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THE PREPARATION AND PROPERTIES OF CAGE POLYCYCLIC SYSTEMS—III[a]

THE CLEAVAGE IN ALKALINE CONDITIONS OF ACETALS DERIVED FROM PENTACYCLO[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]DECANE AND PENTACYCLO[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]NONANE SYSTEMS†

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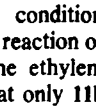
Abstract—The synthesis of some acetals derived from pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane is described. The reductive cleavage of an ethylenedioxy group $\left[\rangle\overline{\text{C.O.CH}_2\text{.CH}_2\text{.O}}\right]$ and a dimethoxy group $\left[\rangle\text{C(OMe)}_2\right]$ in pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane and pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane systems to give the methylene group is shown to occur in alkaline conditions in the presence of hydrazine. Evidence is presented for a mechanism which involves initial cleavage of the acetal by alkali to form the ketone. The substitution of a Br atom in the position neighbouring the CO group of 5-bromo-6,6-ethylenedioxypentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-10-one facilitates the Wolff–Kishner reaction to such an extent that hydrazine hydrate is a sufficiently strong base to induce the decomposition of the hydrazone directly.

The NMR spectrum of pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane (**1**) and the changes in chemical shift of its protons arising from the presence of a CO or an ethylenedioxy group have been studied recently.[1] Unexpectedly, either group causes an upfield shift of the absorption of protons α to the substituent. We are at present studying the proton chemical shift changes caused by introducing a CO or an ethylenedioxy group into pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane (**2**) and related systems to find out whether only the protons at positions α to the substituent behave exceptionally or whether other protons of the strained system behave differently from protons in less strained systems.[2]



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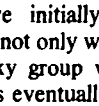

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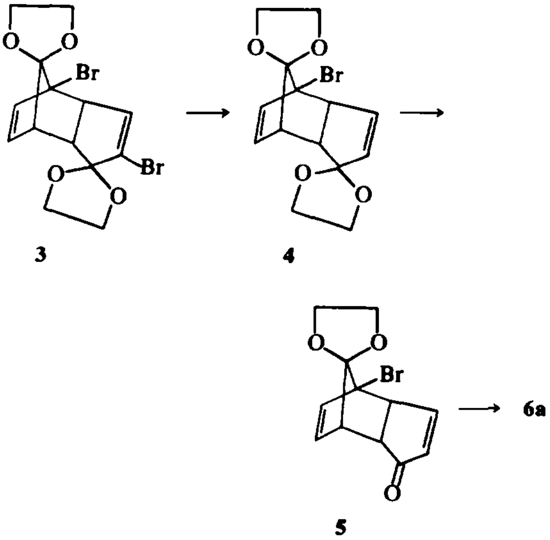
The reaction scheme we had planned for the preparation of the required compounds involved the preparation of **9b** from **6b** (Schemes 1 and 2).[2]‡ However, under the Huang–Minlon conditions we initially used for the Wolff–Kishner reaction of **6b**, not only was the CO group reduced but the ethylenedioxy group was also slowly removed so that only **11b** was eventually isolated in *ca.* 70% yield from a clean reaction mixture. The hydrazone of **6b** (compound **8b**) would decompose readily in Huang–Minlon conditions (p. 000) and **11b** probably arises from **9b** by the subsequent loss of the ethylenedioxy group. This was confirmed by subjecting **9b** (also **17**) to these conditions, which gave **11b**. Compounds **12** and **18** under the same conditions also yield **11b** and so cleavage of a dimethoxy group is also possible. We are not aware of other examples of the cleavage of an acetal in such conditions apart from the possibly related reaction of 1,2,3,4-*endo*-5-pentachloro-7,7-dimethoxynorbornene (**19**) with sodium hydroxide in dimethyl sulphoxide to give 2,3,4-trichlorobenzoic acid.[6] The cleavage of thioacetals with hydrazine has, however, been reported.[7]

We have considered several possible mechanisms for the cleavage of the ethylenedioxy group (mechanisms i–iii) and we have carried out experiments to differentiate between these possibilities.



