STUDIES ON CYCLOOCTANES—I

1,5-BISMETHYLENECYCLOOCTANE

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Abstract—The preparation and the addition reactions of 1,5-bismethylenecyclooctane are described, together with a novel synthesis of the bicyclo[3.3.2]decane ring system.

These researches were undertaken to determine the extent to which the three dimensional structure of an 8-membered ring would lead to interaction between the π-electron systems in 1,5-bismethylenecyclooctane, I. Interaction between non-conjugated double bonds has previously been demonstrated;[1] in particular the formation of a Diels–Alder adduct from tetramethylenecyclooctane,[2] and of the adamantane derivatives IV and V from the bicyclononanes II and III have been reported.[3]

I

II, X = O
III, X = CH₂

IV, X = O
V, X = CH₂

VI
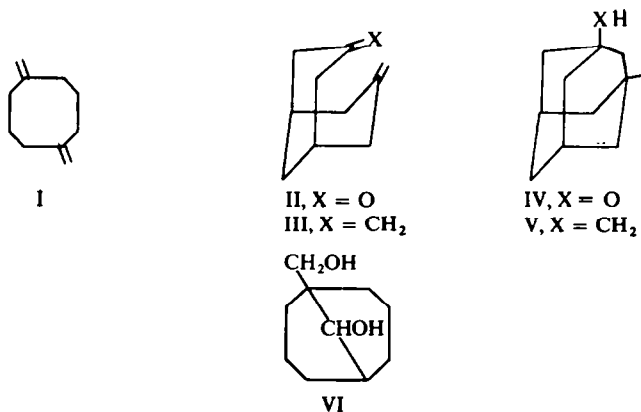
The starting material for the preparation of I was 1-ethoxycarbonylbicyclo[3.3.1]nonan-9-one,[4] reduction led to the diol VI, the monotosylate of which underwent a fragmentation reaction[5] to produce 5-formylmethylenecyclooctane. The structure of the aldehyde was confirmed by conversion (by Wolff–Kishner reduction and oxidation) to 5-methylcyclooctanone[6] and formaldehyde, the series of reactions providing a convenient alternative route to the octanone. (The fission of the exocyclic methylene could be achieved by ozonolysis or by the use of osmic acid-periodate, the latter method gave a purer product[7].) The aldehyde XVIII was converted to the diene I by the successive stages of oximation, aluminohydride reduction, N-methylation and pyrolysis of the methohydroxide. The product from the Hofmann elimination was

homogeneous (GLC), absorbed two moles of hydrogen over Pt or Pd in ethanolic solution (but only 1·5 moles in acetic acid solution) and showed the typical infrared absorptions for terminal methylenes, the out-of-plane bending absorption (885 cm^{-1}) being particularly intense.[5] The PMR spectrum consisted of a 4-proton singlet at τ 5·34, an 8-proton multiplet at τ 7·9 and a further multiplet (4 protons) at τ 8·25. Taking the method of preparation into account, these properties are consistent only with structure I; attempts to provide further evidence by oxidative degradation were unsuccessful.

The diene I failed to react with tetracyanoethylene; the discrepancy between this observation and the results of Benson and Williams[2] is not hard to understand, for the adduct expected from I would include a bicyclo[3.3.0]octane moiety and hence possess several eclipsing interactions, four of which are removed from the Benson and Williams adduct where C_5 and C_{11} are trigonal.[8] The diene I added one mole of bromine to give two bromides in unequal amounts, only the major product was investigated further. It was bicyclic since it analysed for $C_{10}H_{16}Br_2$ and showed no olefinic protons in the PMR spectrum: the presence of a 2-proton singlet at τ 6·8 (CH_2Br) and characteristic additional C-H stretching and scissoring frequencies at 2996 and 1490 cm^{-1} [9] show the dibromide to be the bicyclononane derivative VII. Reaction of I with a mixture of hydrochloric and acetic acids gave an alcohol, $C_{10}H_{18}O$, and a chloride, $C_{10}H_{17}Cl$, (a small amount of acetate ester also was produced but could not be separated from the chloride; this last was obtained pure after mild hydrolysis destroyed the ester). Both had similar PMR spectra with absorptions as highfield as τ 9·6; the absence of olefinic protons, and of any CH_3 or CH_2X groups excluded all simple addition products of I other than bicyclo[3.3.2]-decanes, and bicyclo[3.3.2]decan-1-ol, VIII, was synthesized independently as described below, and shown to be identical with the hydration product of I.
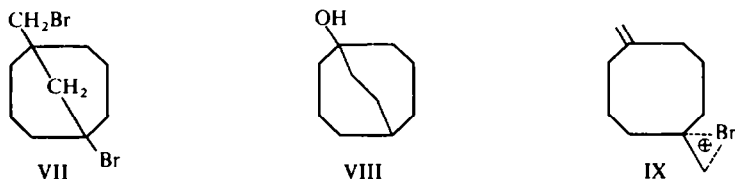

