into an oily mixture showing carboxyl (3400—2700 cm.$^{-1}$), ketone (1705 cm.$^{-1}$), and t-butoxycarbonyl (1735, 1385, 1365, and 1260 cm.$^{-1}$) groups. This mixture was hydrolysed with methanolic potassium hydroxide and the resulting mixture of acids was esterified with diazomethane and fractionally crystallised from light petroleum. This yielded the keto-ester [2] (VII), m. p. and mixed m. p. 80°, and a gummy residue which was rehydrolysed with methanolic potassium hydroxide to the diacid (X) whose i.r. spectrum was identical with that previously obtained.

5-*Methylcyclo-oct*-4-*ene*-1-*carboxylic Acid* (XIV).—The di-acid (X) (1·3 g.) mixed with copper dust (1 g.) was heated in a sealed Carius tube at 270° for 22 hr. The dark oily product was taken up in ether, and extracted with aqueous sodium hydroxide (3 × 10 ml.; 1N). Acidification of the alkaline extract afforded a pale yellow oil which on distillation yielded the monocarboxylic acid (0·84 g.), b. p. 90—92°/0·08 mm. [Found: C, 71·0; H, 8·5%; *M* (mass spec.), 170 ± 3. $C_{10}H_{16}O_2$ requires C, 71·4; H, 9·6%; *M*, 168]. The infrared spectrum showed carboxyl (3330—2800, 1720—1705, and 1260 cm.$^{-1}$) and olefin (830 cm.$^{-1}$) bands. The acid gave an *amide*, m. p. 174° (from ethyl acetate), (Found: C, 71·6; H, 10·3; N, 8·2. $C_{10}H_{17}NO$ requires C, 71·8; H, 10·25; N, 8·4%).[10]

Repetition of the above decarboxylation in the absence of copper dust gave a crystalline acid, m. p. 138—140°, shown to be (VI) [2] by mixed m. p. and by comparison of infrared spectra.

Ozonolysis.—The acid (XIV) (0·55 g.) in chloroform was cooled to −70° and ozone was passed through until a starch–iodide test proved positive. The mixture was allowed to come to room temperature, treated with hydrogen peroxide (3 ml., 30%) and acetic acid (4 ml.), and stirred for 1 hr. on the steam-bath. The mixture was thereafter diluted with water, treated with ferrous sulphate to destroy peroxides, and extracted with ether (4 × 40 ml.). The extract afforded 7-*oxo-octan*-1,3-*dicarboxylic acid* (XVI) (0·44 g.) as a viscous oil, b. p. 138—140/0·3 mm., n_D^{20} 1·4432 (Found: C, 55·4; H, 7·2. $C_{10}H_{16}O_5$ requires C, 55·5; H, 7·5%).

Triethyl Oct-7-*yne*-1,3,3-*tricarboxylate* (XVII).—Triethyl propane-1,1,3-tricarboxylate [11] (6·9 g.) was added to a solution of sodium ethoxide [from sodium (0·62 g.) in ethanol (25 ml.)] and heated to 40°. To the resulting mixture, 5-bromopent-1-yne (3·9 g.) was added dropwise during 20 min. with stirring and the mixture was thereafter heated to reflux for 2 hr., then diluted with water and extracted with ether (3 × 30 ml.), yielding the *acetylenic triester* (5·5 g.), b. p. 154—155°/0·9 mm., n_D^{21} 1·4530 (Found: C, 62·2; H, 7·9. $C_{17}H_{26}O_6$ requires C, 62·6; H, 8·0%); ν_{CO} 1730 cm.$^{-1}$, $\nu_{\equiv CH}$ 3250 cm.$^{-1}$

Triethyl 7-*Oxo-octane*-1,3,3-*tricarboxylate*.—A solution of the acetylenic ester (3·6 g.) in methanol (10 ml.) was added slowly to a catalyst mixture prepared by warming mercuric oxide (0·5 g.), boron trifluoride etherate (0·2 ml.), trichloroacetic acid (10 mg.). and methanol (1 ml.). After being shaken for 2·5 hr. the mixture was poured into sulphuric acid (6N) and extracted with ether, affording the *keto-triester* (2·8 g.), b. p. 140°/0·06 mm., n_D^{23} 1·4489 (Found: C, 59·1; H, 8·2. $C_{17}H_{28}O_7$ requires C, 59·3; H, 8·2%). The i.r. spectrum showed a broad carbonyl band at 1735—1700 cm.$^{-1}$, but no acetylenic C–H band.