Scheme 1

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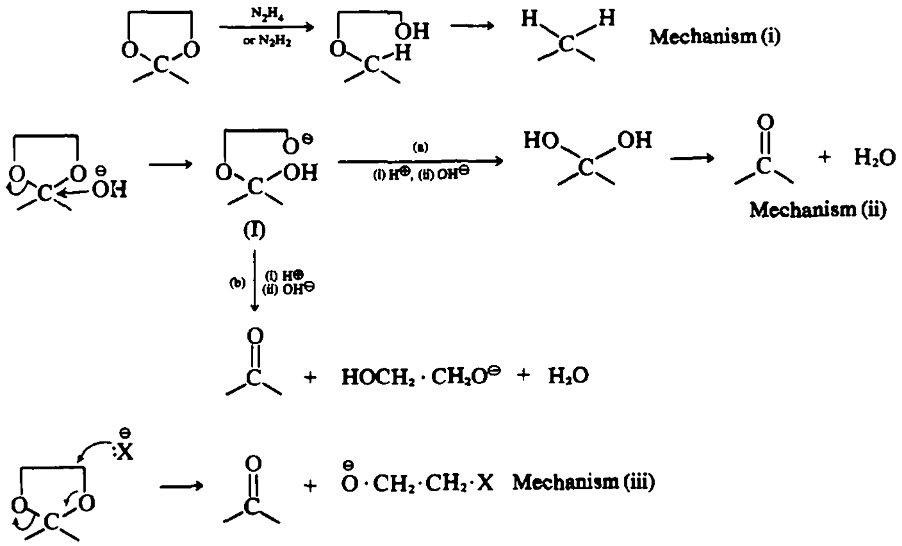
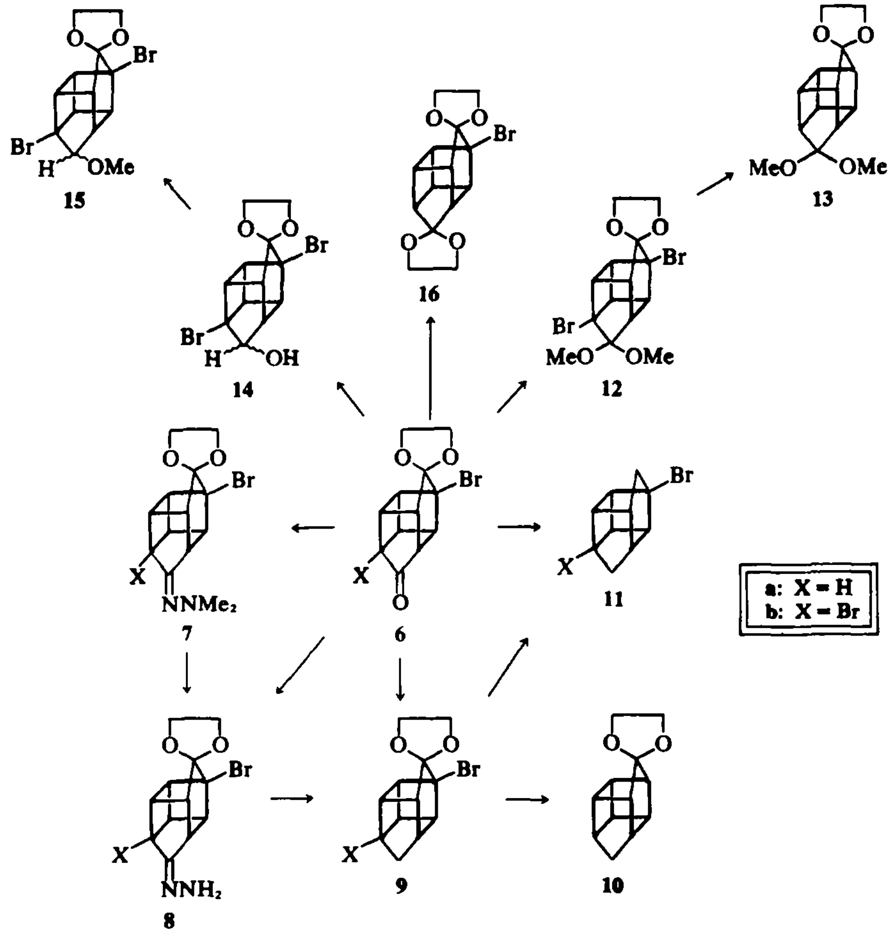
[a] Part II, N. B. Chapman, J. M. Key and K. J. Toyne, *Tetrahedron Letters* 5211 (1970).

†Part of this work was reported to the Autumn Meeting of the Chemical Society at Leicester, 1974.

‡Luh and Stock[3] have reported that they did not experience the difficulties we met in attempting the preparation of the caged systems as outlined by Eaton and Cole.[4] Klunder and Zwanenburg,[5] however, met difficulties and found the procedure we used to be "a great practical improvement".



In mechanism (i) the C–O bonds are directly cleaved by hydrazine (or di-imine) in two stages (Ref. 7). In mechanism (ii), the hydroxide ion attacks C_2 in the dioxolan ring to give the hemi-acetal derivative (I) and a second similar displacement (route a) would give the hydrate of the ketone and ultimately the ketone. Alternatively the intermediate (I) may lose the ethylene glycol anion as shown and yield the ketone (route b). In mechanism (iii), the base attacks C_4 in the dioxolan ring and gives the ketone in a one-stage process. It is suggested that the ketone formed by mechanism (ii) or (iii) would then react with hydrazine and so undergo the Wolff–Kishner reaction, but for either of these mechanisms to be acceptable it is necessary to demonstrate that



Scheme 2

an α-bromo-ketone (e.g. from **17**) formed in the reaction mixture under these conditions (internal temperature *ca.* 210°; strongly basic medium) is capable of reacting with hydrazine (b.p. 113°), and not with the hydroxide or alkoxide ion to give a Favorskii ring-contraction product. We have added **6b** in triethylene glycol to a potassium hydroxide–triethylene glycol–hydrazine hydrate mixture at 215°; the reaction mixture remained clear and **9b** and **11b** were formed, but a Favorskii product was not detected so that mechanisms (ii) and (iii) are acceptable possibilities.

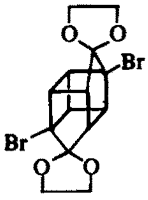
We believe that mechanism (iii) is the most likely mechanism for the following reasons. (a) The reaction of **9b** with anhydrous hydrazine or hydrazine hydrate in digol or trigol at 200–10° in the presence (or absence) of cupric ions and air did not give **11** but only traces of the hydrodebromination products **9a**, **20** and **10** as shown by GLC analysis, GLC/mass spectrometric analysis and GLC analysis respectively.