By analogy with addition to II and III, a bicyclononanol would have been anticipated from the hydration of I; however the bicyclodecane skeleton can permit more flattening round the bridgehead and hence more stabilization of the positive charge. The extra methylene bridge in the tricyclic ions derived from II and III would prevent any increase in flexibility accruing from the bridging of positions 3 and 7 by an ethylene rather than a methylene unit, and the extra endocyclic carbon would serve merely to distort the ideal geometry of the adamantane skeleton. There remains the question of why I forms bicyclononane in additions of bromine. The introduction of a bromine substituent could not affect the relationship between geometry and stability in these bicyclic ions; the intermediate in the bromination of I must therefore be a bromonium ion, IX, derived by reaction at one π-bond only. The gain in stability resulting from the neighbouring group effect of bromine[10] apparently outweighs the more favourable geometry of the bicyclic systems vis-a-vis the 8-membered ring.
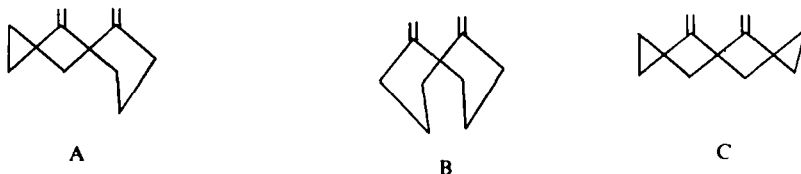
The IR and UV spectra of I do not indicate any interaction between the two π-electron systems, although from models there would seem to be a high likelihood of the two double bonds being aligned roughly parallel to each other. Three models for I can be constructed, all free from eclipsing strain, and all have the same mutual alignment of the double bonds. Model A is mainly of interest in that it is derived from what now seems to be the preferred conformation of cyclooctane by replacing the two 'transannular' methylenes by trigonal carbons: model B would probably be that predicted by conformational theory since the conformation about the four butene units it contains is that predicted for but-2-ene[11] and established for propene[12] and but-1-ene.[13] Model B does have serious transannular interactions but these would not be energetically more expensive than in bicyclo[3.3.1]nonane where the strain is relieved by deformation of bond angles.[14] The PMR spectrum of I tends to support model B as the preferred conformation since the olefinic proton resonance at τ 5·34 is a fairly sharp singlet: for model C appreciable allylic coupling constants (ca. 1 c/s) would be expected with dihedral angles of 60° and 180° subtended by the olefinic and allylic C—H bonds[15] while a somewhat distorted model B with dihedral angles approaching 15 and 135° would give much smaller coupling constants. It is interesting that, like bicyclo[3.3.1]nonane and cyclooctane, I shows in its IR spectrum absorptions at 2976 and 1466 cm^{-1}, on the short wavelength side of the main stretching and scissoring bands. Both bicyclononane and cyclooctane are molecules with transannular strain and in the case of the former at least the anomalous absorptions have been related to the (strained) 3,7-methylenes:[9] a similar explanation has been advanced for the case of cyclooctane too.[15] Rapid interconversion of B and its mirror image would make all the allylic protons equivalent, and similarly for the four protons on C_3 and C_7: the complexity of the signals for $H_{allylic}$ and $H_{methylene}$ suggests that this interconversion may not in fact be rapid at ordinary temperatures.