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[10] Baumgarten, Bowen, and Okamoto, *J. Amer. Chem. Soc.*, 1957, **79**, 3145.

[11] Ruzicka, de Almeida, and Brack, *Helv. Chim. Acta*, 1934, **17**, 183.

7-*Oxo-octan*-1,3-*dicarboxylic Acid* (XVI).—The keto-triester (3·8 g.) was refluxed for 8 hr. with a solution of barium hydroxide (16 g.) in water (200 ml.), then cooled, filtered, acidified with hydrochloric acid (6N), and evaporated to dryness under vacuum. The residue was extracted with boiling ethanol and yielded the keto-dicarboxylic acid (10%), b. p. 170°/0·14 mm., n_D^{21} 1·4440 (Found: C, 55·35; H, 7·6. Calc. for $C_{10}H_{16}O_5$: C, 55·5; H, 7·5%). The i.r. spectrum was identical with that recorded from the ozonolysis product. A better yield (77%) was obtained by using the procedure of Sorm and Dolejs.[12]

An attempted preparation of a *p*-bromophenacyl ester, by the standard method,[13] afforded a solid, m. p. 135—136° (ethanol), identical (mixed m. p.) with bis-*p*-bromophenacyl glutarate (Found: C, 48·05; H, 3·45. Calc. for $C_{21}H_{18}Br_2O_6$: C, 47·9; H, 3·45%). A repetition of this experiment in the absence of *p*-bromophenacyl bromide yielded cyclopropyl methyl ketone, which was extracted from the mixture by ether and identified as its 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 146—151°.

Ethyl 3-*Methyl*-2-*oxocycloheptanecarboxylate* (XX).—A mixture of 2-methylcycloheptanone[14] (75 g.) and diethyl oxalate (103 g.), cooled to −10°, was added dropwise to a stirred solution of sodium ethoxide [from sodium (13·8 g.) in anhydrous ethanol (220 ml.)] cooled to −10°. The resulting solution was stirred overnight at 0° and then at room temperature for 72 hr. The mixture was then poured on crushed ice, acidified, and extracted several times with ether. The combined extracts were washed, dried, and concentrated, affording a clear red oil (XIX), which was decarbonylated by heating it with powdered glass for 6 hr. at 200—220°. Fractional distillation of the resultant black oil furnished the β-*keto-ester* (42 g.), b. p. 80—84°/0·05 mm., n_D^{21} 1·4609 (Found: C, 66·2; H, 8·6. $C_{11}H_{18}O_3$ requires C, 66·6; H, 9·1%). The *pyrazolone* was prepared by heating the ester (2 g.) with hydrazine hydrate (1 g.; 100%) in methanol (10 ml.) for 1·5 hr., followed by removal of the solvent. Crystallised from aqueous ethanol it had m. p. 222—224° (Found: C, 65·2; H, 8·5; N, 17·0. $C_9H_{14}N_2O$ requires C, 65·0; H, 8·5; N, 16·85%).

When an old batch of anhydrous ethanol was used, the clear red oil (XIX) deposited the *lactone* (XXI), m. p. 175—177° (aqueous ethanol) (Found: C, 66·2; H, 6·7. $C_{10}H_{12}O_3$ requires C, 66·65; H, 6·70%). The i.r. spectrum showed bonded OH (3330 cm.$^{-1}$), conjugated lactone (1720 cm.$^{-1}$), and double-bond absorption (1660 and 1640 cm.$^{-1}$); $\lambda_{max.}$ 295 mμ (ε 18,400). The corresponding *acetate*, m. p. 118° (ethyl acetate) (Found: C, 64·7; H, 6·1. $C_{12}H_{14}O_4$ requires C, 64·85; H, 6·35%), showed unresolved carbonyl absorption (1750—1720 cm.$^{-1}$) and double-bond absorption (1680 and 1630 cm.$^{-1}$); $\lambda_{max.}$ 289 mμ (ε 18,000). The related lactone (XXII)[6] showed $\lambda_{max.}$ 290 mμ (ε 19,300), and its acetate $\lambda_{max.}$ 285 mμ (ε 20,200).