The same result was obtained by the reaction of **9b** with dimethyl sulphoxide–potassium t-butoxide–anhydrous hydrazine at 80°. These observations invalidate mechanism (i) and show that the mechanism of the reaction under investigation differs from that for the reductive cleavage of dithioacetals.[7]

(b) Reaction of **12** with anhydrous hydrazine and the sodium salt of triethylene glycol in dry triethylene glycol at 210° (see c below) gave **11b**, **21** and hydrodebromination product(s). Reaction of **15** in these conditions did not give **11b** (or **9b**), as indicated by GLC analysis, but **22** was formed. The cleavage of the dimethoxy group in **12** by mechanism (i) would require the formation and subsequent cleavage of an intermediate methyl ether. The observation that the methyl ether group in **15** is not cleaved in these conditions is therefore incompatible with the operation of mechanism (i).

(c) Both mechanism (ii) and mechanism (iii) are possible with hydroxide as base but only mechanism (iii) is possible when alkoxide ion is used. We have found that reaction of **9b** with anhydrous hydrazine in dry triethylene glycol at 210–20° with the alkoxide formed from dry triethylene glycol and sodium as base, gave **11b** cleanly, in accord with mechansim (iii).† It is possible, however, that traces of moisture may be present which permit mechanism (ii) to operate and the subsequent formation of the hydrazone would produce more water.

(d) Reaction of **12** with anhydrous hydrazine and the sodium salt of decan-1-ol in dry decan-1-ol at 200–10° gave 1-methoxydecane and 2-decoxyethanol. The reaction of **17** in similar conditions gave 2-decoxyethanol. These observations indicate that mechanism (iii) is operating.



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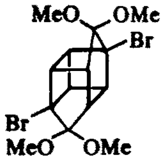

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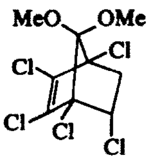

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We have made a few qualitative comparisons of the ease of cleavage of several acetals, by following the formation of products by GLC. Thus for the reaction of **16** we find that an ethylenedioxy group with an α-Br atom is more readily cleaved than the same group without the bromine, and for the reaction of **12** or **13** we find that the cleavage of an ethylenedioxy group is easier than that of a dimethoxy group.

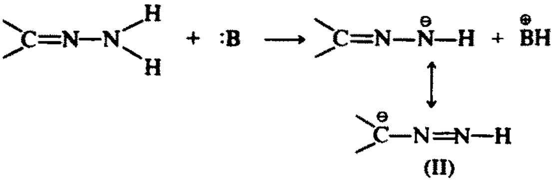
The cleavage of the ethylenedioxy group in 1 - bromo - 4 - methoxymethyl - 9,9 - ethylenedioxypentacyclo [$4.3.0.0^{2,5}.0^{3,8}.0^{4,7}$] nonane (**23**) with the subsequent formation of **24** has also been carried out.

The usual method for the conversion of an acetal group into a CO group requires moderately acidic conditions. For the hydrolysis of acetals of pentacyclo-decane and -nonane systems, however, *strongly* acidic conditions are necessary (e.g. 75–98% sulphuric acid[2]) and structural rearrangements may occur.[8] In addition, the ketone formed often exists as a water-soluble hydrate which makes its isolation troublesome. The reaction we describe here, however, offers the practical advantage that acidic conditions and isolation of the ketone can be avoided in the formation of a cycloalkane from a ketal.

The cleavage of an acetal group in basic conditions by mechanism (iii) involves a change in the hybridisation of the C_2 atom in the acetal from sp^3 to sp^2. Further work will be necessary before it is possible to decide whether such a change of hybridisation is more, or less, favourable in acetals of strained systems than in acetals of non-strained systems.

As our initial attempts to prepare **9b** had been complicated by the cleavage of the acetal group, we then used milder conditions for the decomposition of the hydrazone **8b**, and its decomposition *in situ* or after isolation were carried out. It proved impossible to isolate the hydrazone from the reaction of **6b** with 98–100% hydrazine hydrate or anhydrous hydrazine, even when a low temperature and a short reaction time were used, and an indirect method[9] of preparing the hydrazone had to be adopted. However, in the attempts to prepare hydrazone **8b** from **6b** and 98–100% hydrazine hydrate it was noted that **9b** was being formed and when the mixture was boiled for 1–2 days an almost quantitative yield of **9b** was obtained, presumably by decomposition of the hydrazone with hydrazine hydrate acting as the base.[10,11]

Several structural features of hydrazone **8b** may account for its easy reduction; (*a*) in the initial stage of the Wolff–Kishner reduction, the removal of a proton from the hydrazone may be facilitated because of the relief of strain in the ring system on changing from an sp^2-hybridised carbon atom in the hydrazone to an sp^n-hybridised carbon atom ($2 < n < 3$) in the anion (II), (*b*) the α-bromine atom may stabilise carbanion (II) by electron-withdrawal or destabilise the eclipsed synperiplanar structure of the hydrazone for steric or electronic reasons. Point (b) appears to be the more important factor since hydrazone **8a** (without an α-Br atom) has been prepared directly by using boiling 98–100% hydrazine hydrate. The ability of an α-bromo-substituent to



(II)

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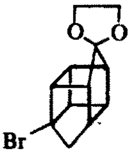
†A practical advantage of this method is that the reaction flask is not etched as badly as for reactions using potassium hydroxide as base. On one occasion, however, the reaction mixture exploded.