Alternative routes to I via molecules of type X and XI were investigated. Bisbromomethylcyclooctane was prepared from 1,5-bismethoxycarbonylcyclooctane by normal reactions. It was observed that partial epimerization accompanied the hydride reduction of the trans diester. Dehydrobromination of the dibromide in refluxing collidine gave 5-bromomethylmethylenecyclooctane, XI (X = Br) and a hydrocarbon mixture. Analysis of the latter by GLC showed three components (45·5, 48·5, and 6% respectively), and integration of the τ 5·32 singlet in the PMR spectrum indicated about 10% of I (which had the same retention time on GLC as the 48·5% component). Nearly half the protons were aromatic, and a triplet at τ 7·0 indicated the group Ar $\underline{C}H_2CH_2$; a sharp peak at τ 7·7 suggested ArCH$_3$. The remaining components of the mixture therefore seemed to be tetralin and/or methylindanes, together with (remembering the high ratio of aromatic protons) naphthalene. Somewhat similar results were obtained with eliminations from compounds of type XI but dehydrobromination of bromomethylcyclooctane in collidine gave methylenecyclooctane in good yield.
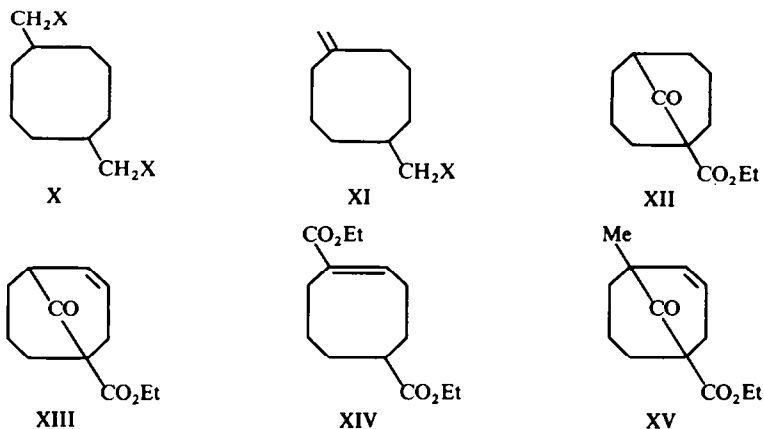
The diesters required for the preparation of X were prepared by alcoholysis of XII with dilute methanolic methoxide: by allowing the reaction to run to about 65% conversion, and removing unreacted XII with Girard's reagent, competing reduction of the C_9 carbonyl of XII was minimized and a good yield of the geometrically isomeric diesters (which could be separated by fractionation on a spinning band column) obtained. The suggestion that such retro-Claisen reactions must be accompanied by double bond migration (as in XIII → XIV) to achieve success[5] thus cannot be correct: the difficulties reported in the alcoholysis of XV may have stemmed from the fact that the intended product was a gem-disubstituted cyclooctene.
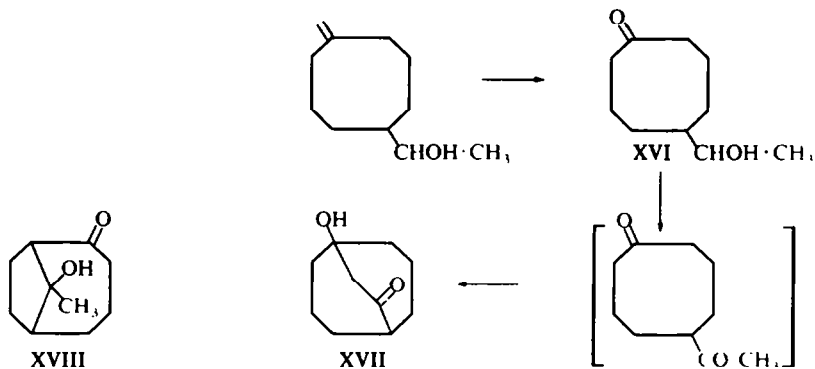
The alcohol VIII could not be synthesized by the obvious route involving diazomethane homologation of XII, because the ketoester failed to reaction with diazomethane even in the presence of boron trifluoride. The route adopted is shown in the reaction scheme; oxidation of the alcohol XVI in acid solution led directly to XVII, which was converted to VIII by aluminohydride reduction of its tosylhydrazone (Wolff–Kishner reduction gave mainly VIII plus a second, unidentified, alcohol). It is noteworthy that only XVII (obtained as a crystalline solid) was formed from XVI, and neither of the isomers XVIII. Models show that the latter would be subject to appreciable steric crowding in the 7-membered ring.