Ethyl 1-2′-*Formylethyl*-3-*methyl*-2-*oxocycloheptanecarboxylate* (XXIII).—Acrolein was condensed with the above β-keto-ester as described[2] for a related compound, furnishing the *aldehyde-ester* in 65% yield, b. p. 130—132°/0·1 mm. n_D^{21} 1·4790 (Found: C, 66·0; H, 9·0. $C_{14}H_{22}O_4$ requires C, 66·1; H, 8·7%). Oxidation of the aldehyde with silver oxide in the usual manner[15] furnished the related *acid ester*, b. p. 161°/0·7, m. p. 30—32°, n_D^{20} 1·4772 (Found: C, 62·1; H, 8·1. $C_{14}H_{22}O_5$ requires C, 62·2; H, 8·2%).

Ethyl 7-*Hydroxy*-6-*methyl*-10-*oxobicyclo*[4,3,1]*decane*-1-*carboxylate* (XXIV).—A mixture of the aldehyde-ester (XXIII) (3 g.), dioxan (20 ml.), and concentrated hydrochloric acid (20 ml.) was heated on the steam-bath for 3 hr., and then left at room temperature for 2 hr. The mixture was poured into saturated brine (100 ml.) and extracted with ether (2 × 50 ml.). The ethereal solution was dried and evaporated, giving the bicyclic alcohol (2·37 g.), b. p. 131°/0·07 mm., n_D^{20} 1·4970, ν_{OH} 3400 cm.$^{-1}$ (Found: C, 65·9; H, 7·4. $C_{14}H_{22}O_4$ requires C, 66·1; H, 8·7%).

Attempted cyclisation of the aldehyde-ester (XXIII) to the bicyclo-olefin (XXVIII) by concentrated sulphuric acid, using the previously described[2] procedure, yielded an intractable neutral fraction and 5,6,7,8-*tetrahydro*-4-*methyl*-1-*naphthoic acid* (20%), m. p. 190—192° (ethyl acetate) (Found: C, 75·6; H, 7·4. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%). The i.r. spectrum showed carboxyl (3100—2800 and 1695 cm.$^{-1}$) and aromatic skeletal (1600 and 1500 cm.$^{-1}$) bands; $\lambda_{max.}$ 242 (ε 8910), and 284 mμ (ε 1260). The same acid (XXX) was the only recognisable product from sulphuric acid dehydration[2] of the bicyclic alcohol (XXIV).

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[12] Sorm and Dolejs, *Coll. Czech. Chem. Comm.*, 1954, **19**, 559.

[13] Vogel, " A Textbook of Practical Organic Chemistry," Longmans, Green and Co., London, 1956, p. 362.

[14] Giraitis and Bullock, *J. Amer. Chem. Soc.*, 1937, **59**, 951.

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

4-*Methyl*-1-*naphthoic Acid.*—A mixture of selenium powder (250 mg.) and 5,6,7,8-tetrahydro-4-methylnaphthoic acid (250 mg.) was heated at 300° for 20 hr.; the cooled melt was then extracted with ether (5 × 5 ml.) and the ethereal solution was washed with aqueous sodium hydroxide (4N). Acidification of the washings afforded the naphthoic acid, m. p. 173—175° (aqueous acetic acid) (83 mg.), undepressed on admixture with authentic 4-methyl-1-naphthoic acid.[16]

5,6,7,8-*Tetrahydro*-4-*methyl*-1-*naphthylamine* (XXXI).—Treatment of the acid (XXX) with hydrazoic acid (4·5 moles) in the usual manner,[17] gave the *naphthylamine*, b. p. 102°/0·8 mm., n_D^{20} 1·5841 (Found: C, 81·7; H, 9·1; N, 8·7. $C_{11}H_{15}N$ requires C, 81·9; H, 9·4; N, 8·7%), which yielded a *benzoyl derivative*, m. p. 207° (methanol) (Found: C, 81·4; H, 7·2; N, 5·1. $C_{18}H_{19}NO$ requires C, 81·5; H, 7·2; N, 5·3%).