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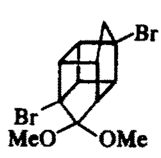

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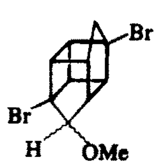

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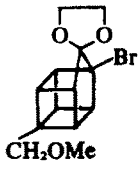

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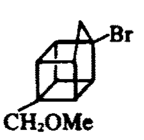

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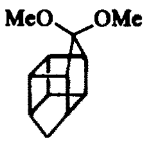

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facilitate Wolff–Kishner reactions cannot be demonstrated for aliphatic systems because elimination or substitution of the substituent occurs. An approximate comparison of the temperatures at which a brisk evolution of nitrogen occurred for reduction of hydrazones **8b**, **8a**, acetophenone hydrazone and benzophenone hydrazone showed that the presence of an α-bromine atom facilitates reaction appreciably and the ease of reaction of the cage compounds and the aromatic compounds is similar.

EXPERIMENTAL

M.ps and b.ps are uncorrected. IR spectra were recorded by using a Perkin-Elmer 457 spectrophotometer. NMR spectra were recorded at 100MHz with a JEOL 4H-100 spectrometer, with TMS as internal standard and $CDCl_3$ as solvent. Mass spectra were recorded with an A.E.I. MS902 spectrometer; *m/e* values are given for the bromine 79 isotope. GLC analyses, unless otherwise stated, were done with a Perkin-Elmer F11 gas–liquid chromatograph fitted with a glass column (2·0 m × 0·3 cm i.d.) packed with 20% silicone gum rubber (SE-301) on Chromosorb W, at a column temp. of 180°. TLC plates were coated with silica gel F_{254} (Merck), eluted with 19 : 1 benzene–methanol and developed by spraying them with an ethanolic solution of phosphomolybdic acid and heating them to 180–200° for 30 min.

Acetophenone hydrazone,[9] benzophenone hydrazone,[12] 1-methoxydecane,[13] and 2-decoxyethanol[14] were prepared by methods previously reported. Compounds **2**, **3**, **6b**, **17**, **18** were prepared as described in Ref. 2.

endo - 1 - *Bromo* - *5,5,10,10* - *bisethylenedioxytricyclo* [5.2.1.0^{2,6}]*deca* - *3,8* - *diene* (**4**). Compound **3**[2] (40·0 g, 0·099 mol) was added to dry THF (300 ml) under dry N_2. N_2 was passed slowly through and the flask and contents were cooled to −60°. The mixture was stirred briskly and BuLi (200 ml of a 5·44% w/w soln in hexane) was added dropwise during 2 hr keeping the temp. below −40°. Water (100 ml) was then added dropwise and the mixture was allowed to attain room temp. The organic layer was separated and the aqueous layer was washed with ether (2 × 150 ml). The combined organic layer and ether washings were washed with water until they were colourless (3 × 150 ml), dried ($MgSO_4$), and the solvents were removed *in vacuo* to leave a white solid which was recrystallised twice (light petroleum, b.p. 80–100°, with a little chloroform) to give endo - 1 - *bromo* - *5,5,10,10* - *bisethylenedioxytricyclo*[5.2.1.0^{2,6}]*deca* - *3,8* - *diene* (**4**) (25·0 g, 78%), m.p. 121–3°, ν_{max} (CCl_4) 2980, 2880, 1616, 1260, 1078, 1030 cm^{-1}; δ 2·71 (1H, m), 3·02 (1H, q), 3·60 (1H, q), 3·88–4·26 (8H, m), 5·68–5·84 (2H, m), 5·94 (1H, q), 6·13 (1H, q); *m/e* 326 (M^+), 281, 247, 175, 131, 103 (Found: C, 51·1; H, 4·6; Br, 24·6. $C_{14}H_{15}BrO_4$ requires: C, 51·4; H, 4·6; Br, 24·4%).

The potential of this reaction for the synthesis of substituted pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decanes and pentacyclo-[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonanes is now being investigated.

endo - 1 - *Bromo* - *10,10* - *ethylenedioxytricyclo*[5.2.1.0^{2,6}]*deca* - *3,8* - *dien* - *5* - *one* (**5**) was prepared from compound **4** by a standard procedure[2]; yield 90%, m.p. 117–9°, ν_{max} (KCl) 3080, 2900, 1700, 1265, 1142, 780 cm^{-1}; δ 2·96–3·10 (2H, m), 3·67 (1H, m), 3·76–4·30 (4H, m), 5·75–5·98 (2H, m), 6·17 (1H, q), 7·47 (1H, q); *m/e* 282 (M^+), 203, 175, 131, 103, 77 (Found: C, 50·8; H, 3·7; Br, 28·0. $C_{12}H_{11}BrO_3$ requires: C, 50·9; H, 3·9; Br, 28·2%).

5 - *Bromo* - *6,6* - *ethylenedioxypentacyclo*[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}] *decan* - *10* - *one* (**6a**) was prepared from compound **5** by a standard procedure[2]; yield 89%, m.p. 84–6°, ν_{max} (KCl) 3000, 2878, 1760, 1303, 1146, 1039 cm^{-1}; δ 2·53 (1H, m), 2·73 (1H, m), 2·86 (1H, m), 3·28 (4H, m), 3·93–4·28 (4H, m); *m/e* 282 (M^+), 203, 175, 131, 103, 77 (Found: C, 50·6; H, 3·7; Br, 28·4. $C_{12}H_{11}BrO_3$ requires: C, 50·9; H, 3·9; Br, 28·2%).