EXPERIMENTAL

1-Hydroxymethylbicyclo[3.3.1]nonan-9-ol, VI

1-Ethoxycarbonylbicyclononan-9-one (36·4 g) was reduced with LAH (6·7 g) in the usual way to give the diol (26·9 g) as a colourless oil, b.p. 124°/0·4 mm, which solidified on standing, and had no CO absorptions in its IR spectrum. It was not purified further but was immediately converted to the *toluenesulphonate ester*, m.p. 65–66°. (Found: C, 62·83; H, 7·32; S, 9·95. $C_{17}H_{24}O_4S$ requires: C, 62·96; H, 7·41; S, 9·88%).

5-Formylmethylenecyclooctane. Potassium (7·2 g) was dissolved in refluxing dry t-BuOH (350 ml) under dry N_2 and cooled to about 30° when the monotosylate of VIII (25 g) was added in one portion. The mixture was then stirred at 25–30° for 30 min under N_2, and then poured into water (1000 ml). After extracting and working-up in the usual way, the combined products of two runs gave the *aldehyde* (16·5 g), b.p. 60°/0·5 mm, n_D^{25} 1·4880, IR maxima at 3067, 1637 and 977 cm^{-1} (=CH_2) and 2710 and 1724 cm^{-1} (CHO). (Found: C, 78·74; H, 10·41. $C_{10}H_{16}O$ requires: C, 78·89; H, 10·59%). 2,4-*Dinitrophenylhydrazone*, chromatographed on bentonite/kieselguhr, yellow needles from benzene/petrol m.p. 129·5–130°. (Found: C, 57·56; H, 6·14; N, 17·06. $C_{10}H_{20}N_4O_4$ requires: C, 57·84; H, 6·02; N, 16·89%). *Semicarbazone*, white prisms from EtOH m.p. 161°. (Found: C, 63·01; H, 9·16; N, 19·79. $C_{11}H_{19}N_3O$ requires: C, 63·15; H, 9·15; N, 20·08%). *Oxime*, colourless viscous oil b.p. 104–105°/0·5 mm, n_D^{25} 1·5108; IR maxima at 3597, 3077, 1664, 1639 and 893 cm^{-1}. (Found: C, 71·84; H, 10·30; N, 8·48. $C_{10}H_{17}NO$ requires: C, 71·83; H, 10·25; N, 8·38%).

5-Methylmethylenecyclooctane. 5-Formylmethylenecyclooctane (15 g) was refluxed for 1 hr with a soln of Na (6·9 g) and 99% hydrazine hydrate (15 g) in diethylene glycol (250 ml), then the mixture was distilled till the temp of the vapour reached 190°, and refluxing continued for 3 hr. The mixture was cooled and diluted with water (700 ml), extracted with ether (2 × 100 ml), the extracts combined with the distillate, washed, dried, and distilled to give the *olefin* (6·55 g), b.p. 170–172°, n_D^{25} 1·4620, IR maxima at 3077, 1639, 1383, 894, and 884 cm^{-1}. (Found: C, 86·90; H, 13·13. $C_{10}H_{18}$ requires: C, 86·87; H, 13·12%).

5-Methylcyclooctanone a. Ozone (0·0145 moles) was passed through a soln of the above olefin (1·88 g) in EtOAc (20 ml) at 0°. Solvent was removed, and the ozonides were decomposed by steam distillation in the presence of Zn dust; extraction of the distillate gave a ketonic fraction (0·95 g), b.p. 100° (bath temp)/10 mm, IR max at 1698 cm^{-1} with a shoulder at 1730 cm^{-1}. (From the aqueous phase of the steam distillate formaldehyde dimethone, m.p. and mixed m.p. 185–187°, was isolated). The crude ketone was converted to its semicarbazone, m.p. 172·5–174° (lit. 176·8–177·4), and hydrolysis of this gave pure 5-methylcyclo-octanone, n_D^{25} 1·4642 (lit. 1·4642), single C=O stretch at 1698 cm^{-1}. (Found: C, 76·97; H, 11·54. Calc for $C_9H_{16}O$: C, 77·09; H, 11·50%). 2,4-Dinitrophenylhydrazone, orange plates from EtOH m.p. 125–126° (lit. 131·6–132°). (Found: C, 56·01; H, 6·12; N, 17·69. $C_{15}H_{20}N_4O_4$ requires: C, 56·26; H, 6·24; N, 17·50%).

b. The olefin (0·27 g) was allowed to stand for 24 hr with osmic acid (0·5 g) and AnalaR pyridine (1 ml) in dry ether (135 ml), the light brown complex (0·94 g) was then filtered off and hydrolysed with mannitol (8 g) and 5% NaOH aq (50 ml) in the usual way to give diol (0·17 g) as a white crystalline solid which was immediately used for the next stage. A soln of the diol (0·2 g) in CH_2Cl_2 (10 ml) was boiled for 2 hr in an extraction apparatus the thimble of which was charged with lead tetraacetate (0·9 g) normal work-up yielded the ketone (0·16 g), CO stretching frequency at 1698 cm^{-1} with no shoulder. 2,4-Dinitrophenyl-hydrazone m.p. 124·5–126° undepressed on admixture with that prepared as above.