4-*Methyl*-5,6,7,8-*tetrahydro*-1-*naphthol* (XXXII). The naphthylamine (0·1 g.) dissolved in sulphuric acid [concentrated acid (0·1 ml.) diluted with water (2 ml.)] was cooled to 0° and treated with sodium nitrite (0·1 g.) in water (1 ml.), with stirring. The mixture was stirred at 0° for 30 min. and then at 50° for 20 min. and finally steam-distilled. The distillate was extracted with ether, affording the naphthol, m. p. 83—84° (light petroleum), undepressed on admixture with a genuine specimen.[7]

Diethyl 5-*Methylcyclo-oct*-4-*ene*-1,1-*dicarboxylate* (XXXIII).—A solution of the bicyclic alcohol[2] (XXVI) (2·1 g.) and toluene-*p*-sulphonyl chloride (2·1 g.) in dry pyridine (10 ml.) was kept at room temperature for 5 days, poured on ice (10 g.), and kept for a further 2 days. The mixture was extracted with ether (3 × 10 ml.), washed with mineral acid, sodium hydrogen carbonate solution, and water, and dried. Removal of the solvent left the crude tosylate (XXVII) as a yellow gum (ν 1605, 1500, 1360, and 1180 cm.$^{-1}$) which was added to a solution of sodium ethoxide [from sodium (0·64 g.) in anhydrous ethanol (11 ml.)] and stirred for 5 min. at room temperature and then under reflux for a further 2 hr. The mixture was thereafter diluted with water (75 ml.), acidified, and extracted with ether. The ethereal solution was washed, dried, and evaporated, giving the crude diester (XXXIII), contaminated with unchanged tosylate. The mixture was chromatographed in benzene on Woelm grade 1 neutral alumina; the diester was eluted with benzene, and the unchanged tosylate with 50% benzene–chloroform. Alternatively, direct distillation of the mixture afforded the *diester*, b. p. 120—122°/0·2 mm., n_D^{25} 1·4722 (0·84 g.) (Found: C, 67·6; H, 8·7. $C_{15}H_{24}O_4$ requires C, 67·2; H, 9·0%), the unchanged tosylate being left as a black, intractable glass. The pure diester showed i.r. spectral absorption at 1725, 1260 cm.$^{-1}$ (ester), and 830 cm.$^{-1}$ (double bond).

5-*Hydroxymethyl*-1-*methylbicyclo*[3,3,1]*non*-2-*en*-9-*ol* (XXXVI).—A solution of the diester (XXXIII) (5 g.) in anhydrous ether (25 ml.) was added during 1 hr. to a stirred solution of lithium aluminium hydride (10 g.) in ether (350 ml.). The mixture was refluxed for 10 hr., excess of hydride was destroyed by the addition of ethyl acetate, and saturated aqueous sodium sulphate was then added to aggregate the inorganic salts. The ethereal solution, with the ether washings of the solid inorganic precipitate, was washed, dried and evaporated, yielding the *diol*. m. p. 134—136° (benzene–light petroleum) (Found: C, 72·8; H, 9·45. $C_{11}H_{18}O_2$ requires C, 72·5; H, 10·0%). It showed hydroxyl (3400 and 1050 cm.$^{-1}$) and *cis*-disubstituted double bond (710 cm.$^{-1}$) absorption in the infrared region, identical with the slightly less pure product obtained by similar reduction of the bicyclic keto-ester (V).