5 - *Bromo* - *6,6* - *ethylenedioxypentacyclo*[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}] *decan* - *10* - *one dimethylhydrazone* (**7a**) was prepared from **6a** by a method similar to that used for the preparation of **7b**. The product (74%) had b.p. 180–2°/1·5 mm Hg, ν_{max} (film) 2990, 1680, 1302, 1078, 1040 cm^{-1}; δ 2·35–2·45 (1H, m), 2·48 (3H, s), 2·52 (3H, s), 2·95–3·35 (5H, m), 3·46–3·57 (0·5H, m), 3·70–3·81 (0·5H, m), 3·96–4·35 (4H, m); *m/e* 324 (M^+), 280, 245, 143 (Found: C, 51·5; H, 5·3; Br, 24·4; N, 8·6. $C_{14}H_{17}BrN_2O_2$ requires: C, 51·7; H, 5·3; Br, 24·6; N, 8·6%). The product appears to be an equimolecular mixture of the two possible geometrical isomers.

5,9 - *Dibromo* - *6,6* - *ethylenedioxypentacyclo*[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}] *decan* - *10* - *one dimethylhydrazone* (**7b**). A mixture of **6b**[2] (1·0 g, 0·0028 mol), glacial acetic acid (0·5 ml) and N,N-dimethylhydrazine (15·0 ml, 0·20 mol) in dry benzene (30 ml) was boiled overnight and then allowed to cool. (GLC analysis showed the absence of **6b** and a single product peak.) The mixture was poured into water (100 ml), washed with ether (3 × 50 ml) and the combined ethereal solns were then washed first with $NaHCO_3$ aq. (100 ml of an 8% w/v soln) until just alkaline to litmus, then with water, and dried ($MgSO_4$). Evaporation of the ether *in vacuo* gave a colourless oil which solidified at room temp. Two recrystallisations (light petroleum, b.p. 80–100°) gave *5,9* - *dibromo* - *6,6* - *ethylenedioxypentacyclo*[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]*decan* - *10* - *one dimethylhydrazone* (**7b**) (0·81 g, 73%), m.p. 150–1°, ν_{max} (KCl) 2980, 2950, 2881, 2860, 1680, 1303, 949, 938 cm^{-1}; δ 2·44–2·55 (1H, m), 2·61 (6H, s), 3·24–3·38 (4H, m), 3·63–3·73 (1H, m), 3·93–4·23 (4H, m); *m/e* 402 (M^+), 358, 323, 198, 197 (Found: C, 41·4; H, 4·0; Br, 39·5; N, 7·1. $C_{14}H_{16}Br_2N_2O_2$ requires: C, 41·6; H, 4·0; Br, 39·6; N, 6·9%).

5 - *Bromo* - *6,6* - *ethylenedioxypentacyclo*[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}] *decan* - *10* - *one hydrazone* (**8a**). *Method A*. Compound **8a** was prepared from **7a** by a method similar to that used for the preparation of **8b** and the product (77%) had m.p. 57–60%, ν_{max} (KCl) 3500–3300, 2980, 1300, 1078, 1040 cm^{-1}; δ 2·37 (1H, m), 2·90–3·30 (7H, m), 3·37–3·46 (0·5H, m), 3·55–3·70 (0·5H, m), 3·90–4·35 (4H, m); *m/e* 296 (M^+), 280, 227, 217, 200, 189, 128, 115. The product appears to be an equimolecular mixture of the two possible geometrical isomers. *Method B*. Compound **8a** was prepared by heating **6a** and hydrazine hydrate under reflux for 17 hr.

5,9 - *Dibromo* - *6,6* - *ethylenedioxypentacyclo*[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}] *decan* - *10* - *one hydrazone* (**8b**). A soln of **7b** (0·5 g, 0·00124 mol) in anhyd hydrazine (0·16 g, 0·0050 mol) and dry EtOH (2·5 ml) was heated under reflux for 24 hr. The soln was allowed to cool and the volatile components were removed *in vacuo* below 20°. The light brown oil solidified on being kept at 0° to give *5,9* - *dibromo* - *6,6* - *ethylenedioxypentacyclo*[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]*decan* - *10* - *one hydrazone* (**8b** 0·41 g, 88%), m.p. 64–7°, ν_{max} (KCl) 3300–3400, 2985, 2885, 1610, 1470, 1300 cm^{-1}; δ 2·50–2·67 (1H, m), 2·93–3·35 (7H, m), 3·94–4·25 (4H, m); *m/e* 376 (M^+ + 2), 358, 267 (Found: C, 38·3; H, 3·1; Br, 42·2; N, 7·4. $C_{12}H_{12}Br_2N_2O_2$ requires: C, 38·3; H, 3·2; Br, 42·5; N, 7·5%).

5 - *Bromo* - *6,6* - *ethylenedioxypentacyclo*[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}] *decane* (**9a**). Compound **8a** (3·0 g, 0·010 mol) and KOH (3·0 g, 0·054 mol) were added to triethylene glycol (100 ml) in a 3-necked flask fitted with a stirrer, thermometer and reflux condenser. The flask was heated in an oil bath to 140° over 45 min and when the internal temp. reached 130° a brisk evolution of N_2 ensued. The mixture was cooled, poured into water (200 ml) and washed with

ether (3 × 50 ml). The ethereal washings were combined, washed with water (2 × 50 ml) and dried ($MgSO_4$). The ether was removed *in vacuo* to leave an oil which was distilled to give 5 - *bromo* - 6,6 - *ethylenedioxypentacyclo*$[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]$*decane* (**9a**) (2·0 g, 74%), b.p. 98–100°/0·15 mm Hg, ν_{max} (film) 2980, 1310, 1300, 1290, 1090, 1040 cm^{-1}; δ 1·45 (1H, d), 1·67 (1H, d), 2·10 (1H, m), 2·88–3·12 (6H, m), 3·83–4·35 (4H, m); *m/e* 268 (M^+), 189, 145, 117 (Found: C, 53·5; H, 4·9; Br, 29·6. $C_{12}H_{13}BrO_2$ requires: C, 53·5; H, 4·9; Br, 29·7%).