5-Trimethylammoniummethylmethylenecyclooctane, XI X = $N(CH_3)_3$

The oxime of the foregoing aldehyde (6·48 g) was reduced with LAH (2·4 g) in refluxing ether in the usual way. Wet ether was then added to destroy complexes and excess of reagent, and the whole continuously extracted with ether for 7 hr. Removal of the ether, after drying, gave 5-aminomethylmethylene-cyclooctane (4·41 g), colourless oil b.p. 74–75°/0·5 mm, n_D^{25} 1·4941, IR maxima at 3378, 3289, 1639, and 893 cm^{-1}. (Found: C, 78·74; H, 12·26. $C_{10}H_{19}N$ requires: C, 78·36; H, 12·49%). A mixture of the above amine (3·46 g), NaHCO$_3$ (6·8 g), and MeI (11·5 g) in MeOH (50 ml) was refluxed for 79 hr; MeI was added after 24 and 48 hr (using in total 2·0 g). The mixture was evaporated to dryness (on a rotary evaporator) and the residue extracted with boiling CHCl$_3$ (3 × 40 ml). Evaporation of the combined extracts gave the *ammonium salt* (5·5 g), white needles m.p. 250° from EtOH. (Found: C, 48·39; H, 8·05; N, 4·08. $C_{13}H_{20}NI$ requires: C, 48·29; H, 8·11; N, 4·33%).

1,5-Bismethylenecyclooctane, I. A slurry of freshly pptd Ag_2O (2·8 g) in water (20 ml) was added to a soln of the above methiodide (6 g) in water (100 ml) and MeOH (50 ml), and the whole stirred at room temp for 4 hr, then allowed to remain overnight. Solids were filtered off, the filtrate evaporated at reduced press and the residue pyrolysed at 100–120°/1 mm for 1 hr, products being collected in a trap cooled by liquid air. The pyrolysate was taken up in ether (50 ml), washed with 0·5N HCl, NaHCO$_3$ aq, water, and

dried. Distillation gave the *diene* (1·13 g) colourless oil b.p. 64°/25 mm, n_D^{25} 1·4819; IR maxima at 3072, 2976, 1639, 1466 and 885 cm^{-1}. The PMR spectrum consisted of a singlet (4 protons) τ 5·34, multiplet (8 protons) centred on τ 7·9 and multiplet (4 protons) centred on τ 8·25. (Found: C, 87·95; H, 11·91. $C_{10}H_{16}$ requires: C, 88·18; H, 11·82%). The diene in EtOH absorbed 2 molar equivs H_2 over 5% Pd/C, and over Adams Pt. The diene (0·1 g) and tetracyanoethylene (0·1 g) in THF (1 ml) were left at room temp for some months, no adduct crystallized out. Heating the soln caused the colour to darken and removal of solvent then left a tarry residue.

Reaction of diene, I, *with bromine*. To the diene (0·5096 ml) in AnalaR CCl_4 (2 ml) was added Br_2 (1·2 g) in CCl_4 (2 ml), when the soln became warm. After the soln had been left at room temp overnight, it was washed with NaOH aq, water and dried. Removal of solvent left a residue (1·19 g) which had two components (TLC). Chromatography of the mixture (0·6 g) on alumina (30 g) gave the *dibromide* VII (0·47 g) eluted with cyclohexane, and a second bromide (0·07 g) eluted with ether/cyclohexane (1:10) and not investigated further. The dibromide VII was distilled at 0·5 mm, bath temp 100°, n_D^{25} 1·5622. (Found: C, 41·25; H, 5·44; Br, 53·70. $C_{10}H_{16}Br_2$ requires: C, 40·37; H, 5·45; Br, 53·98%); IR maxima at 2996, 1490, and 784 cm^{-1}. The PMR spectrum showed a singlet (2 protons) at τ 6·8 as well as methylene absorption between τ 7·6 and 8·5.