5-*Methylcyclo-oct*-4-*ene*-1-*carboxylic Acid* (XIV).—A solution of the diester (12·6 g.) and potassium hydroxide (20 g.) in water (50 ml.) and methanol (400 ml.) was boiled under reflux for 16 hr., distilled under vacuum to remove the methanol, diluted with water, and washed with ether. The aqueous solution was then acidified with mineral acid and extracted with ether. Evaporation left an oil which distilled with decomposition, b. p. 166—200°/0·8 mm. (5·25 g.). The product deposited a solid (0·35 g.), m. p. 137—140° (benzene), identical (i.r. spectra and mixed m. p.) with the bicyclic acid (VI). The i.r. spectrum of the residual oil showed carboxyl (3500—2700 and 1725 cm.$^{-1}$) and lactone (1745 cm.$^{-1}$) absorption, and the proportion of lactone increased with further distillation. Separation was conveniently deferred to a later stage. The acid was identified as that previously obtained from (X), by comparison of their i.r. spectra and by comparison of the amide (m. p. and mixed m. p. 174°) obtained from both sources. The acid also furnished a pure *methyl ester* (diazomethane), b. p. 69°/0·1 mm., n_D^{25} 1·4650 (Found: C, 72·3; H, 9·85. $C_{11}H_{18}O_2$ requires C, 72·5; H, 10·0%).

[16] Cook and Galley, *J.*, 1931, 2012.

[17] Wolff, "Organic Reactions," Vol. III, John Wiley and Sons, London, 1947, p. 307.

5-*Hydroxymethyl*-1-*methylcyclo-oct*-1-*ene* (XXXIX).—A solution of the methyl ester of (XIV) (3·25 g.) in dry ether (20 ml.) was added dropwise to a stirred slurry of lithium aluminium hydride (2·1 g.) in ether (50 ml.). Stirring was continued under gentle reflux for 2 hr. and for a further 18 hr. at room temperature. Excess of hydride was then decomposed with ethyl acetate and sulphuric acid (6N) added. The ethereal layer was washed, dried, and evaporated, leaving *alcohol* (2·2 g.), b. p. 104—106°/12 mm., n_D^{18} 1·4938 (Found: C, 77·7; H, 11·4. $C_{10}H_{18}O$ requires C, 77·9; H, 11·8%). The i.r. spectrum showed hydroxyl (3500 cm.$^{-1}$) and trisubstituted double-bond (830 cm.$^{-1}$) absorption. The *acetate*, b. p. 135°/19 mm., n_D^{21} 1·4730 (Found: C, 73·35; H, 10·3. $C_{12}H_{20}O_2$ requires C, 73·4; H, 10·3%), showed bands at 1740 and 832 cm.$^{-1}$.

Boric Acid Dehydration.—A mixture of the alcohol (XXXIX) (0·38 g.) and boric acid (0·14 g.) was heated slowly to 300° and kept at that temperature for 40 min. The cooled mixture was extracted with ether to give a yellow oil (0·18 g.) which distilled at 175—185° as a mixture of *olefins* (Found: C, 88·2; H, 11·1. $C_{10}H_{16}$ requires C, 88·2; H, 11·8%). G.l.c. showed two components only, in 25—40% and 60—75% abundance. The i.r. spectrum (in CS_2) showed exocyclic methylene absorption (3063, 1633, and 884 cm.$^{-1}$) and trisubstituted double-bond absorption (3008, 1665, and 814 cm.$^{-1}$). The low value of ε_{884} (43) compared with that found for caryophyllene (160) and for pure (II)—(see below) indicated that (II) was the minor component. The n.m.r. spectrum shows the exomethylene protons as a doublet at τ 5·2 and 5·3.

Acetate Pyrolysis.—The acetate (0·5 g.) of the alcohol (XXXIX) was passed through a 1-m. column filled with glass helices heated to 500—550°, in a slow stream of nitrogen. The condensate was taken up in ether, washed with aqueous sodium hydrogen carbonate, dried, and evaporated. The residue (0·2 g.), b. p. 136—139°, n_D^{17} 1·4700, showed two equally intense spectral bands at 890 and 910 cm.$^{-1}$. These were assigned to *exo*-methylene and vinyl groups, respectively, and indicated the probable structure (XL) for the product.