5,9 - *Dibromo* - 6,6 - *ethylenedioxypentacyclo*$[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]$ *decane* (**9b**). A soln of **6b**[2] (20·0 g, 0·55 mol) in hydrazine hydrate (100 ml of 98–100%) was heated under reflux for 2 days (hydrazine hydrate has b.p. 118·5°). The soln was cooled, diluted with water, and shaken with ether (3 × 150 ml). The combined ethereal solns were washed with 2N HCl (2 × 50 ml), water (3 × 100 ml) and then dried ($MgSO_4$). Evaporation of the ether *in vacuo* and two recrystallisations (aqueous MeOH) of the residue gave 5,9 - *dibromo* - 6,6 - *ethylenedioxypentacyclo* $[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]$ *decane* (**9b**, 18·5 g, 96%), m.p. 65–7°, ν_{max} (KCl) 3000, 2980, 2892, 1310, 1292, 1048, 980 cm^{-1}; δ 1·97 (1H, d), 2·10 (1H, d), 2·37 (1H, m), 2·90–3·00 (1H, m), 3·10–3·22 (4H, m), 3·95–4·25 (4H, m); *m/e* 346 (M^+), 267, 188, 187, 116, 115 (Found: C, 41·4; H, 3·5; Br, 45·8. $C_{12}H_{12}Br_2O_2$ requires: C, 41·4; H, 3·5; Br, 45·9%). **9b** was also prepared from **8b** by a procedure similar to that described for the preparation of **9a**.

6,6 - *Ethylenedioxypentacyclo*$[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]$*decane* (**10**). Compound **9b** (9·0 g, 0·026 mol), t-BuOH (7·5 g, 0·101 mol) and dry THF (200 ml) were placed in a flask fitted with a condenser, glandular stirrer and N_2 inlet tube and small pieces of freshly cut Li (1·1 g, 0·159 mol) were added during 40 min to the stirred soln under N_2. The mixture was heated under reflux for 3 hr and a sample was then analysed (GLC). This showed the absence of starting material and a single product peak. The mixture was cooled and water (150 ml) was added during 15 min to destroy the excess of Li. The soln was then poured into water (400 ml), washed with ether (3 × 125 ml) and the combined ethereal solns were washed with water and dried ($MgSO_4$). The ether was evaporated *in vacuo* to give a colourless oil, which was distilled to give 6,6 - *ethylenedioxypentacyclo*$[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]$*decane* (**10**; 4·6 g, 94%), b.p. 78–80°/0·3 mm Hg, ν_{max} (film) 2975, 1330, 1103 cm^{-1}; δ 1·33 (1H, d), 1·62 (1H, d), 2·05–2·17 (1H, m), 2·30–2·47 (1H, m), 2·60–2·95 (6H, m), 3·82–3·95 (4H, m); *m/e* 190 (M^+), 125, 118, 117, 115, 91 (Found: C, 75·5; H, 7·4. $C_{12}H_{14}O_2$ requires: C, 75·8; H, 7·4%).

5,9 - *Dibromopentacyclo*$[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]$*decane* (**11b**). A mixture of **9b** (17·6 g, 0·051 mol), KOH pellets (30·0 g, 0·54 mol) and hydrazine hydrate (50 ml of 98–100%) in triethylene glycol (300 ml) was placed in a flask fitted with a thermometer and a stirrer, and arranged for distillation. The mixture was heated so that the internal temp increased to 180° during 2 hr. At this point most of the hydrazine hydrate had distilled out of the flask and the temp of the mixture was raised to and maintained at 200–10° for a further 6 hr. (Samples of the reaction mixture were analysed periodically by using GLC and heating was continued until no trace of **9b** remained.) The mixture was then allowed to cool, poured into water (500 ml) and washed with ether (3 × 150 ml). The distillate was also washed with ether and the combined ethereal extracts were successively washed with 2N HCl (2 × 100 ml) and with water (2 × 100 ml) and then dried ($MgSO_4$). The ether was evaporated *in vacuo* to give a colourless oil which solidified on being cooled. Two recrystallisations (aqueous MeOH) gave **11b** (10·6 g, 72%), m.p. 82–4° (lit.,[15] m.p. 81–2°), ν_{max} (KCl) 3010, 2990, 1253, 1182, 1096, 978 cm^{-1}; δ 1·92 (2H, d), 2·10 (2H, d), 2·62–2·70 (2H, m), 3·04 (4H, m); *m/e* 288 (M^+), 209, 144, 65. **11b** was also prepared by a similar procedure from **6b**, **12**, **17** and **18**.