Reaction of diene I *with hydrochloric acid*. Conc HCl (0·4 ml) was added dropwise to I (0·5 g) in glacial AcOH (5 ml), and the mixture became warm: it was then left at room temp for 4 days before being poured into water. Ether extraction and the usual working up gave an oil (0·63 g) which was warmed with N NaOH aq (10 ml) at 60–80° for 1 hr. Extraction, drying, and chromatography on alumina (30 g) eluting with CH_2Cl_2 gave a *chloride*, (0·28 g) b.p. 80° (bath temp)/8 mm, n_D^{22} 1·4892; IR maxima at 2994, 1493, and 794 cm^{-1}: no absorptions at higher frequency than 2994, between 2000 and 1500, or strong absorptions near 910–850 cm^{-1}. The PMR spectrum showed only complex absorption between τ 8·5 and 9·75. (Found: C, 70·05; H, 10·05; Cl, 20·00. $C_{10}H_{17}Cl$ requires: C, 69·55; H, 9·93; Cl, 20·52%). Elution with ether/CH_2Cl_2 (1:1) gave the *alcohol* VIII (0·3 g), m.p. 64–65° purified by sublimation *in vacuo*; IR maxima at 3160, 2994, 1493, 1136, and 1010 cm^{-1}. The PMR spectrum showed complex absorption between τ 8·8 and τ 9·7 and was very similar to that of the chloride. (Found: C, 77·45; H, 11·28. $C_{10}H_{18}O$ requires: C, 77·87; H, 11·76%).

1,5-*Bismethoxycarbonylcyclooctanes*

1-Ethoxycarbonylbicyclononan-9-one (61·9 g), NaOMe (from 3·6 g Na) and abs MeOH (620 ml) were refluxed for 15·5 hr, cooled, and just acidified to Congo Red with dil HCl aq. Most of the MeOH was removed *in vacuo*, the residue partitioned between water and ether, and worked up in the normal way to give a mixture of esters (54 g). The combined products from two such runs were refluxed in abs EtOH (800 ml) with Girards reagent P (70 g) and glacial AcOH (6 ml) for 2 hr, then EtOH was removed *in vacuo* and the residue diluted with water (to 2·5 l.) and extracted with ether (4 × 200 ml). Removal of the ether after drying gave a mixture of diesters (71·88 g) which was distilled to gave *cis*-diester (33 g), b.p. 98–100°0·2 mm n_D^{25} 1·4723, and *trans* diester (31 g), b.p. 119–120°/0·3 mm, which partially crystallized on standing, recrystallization from petrol gave needles m.p. 35·5–38°. Hydrolysis of each ester fraction gave the corresponding dicarboxylic acids m.p. 167–168° (lit.[10] 169–171°) and m.p. 168·5–169° (lit.[10] 171–172°) respectively. From the aqueous phase was recovered 1-*methoxycarbonylbicyclononan-9-one* (19 g), m.p. 42–44°. (Found: C, 67·28; H, 8·16. $C_{11}H_{16}O_3$ requires: C, 67·32; H, 8·22%).

1,5-*Bishydroxymethylcyclooctanes* (3 g). Reduction of the *cis*-diester (9·3 g) with LAH in the usual way gave diols (7·3 g) as a colourless viscous oil. (Found: C, 67·55; H, 11·61. $C_{10}H_{20}O_2$ requires: C, 67·71; H, 11·70%). *Bis*(1-*naphthyl*)*urethane*, m.p. 133·5–134°. (Found: C, 75·4; H, 6·8; N, 4·9. $C_{32}H_{34}N_2O_4$ requires: C, 75·3; H, 6·7; N, 5·5%). From the mother liquors of the recrystallization of this urethane was obtained impure urethane of the *trans*-diol, m.p. 148–150°. Similar reduction of the *trans*-diester (4·3 g) with LAH (1·5 g) gave diol (3 g) as a viscous colourless oil. (Found: C, 67·95; H, 11·85. $C_{10}H_{20}O_2$ requires: C, 67·71; H, 11·70%). *Bis*(1-*naphthyl*)*urethane*, m.p. 156·5–157° after several recrystallizations. (Found: C, 75·2; H, 7·0; N, 5·2. $C_{32}H_{34}N_2O_4$ requires: C, 75·3; H, 6·7; N, 5·5%).