5-*Dimethylaminomethyl*-1-*methylcyclo-oct*-1-*ene* (XLI).—The acid (XIV) (4·7 g.) and oxalyl chloride (4·7 ml.) in anhydrous benzene (50 ml.) were kept overnight at room temperature and thereafter the solvent was removed under vacuum. The residual acid chloride (ν 1815 cm.$^{-1}$) which was contaminated with lactone (ν_{CO} 1745 cm.$^{-1}$), was added during 15 min. to concentrated aqueous ammonia (25 ml.). The tacky solid was washed with water and then triturated with light petroleum, giving 5-*methylcyclo-oct*-4-*en*-1-*carboxamide* (3·73 g.), m. p. 174—175° (ethyl acetate) (Found: C, 71·6; H, 10·3; N, 8·2. $C_{10}H_{17}NO$ requires C, 71·8; H, 10·25; N, 8·4%), ν_{CO} 1660. The light petroleum washings afforded the *lactone* (XXXVIII) (0·45 g.), b. p. 66°/0·5 mm., n_D^{22} 1·4770 (Found: C, 71·5; H, 9·0. $C_{10}H_{16}O_2$ requires C, 71·4; H, 9·6%), ν_{CO} 1745 cm.$^{-1}$. Similar use of aqueous dimethylamine (33%) afforded a crude dimethylamide which could not be purified (ν_{CO} 1650 and 1745 cm.$^{-1}$). The crude dimethylamide (4·6 g.) was dissolved in dry ether (35 ml.) and added slowly to a stirred suspension of lithium aluminium hydride (1 g.) in anhydrous ether (35 ml.). The mixture was stirred for 24 hr. at room temperature and excess of hydride was decomposed with ethyl acetate. Saturated sodium sulphate was then added to aggregate the inorganic salts and these were filtered off. The ethereal layer and the inorganic precipitate were separately extracted with sulphuric acid and the combined extract was basified and re-extracted with ether, affording the *tertiary amine* (XLI) (3·5 g.), b. p. 108—109°/14 mm., n_D^{20} 1·4760 (Found: C, 79·3; H, 12·6; N, 7·45. $C_{12}H_{23}N$ requires C, 79·5; H, 12·8; N, 7·7%); *picrate*, m. p. 123—124° (ethanol) (Found: C, 52·4; H, 6·4; N, 13·5. $C_{18}H_{26}O_7N_4$ requires C, 52·7; H, 6·4; N, 13·65%).

The same tertiary amine was obtained from the primary amide of (XIV) by reduction to the primary amine, b. p. 114—116°/22 mm., n_D^{17} 1·4978 (Found: C, 78·1; H, 12·7; N, 8·9. $C_{10}H_{19}N$ requires C, 78·35; H, 12·5; N, 9·1%), followed by methylation, but, contrary to recent reports,[10] this route offered no advantage in yield.

1-*Methyl*-5-*methylenecyclo-oct*-1-*ene* (II).—Hydrogen peroxide (2 g., 35%) was added during 20 min. to the tertiary amine (XLI) (1·0 g.) in methanol (2 ml.) at 0° and this solution was kept at room temperature for 48 hr. A trace of platinum black was then added and the mixture was stirred for 24 hr. and filtered. Evaporation of the filtrate at 35°, under vacuum, gave crude amine *N*-oxide (0·94 g.) which afforded a *picrate*, m. p. 115—116° (ethanol) (Found: C, 50·7; H, 6·2; N, 13·2. $C_{18}H_{26}N_4O_8$ requires C, 50·7; H, 6·15; N, 13·2%). The *N*-oxide (0·9 g.) and water (1 ml.) in a 10-ml. flask lightly packed with glass wool, and connected to two traps in series, each cooled to —10°, was heated slowly to 100° and then to 160° over a further 20 min., the system being under reduced pressure (15 min.). The distillate was taken up in ether, washed with sulphuric acid (2N), dried, and evaporated, yielding the diene (II) (0·435 g.), b. p. 138—140°, n_D^{26} 1·4822. The infrared spectrum (CS_2) showed exocyclic methylene (3064, 1639, and 890 cm.$^{-1}$; ε_{890} 186, $\Delta_{\frac{1}{2}}^{a}$ 7 cm.$^{-1}$) and trisubstituted double-bond (3032, 1668, and 822 cm.$^{-1}$; ε_{882} 70, $\Delta_{\frac{1}{2}}^{a}$ 11 cm.$^{-1}$) absorption bands.