5,9 - *Dibromo* - 6,6 - *ethylenedioxy* - 10,10 - *dimethoxypentacyclo* $[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]$ *decane* (**12**). A soln of **6b**[2] (15·0 g, 0·041 mol) and toluene-*p*-sulphonic acid monohydrate (0·2 g) in "Analar" MeOH (150 ml) was heated under reflux (*ca.* 10 days) until starting material could not be detected by TLC or GLC analysis. The soln was then poured into water (500 ml) and washed with ether (3 × 200 ml) and the ethereal solns were washed with NaOH aq (2 × 50 ml of 10%), followed by water, and then dried ($MgSO_4$). The ether was removed *in vacuo* to leave a colourless oil which solidified when kept at room temp. The crude solid was recrystallised twice (light petroleum, b.p. 80–100°) to give 5,9 - *dibromo* - 6,6 - *ethylenedioxy* - 10,10 - *dimethoxypentacyclo* $[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]$*decane* (**12**; 13·5 g, 80%), m.p. 89–91°, ν_{max} (KCl), 3000, 2900, 1308, 1295, 1136, 1110, 1082, 1041 cm^{-1}; δ 2·44–2·57 (1H, m), 2·79–2·94 (1H, m), 3·17–3·32 (4H, m), 3·45 (6H, s), 3·94–4·34 (4H, m); *m/e* 406 (M^+), 391, 375, 327, 248, 233, 103 (Found: C, 41·2; H, 3·9; Br, 39·3. $C_{14}H_{16}Br_2O_4$ requires: C, 41·2; H, 4·0; Br, 39·2%).

6,6 - *Ethylenedioxy* - 10,10 - *dimethoxypentacyclo* $[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]$*decane* (**13**) was prepared from **12** by a procedure similar to that described for the preparation of **10**. The crude product was distilled to give 6,6 - *ethylenedioxy* - 10,10 - *dimethoxypentacyclo* $[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]$ *decane* (**13**) (76%), b.p. 110–2°/0·1 mm Hg, ν_{max} (film) 2990, 1329, 1314, 1105, 1084, 1058, 1010 cm^{-1}; δ 2·40–2·50 (2H, m), 2·72–3·00 (6H, m), 3·18 (3H, s), 3·27 (3H, s), 3·86–3·94 (4H, m); *m/e* 250 (M^+), 235, 219, 131, 103 (Found: C, 67·0; H, 7·2. $C_{14}H_{18}O_4$ requires: C, 67·2; H, 7·2%).

5,9 - *Dibromo* - 6,6 - *ethylenedioxypentacyclo* $[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]$ *decan* - 10 - *ol* (**14**). A mixture of **6b**[2] (1·1 g, 0·0030 mol) and $NaBH_4$ (0·49 g, 0·013 mol) in "AnalaR" MeOH (17·0 ml) and water (3·5 ml) was heated under reflux overnight. The soln was allowed to cool and starting material could not be detected in a sample which was tested by TLC. Water (50 ml) was added dropwise to destroy the excess of $NaBH_4$ and the mixture was then poured into water (100 ml), washed with chloroform (3 × 50 ml) and the combined washings were dried ($MgSO_4$). The chloroform was removed *in vacuo* and the crude product was recrystallised (light petroleum, b.p. 80–100°, and a little chloroform) to give 5,9 - *dibromo* - 6,6 - *ethylenedioxypentacyclo* $[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]$ *decan* - 10 - *ol* (**14**; 1·0 g, 90%), m.p. 134–6°, ν_{max} (Nujol) 3440, 2910, 1305, 1150, 1106, 1082, 970 cm^{-1}; δ 2·07 (1H, s), 2·78–3·25 (6H, m), 3·97 (1H, s), 3·89–4·29 (4H, m); *m/e* 362 (M^+), 283, 265, 204, 203, 132, 131 (Found: C, 39·4; H, 3·3; Br, 43·7. $C_{12}H_{12}Br_2O_3$ requires: C, 39·6; H, 3·3; Br, 43·9%). The product gave a single peak on GLC analysis and the NMR spectrum is consistent with that expected for a single isomer; it is not known which C_{10}-alcohol has been formed.

5,9 - *Dibromo* - 6,6 - *ethylenedioxy* - 10 - *methoxypentacyclo* $[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]$ *decane* (**15**). A mixture of **14** (1·21 g, 0·0033 mol) and NaH (50% dispersion in mineral oil, 2·5 g, 0·052 mol) in 1,2-dimethoxyethane (35 ml) was heated at 90° with stirring for 3 hr in a flask fitted with a condenser and guard tube ($CaCl_2$). MeI (25 ml) was added to the cooled mixture which was then stirred at 60° for 60 hr. The cooled mixture was diluted with water (200 ml), washed with chloroform (3 × 60 ml) and the combined washings were washed with water and dried ($MgSO_4$). The chloroform was removed *in vacuo* to leave an oil which was twice recrystallised (light petroleum, b.p. 80–100°) to give 5,9 - *dibromo* - 6,6 - *ethylenedioxy* - 10 - *methoxypentacyclo* $[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]$ *decane* (**15**; 0·89 g, 71%), m.p. 82·5–3·5°, ν_{max} (KCl) 2990, 1302, 1110, 1100, 1037, 982 cm^{-1}; δ 2·60–2·80 (1H, m), 2·96–3·36 (5H, m), 3·44 (3H, s), 3·62 (1H, s), 3·90–4·36 (4H, m); *m/e* 376 (M^+), 297, 265, 115, 103 (Found: C, 41·8; H, 3·9; Br, 42·1. $C_{13}H_{14}Br_2O_3$ requires: C, 41·3; H, 3·7; Br, 42·3%). The product gave a single peak on GLC analysis and the NMR spectrum is consistent with that expected for a single isomer; it is not known which C_{10}-methoxy compound has been formed.