1,5-*Bisbromomethylcyclooctanes*. Br_2 (11·7 g) was added dropwise with stirring to a mixture of triphenylphosphite (24·8 g) and the above mixture of diols (6·3 g), the mixture was kept at room temp for 1 hr, and warmed on the water bath for a further hr, then taken up in $CHCl_3$, washed with NaOH aq, water, and dried. Distillation gave the *dibromides* (7·8 g), b.p. 115–117/0·3 mm. (Found: C, 40·37; H, 6·35. $C_{10}H_{18}Br_2$ requires: C, 40·28; H, 6·07%). Two α-naphthyl ethers were separated by fractional crystallization from acetone. The *trans*-isomer (also prepared from *trans*-diol), m.p. 158°. (Found: C, 89·1; H, 7·8. $C_{30}H_{32}O_2$

requires: C, 84·9; H, 7·55%). The *cis-isomer*, m.p. 123° (Found: C, 84·5; H, 7·65. $C_{30}H_{32}O_2$ requires: C, 84·9; H, 7·55%).

5-*Iodomethylmethylenecyclooctane*

5-Hydroxymethylmethylenecyclooctane (1 g) was reacted with toluene-*p*-sulphonyl chloride (2 g) in pyridine (15 ml) at 5° for 12 hr. The usual work-up gave the tosylate ester (1·8 g) as an oil which decomposed on attempted distillation: IR maxima at 3067, 1639, 1600, 1361, 1190, 1176, and 889 cm^{-1}. This tosylate (5 g) was refluxed with NaI (5 g) in acetone (30 ml) for 20 hr. Normal work-up gave the iodide (2·6 g) as an oil which decomposed on attempted distillation; IR maxima at 897 and 730 cm^{-1}, no characteristic tosylate absorptions.

Elimination reactions in collidine. The compound, X, (10 g) and collidine (59 g) were boiled for 3 hr, cooled, filtered from salts which were washed with ether, and the combined filtrates partitioned between ether and N HCl aq. Washing, drying, and distillation of the ether gave a hydrocarbon fraction 4·12 g) b.p. 56–58°/8 mm, and 5-*bromomethylmethylenecyclooctane* (1 g) b.p. 108–110°/8 mm, n_D^{20} 1·5141. (Found: C, 44·23; H, 7·75. $C_{10}H_{17}Br$ requires: C, 43·91; H, 7·89%); IR maxima at 3067 and 889 cm^{-1}. The hydrocarbon fraction had IR maxima at 3086, 3063, 3035, 772, and 751 cm^{-1}, but only weak absorption at 893 cm^{-1}. The PMR spectrum showed a complex set of peaks between τ 2·4 and τ 3·3, singlets at τ 5·23 and τ 5·34 (the latter corresponding to ca. 5% I), a triplet (J = 7 c/s) centred on τ 7·05, and a singlet at τ 7·7 superimposed on broad methylene absorption. GLC (on silicone oil at 133°) showed three peaks integrating for 45·5, 48·5, and 6% in order of increasing retention time; the middle peak had the same retention time as I. Treatment of the compounds XI, X = $C_7H_7SO_3$, and XI, X = I, with collidine in the same way gave the same three components in the ratios 51:43·5:5·5 and 46·5:5:48·5 respectively.

Hydroxymethylcyclooctane (14·1 g) was prepared by LAH reduction of methoxycarbonylcyclooctane (19 g), b.p. 111–113°/13 mm, n_D^{22} 1·4834. (Found: C, 75·3; H, 12·4. $C_9H_{18}O$ requires: C, 76·0; H, 12·8%). *Dinitrobenzoate*, m.p. 71° (Found: C, 57·2; H, 5·9; N, 8·3. $C_{16}H_{20}N_2O_6$ requires: C, 57·1; H, 6·0; N, 8·3%).

Bromomethylcyclooctane. Br_2 (30 g) was added over 30 min to a stirred, ice-cooled mixture of hydroxymethylcyclooctane (38 g) and triphenyl phosphite (84 g); after a further hr at room temp the mixture was heated on the steam bath for 90 min, cooled, taken up in ether (150 ml) and washed with 2N NaOH, water and dried. Distillation gave the *bromide* (45·2 g), b.p. 96–98°/8 mm, n_D^{19} 1·5058. (Found: C, 53·2; H, 8·2; Br, 37·2. $C_9H_{17}Br$ requires: C, 52·7; H, 8·4; Br, 38·9%). α-*Naphthyl ether*, m.p. 56°. (Found: C, 84·7; H, 8·9. $C_{19}H_{24}O$ requires: C, 85·0; H, 9·0%).