Diethyl 5-*Methylcyclonon*-4-*ene*-1,1-*decarboxylate* (XXXIV).—By using the procedure described for (XXXIII), the hydroxyketo-ester (XXIV) was converted into the tosylate (XXV) which was then used without purification in the bridge-fission reaction. Distillation gave the required diester (20%), b. p. 114/0·7 mm., n_D^{20} 1·4812 (Found: C, 68·4; H, 9·5. $C_{16}H_{26}O_4$ requires C, 68·05; H, 9·5%). Alternatively, the crude product was chromatographed on Woelm grade 1 neutral alumina. The impure diester, its i.r. spectrum showing evidence of a *cis*-disubstituted double bond (710 cm.$^{-1}$) and the fine structure typical of the bicyclo-series, was eluted with benzene, and the unchanged tosylate with chloroform. The benzene eluate showed two spots on thin-layer chromatography and the components were identified as follows: (*a*) The impure ester (0·5 g.) in hydrazine hydrate (0·5 g., 100%) in methanol (5 ml.) was refluxed for 2 hr., and then concentrated; the resulting *pyrazolone* (XLII) sublimed at 140°/0·7 mm., m. p. 163—164° (Found: C, 70·8; H, 7·9; N, 13·6. $C_{12}H_{16}N_2O$ requires C, 70·6; H, 7·9; N, 13·7%). (*b*) The *barbiturate* (XLIII), prepared by the standard method,[18] had m. p. 257—259° (from aqueous methanol) (Found: C, 62·6; H, 7·0; N, 11·1. $C_{13}H_{18}N_2O_3$ requires C, 62·4; H, 7·25; N, 11·2%).

Hydrolysis of the pure diester (XXXIV) with methanolic potassium hydroxide (16 hr.; reflux) gave a yellow gum which crystallised from benzene–light petroleum and then had m. p. 145—146°. The i.r. spectrum of this bicyclic *oxo-acid* (XXIX) showed carboxyl (3300—2800 and 1740 cm.$^{-1}$), ketone (1700 cm.$^{-1}$), and *cis*-disubstituted double-bond (710 cm.$^{-1}$) absorption bands (Found: C, 69·2; H, 7·5. $C_{12}H_{16}O_3$ requires C, 69·2; H, 7·7%). It afforded a *methyl ester*, m. p. 63—64° (hexane) (Found: C, 70·4; H, 8·2. $C_{13}H_{18}O_3$ requires C, 70·2; H, 8·2%), which was reduced by sodium borohydride and subsequently hydrolysed to 10-*hydroxy*-6-*methylbicyclo*[4,3,1]*dec*-7-*ene*-1-*carboxylic acid*, m. p. 103—105° (light petroleum) (Found: C, 68·8; H, 8·6. $C_{12}H_{18}O_3$ requires C, 68·5; H, 8·6%). This methyl ester (100 mg.) in concentrated sulphuric acid (5 ml.) was left for 30 hr. at room temperature and then poured on ice, affording 5,6,7,8-tetrahydro-4-methyl-1-naphthoic acid (XXX) (20 mg.), m. p. and mixed m. p. 190°, as the only acidic product.

5-*Hydroxymethyl*-1-*methylcyclonon*-1-*ene* (XLVI) *and* 1-*Hydroxymethyl*-6-*methylbicyclo*[4,3,1]-*dec*-7-*en*-10-*ol* (XLVII).—The ester mixture (XXXIV) and (XXVIII) (4·77 g.) and potassium hydroxide (2·8 g.) in methanol (50 ml.) were kept at room temperature for 5 days, diluted with water, washed with ether, and acidified. The mixture of acids was extracted with ether, dissolved in pyridine (25 ml.), and refluxed gently for 2 hr. with glass powder (0·5 g.). The mixture was poured into excess of hydrochloric acid (6N) and extracted with ether, yielding a semi-solid mixture of acids (XV and XXXIX) which could not be separated completely. The mixture was esterified (diazomethane) and reduced with lithium aluminium hydride in ether by the general procedure already described. The products which showed no carbonyl absorption in the infrared spectrum, were chromatographed on Woelm grade 1 neutral alumina (60 g.). The *alcohol* (XLVI) (0·61 g.), eluted with chloroform, had b. p. 88—89°/0·8 mm., n_D^{18} 1·4998 (Found: C, 78·8; H, 11·9. $C_{11}H_{20}O$ requires C, 78·5; H, 12·0%) and showed spectral bands at 3400 and 820 cm.$^{-1}$. The *diol* (XLVII) (0·84 g.), eluted with 50% methanol–chloroform, had m. p. 97—99° (ethyl acetate–light petroleum) (Found: C, 73·5; H, 10·3. $C_{12}H_{20}O_2$ requires C, 73·4; H, 10·3%) and showed spectral absorption at 3300—3250 and 710 cm.$^{-1}$.