5 - *Bromo* - 6,6,10,10 - *bisethylenedioxypentacyclo* $[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]$ *decane* (**16**) was prepared from compound **6a** by a standard procedure[2]; yield 64%, b.p. 163–5°/0·35 mm Hg, ν_{max} (film) 2985, 2885, 1330, 1305, 1085, 1040 cm^{-1}; δ 2·50–2·75 (3H, m), 2·98–3·28 (4H, m) 3·85–4·30 (8H, m); *m/e* 326 (M^+), 282, 247, 175, 131 (Found: C, 51·6; H, 4·8; Br, 24·2. $C_{14}H_{15}BrO_4$ requires: C, 51·4; H, 4·6; Br, 24·4%).

1 - *Bromo* - 4 - *methoxymethylpentacyclo*$[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]$ *nonane* (**24**). Compound **23**[16] (0·39 g, 0·0013 mol), KOH (0·96 g, 0·017 mol) and hydrazine hydrate (4 ml of 98–100%) in triethylene glycol (8 ml) were heated as described for the preparation of **11b** and a solid (0·34 g) sublimed into the condenser. The solid was resublimed at 150° and atmospheric pressure to give 1 - *bromo* - 4 - *methoxymethylpentacyclo*$[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]$*nonane* (**24**; 0·26 g, 83%), m.p. 44–6°, ν_{max} (KCl) 2980, 1169, 1120, 1104, 1097, 996, 829 cm^{-1}; δ 2·12 (2H, d), 3·00–3·20 (1H, m), 3·23–3·45 (10H, m;

includes two peaks at 3·30 [~3H] and 3·39 [~2H]); *m/e* 240 (M^+), 225, 209, 195, 161, 129, 116, 115 (Found: C, 54·6; H, 5·3; Br, 33·4. $C_{11}H_{13}BrO$ requires: C, 54·8; H, 5·4; Br, 33·1%).

Reaction of **6b** *with a mixture of potassium hydroxide, hydrazine hydrate, and triethylene glycol.* A mixture of KOH (1·01 g, 0·018 mol), hydrazine hydrate (6 ml of 98–100%) and triethylene glycol (8 ml) was placed in an apparatus arranged for distillation as described for the preparation of **11b**. The mixture was heated during 2 hr until the internal temp. reached 215°, at which point **6b** (0·40 g, 0·0011 mol) in triethylene glycol (5 ml) was added. The mixture remained clear and after 7 min the mixture was cooled, diluted with water, washed with ether and the ethereal extracts were dried ($MgSO_4$) (basic extract). The aqueous phase was acidified at 0° with conc HCl and then washed with ether and the ethereal extracts were dried ($MgSO_4$) (acidic extract). The basic extract yielded a crude product (0·37 g) which was shown by GLC analysis (180°) to be mainly **9b** mixed with a little **11b**. The ether was removed from the acidic extract and the trace of crude product was treated with ethereal diazomethane; GLC analysis (180°) did not show a single peak.

Reaction of **9b**, **12**, **13**, **15**, **16** *with a mixture of sodium, triethylene glycol and anhydrous hydrazine.* (a) Na (0·3 g, 0·013 g atom) was treated with warm triethylene glycol (10 ml) and then **9b** (0·10 g, 0·00029 mol) and anhyd hydrazine (3·0 ml) were added and the mixture was heated in an apparatus arranged for distillation as described for the preparation of **11b**. After 3 hr at 210–220°, GLC analysis showed that reaction was almost complete; the product was mainly **11b** with small amounts of **9a** and **20** (which was identified by GLC/mass spectrometry).

(b) In similar reactions, (i) **12** gave **11b**, **21** (identified by GLC/mass spectrometry; also formed in the reaction with **18**) and hydrodebromination product(s) of **21** (identified by GLC/mass spectrometry); (ii) **16** gave **20** and **9a** (~2:1); **20** was identified by GLC/mass spectrometry; (iii) **13** gave **10**, **25** (~1:10) and **2**; **25** was identified by GLC/mass spectrometry; (iv) **15** gave **22** (identified by GLC/mass spectrometry); **9b** or **11b** were not detected by GLC analysis on 20% silicone gum-rubber or 3% ECNSS/M.

Reaction of **17** *or* **12** *with a mixture of sodium, decan-1-ol and anhydrous hydrazine.* (a) Na (0·2 g, 0·0087 g atom) was treated with warm decan-1-ol (10 ml) and then **17** (0·10 g, 0·00025 mol) and anhyd hydrazine (5 ml) were added and the mixture was heated in an apparatus arranged for distillation as described for the preparation of **11b**. After 3 hr at 200–210°, GLC analysis on 20% silicone gum-rubber or 10% Carbowax 20M showed the presence of 2-decoxyethanol. A similar reaction with omission of **17** and addition of ethylene glycol (1 ml) did not give 2-decoxyethanol. (b) In a similar reaction, **12** gave 1-methoxydecane and 2-decoxyethanol. Neither of these products was formed when **12** was omitted from and methanol (1 ml) and ethylene glycol (1 ml) were added to the mixture.

Reaction of acetophenone hydrazone, benzophenone hydrazone, **8a** *and* **8b** *with potassium hydroxide in triethylene glycol.* These hydrazones were reduced following the procedure described for the preparation of **9a**. The temp of the oil bath was raised slowly and the internal temps at which a brisk evolution of N_2 occurred were as follows: **8b**, 100–110°; benzophenone hydrazone, 105–115°; **8a**, 130–140°; acetophenone hydrazone, 135–145°.

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