Methylenecyclooctane. Reaction of the bromide (7·5 g) and collidine (40 g) as described above gave the olefin (3 g), b.p. 57–60°/13 mm, n_D^{15} 1·4800. (Found: C, 87·0; H, 12·8. Calc for C_9H_{16}: C, 87·0; H, 13·0%); IR maxima at 3077, 1638, and 882 cm^{-1}. By ozonolysis of the olefin (1 g) cyclooctanone (0·55 g) was isolated (identified as its semicarbazone, m.p. and mixed m.p. 167–168°) together with formaldehyde (isolated and identified as its dimethone, m.p. and mixed m.p. 188–189°).

5-(α-*hydroxyethyl*)*methylenecyclooctane*

5-Formylmethylenecyclooctane (20 g) was reacted with the Grignard reagent from MeI (25 g) and the complex decomposed with sat'd NH$_4$Cl aq. The usual work-up gave the *secondary alcohol* (19·1 g), b.p. 72–73°/0·9 mm, n_D^{25} 1·4916, IR maxima (film) at 3350 (broad), 3065, 1630, 895 cm^{-1}. (Found: C, 78·20; H, 11·90. $C_{10}H_{16}O$ requires: C, 78·48; H, 11·97%).

5-(α-*hydroxyethyl*)*cyclooctanone*, XVI. A soln of the above secondary alcohol (8 g) and OsO$_4$ (0·5 g) in THF (80 ml) and water (120 ml) was stirred at room temp for 15 min, then sodium metaperiodate (24 g) added in portions over 30 min, and the mixture stirred till it became yellow (2·5 hr). Solids were filtered off and washed with ether, combined filtrates and washings evaporated and partitioned between 2N NaOH aq and CH$_2$Cl$_2$. The organic phase was washed, dried, and evaporated to leave the crude *ketoalcohol* (7·3 g) as a viscous liquid: IR maxima (film) 3450 (broad), 1689 cm^{-1}, none at 3065, 1630 or 890 cm^{-1}. (Found: C, 70·72; H, 10·46. $C_{10}H_{18}O_2$ requires: C, 70·58; H, 10·65%).

1-*Hydroxybicyclo*[3,3,2]*decan-10-one*, XVII. Sodium dichromate (17 g) and H$_2$SO$_4$ (20 ml) in water (120 ml) were added dropwise with stirring to XVI (7 g) in ether (100 ml), and then the solns were refluxed for 4 hr. Normal work-up gave *ketoalcohol* XVII (4·2 g), b.p. 58–60°/1 mm, white cubes from benzene/petrol (1:1) m.p. 92°; IR maxima (CCl$_4$ solution) at 3617, 2994, 1704, 1020, and 893 cm^{-1}; PMR spectrum showed singlet at τ 7·78 superimposed on methylene envelope. Satisfactory analyses could not be obtained for this material.

Bicyclo[3.3.2]*decan-1-ol*, VIII. The ketoalcohol, XVII (0·1 g) and toluene-*p*-sulphonylhydrazide (0·11 g)

in abs EtOH (10 ml) were boiled for 30 min; the tosylhydrazone crystallized on cooling (0·15 g), m.p. 189° (dec) (not analysed). To a soln of the tosylhydrazone (0·075 g) in MeOH (20 ml) was added NaBH₄ (0·07 g) and after the initial reaction had subsided, the whole was boiled for 3 hr. The usual work-up yielded VIII (0·018 g), m.p. 64°, not depressed on admixture with the hydration product of I. The IR spectra of both samples were identical and both had the same retention time on GLC (on butanediol succinate, and on tricyanoethoxypropane). The ketoalcohol XVII (0·05 g) and 99% hydrazine hydrate (1 ml) were refluxed for 3 hr with a soln of Na (0·025 g) in digol (2 ml), hydrazine was distilled off and the residue was poured into water. Extraction, washing, drying, and removal of solvent, followed by molecular distillation gave a semi-solid gum which consisted of VIII and a second compound (5·5 : 1), GLC on butanediol succinate, and on tricyanoethoxypropane at 80°.

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