1-*Hydroxymethyl*-6-*methylbicyclo*[4,3,1]*decan*-10-*ol* (XLVIII).—(*a*) The tosylate (XXVII) (14 g.) in ether (100 ml.) was added during 30 min. to a stirred suspension of lithium aluminium hydride (14 g.) in ether (250 ml.) and thereafter refluxed with stirring for 24 hr. The product, isolated by the usual procedure, showed traces of carbonyl absorption (i.r.) and could not be purified by chromatography. It was re-reduced with lithium aluminium hydride (10 g.) for 30 hr., distilled (b. p. 130°/1 mm.), and chromatographed on Woelm grade 1 neutral alumina. Elution with benzene and with 10% ether in benzene gave intractable oils; elution thereafter with 50% ether–benzene and with ether gave the solid *diol* (1·58 g.), m. p. 86—88° (hexane–light petroleum) (Found: C, 72·6; H, 10·9. $C_{12}H_{22}O_2$ requires C, 72·7; H, 11·2%).

(*b*) The unsaturated diol (XLVII) (35 mg.) in ethanol (5 ml.) was reduced in the presence of

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[18] Vogel, " A Textbook of Practical Organic Chemistry," Longmans, Green and Co., London, 1956, p. 1001.

palladium–charcoal (20 mg., 10%), affording the solid diol, m. p. and mixed m. p. 85—88°.

1-*Methyl*-5-*methylenecyclonon*-1-*ene* (III).—A solution of the alcohol (XLVI) (1·43 g.) and toluene-*p*-sulphonyl chloride (1·65 g.) in dry pyridine (25 ml.) was kept for 4 days at room temperature, and worked up by the method described for (XXVII), affording crude tosylate (2·28 g.) with the expected infrared spectrum. A mixture of this tosylate (2 g.) and aqueous dimethylamine (30%; 20 ml.) was boiled for 16 hr., cooled, diluted with water and extracted with ether (3 × 50 ml.). The ethereal solution was extracted with hydrochloric acid (6N; 5 × 20 ml.) and on basification this extract afforded 5-*dimethylaminomethyl*-1-*methylcyclonon*-1-*ene* (0·46 g.), b. p. 116°/17 mm., n_D^{24} 1·4800 (Found: C, 79·7; H, 13·0; N, 7·0. $C_{13}H_{25}N$ requires C, 79·9; H, 12·9; N, 7·2%). The infrared spectrum showed *N*-methyl (2725 cm.$^{-1}$) and double-bond (825 cm.$^{-1}$) absorption bands. The corresponding *N*-oxide, prepared by the general method already described, was characterised as its *picrate*, m. p. 107—110° (aqueous ethanol) (Found: C, 51·8; H, 6·2; N, 12·85. $C_{19}H_{28}N_4O_8$ requires C, 51·8; H, 6·4; N, 12·7%), and pyrolysed in the manner already described for the preparation of (II), yielding the *diene* (III), b. p. 166—168° (Found: C, 87·7; H, 12·1. $C_{11}H_{18}$ requires C, 87·9; H, 12·1%).

Micro analyses were by Mr. J. M. L. Cameron, B.Sc., and his staff, mass spectra were measured by Dr. R. I. Reed and his associates, and n.m.r. spectra (neat) on an A.E.I. R.S.2 instrument by Miss M. Mackay unless otherwise acknowledged. Infrared spectra of solutions were measured by Mrs. F. Lawrie on a Unicam S.P. 100 instrument; where no solvent is mentioned the spectra were recorded on liquid films or Nujol mulls on a Perkin-Elmer model 137 Infracord. We are indebted to the D.S.I.R. and to The Salters' Company for the awards of scholarships (to A. McK.).

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