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CHEMISTRY OF STRAINED POLYCYCLIC COMPOUNDS—V[1]

THE STEREOSPECIFIC CATIONIC CAGE EXPANSION REACTION OF 4-HOMOCUBANE CARBINOLS TO 1,3-BISHOMOCUBANE BRIDGEHEAD ALCOHOLS

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Abstract—The cationic rearrangement of four homocubane bridgehead carbinols *viz* dimethyl 4-(1-bromopentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonyl-9-one ethylene ketal) carbinol **2**, diphenyl 4-(1-bromopentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonyl-9-one ethylene ketal) carbinol **3**, 4-(1-bromopentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonyl-9-one ethylene ketal) carbinol **4** and 4-(1-bromopentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonyl) carbinol **16**, has been studied under various conditions.

Exclusive migration of the C_4—C_7 (or the equivalent C_3—C_4 bond) in the homocubane skeleton was observed leading to 1,3-bishomocubane bridgehead alcohols. Relief of cage constraint governs the selective course of these cage expansions.

Anions adjacent to a bridgehead position in strained polycyclic systems can induce stereospecific rearrangements of these compounds, as exemplified by the homoketonization of a homocubane bridgehead alcohol.[2] In order to study this interesting rearrangement in more detail, particularly the influence of ring strain, a number of cage alcohols was required, which show a diversity in strain energy.

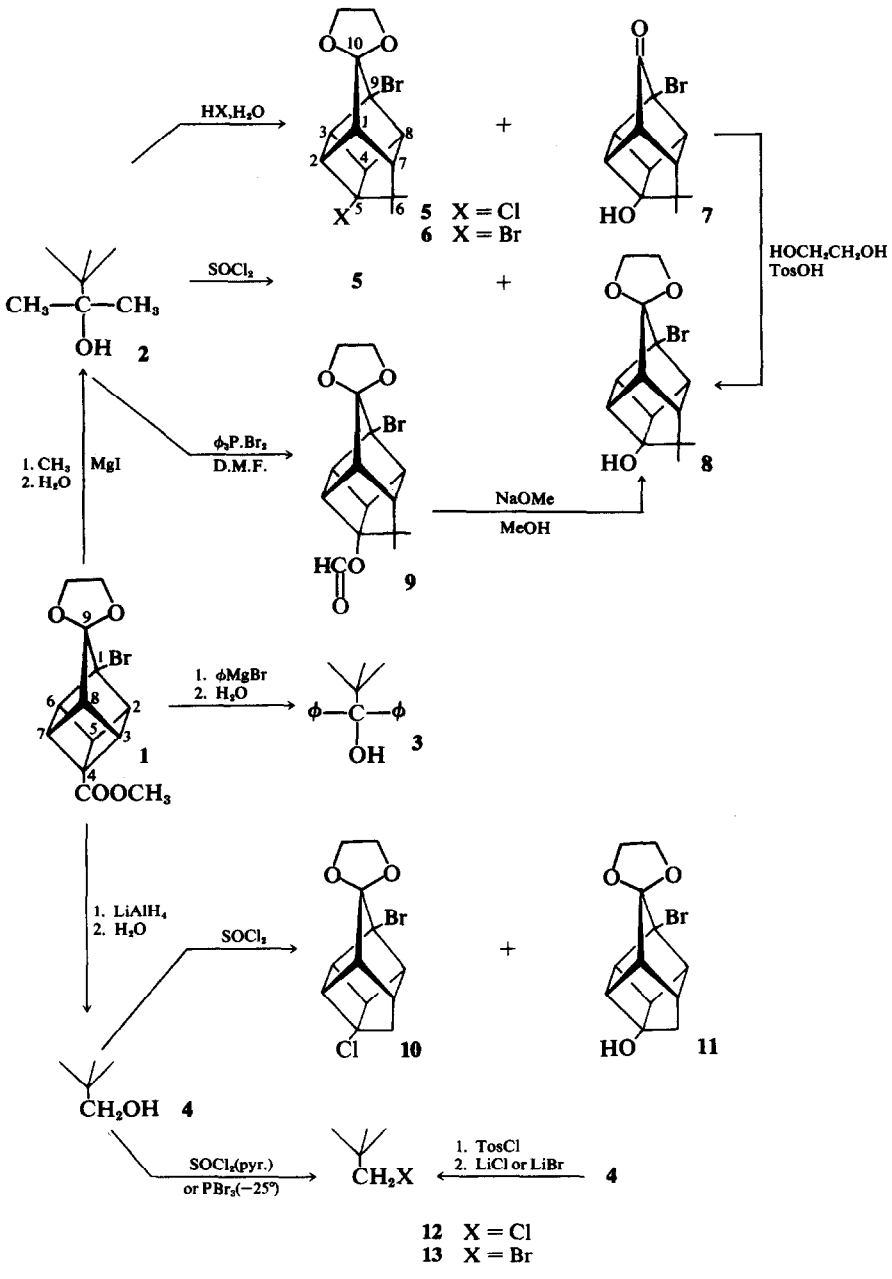
In a previous paper we described the synthesis of cubane and homocubane alcohols.[3] This paper deals with the preparation of 1,3-bishomocubane bridgehead alcohols by a stereospecific cationic cage expansion reaction of homocubane bridgehead carbinols.

The required carbinols, i.e. **2**, **3**, **4** and **16** were easily accessible from the homocubane-4-carboxylic acid **14** or its ester **1**[4] (Schemes I and II).

The cationic rearrangement of the carbinols **2**, **3**, **4** and **16** was studied under a variety of conditions (Schemes I and II). Upon treatment with HCl aq dimethylcarbinol **2** gave a mixture of two main products **5** and **7**. Alcohol **7** was obtained in 57% yield and characterized by an OH absorption at 3400 cm^{-1}, a C=O absorption at 1775 cm^{-1} in the IR spectrum and by two singlets for the Me groups at δ 0·78 and δ 0·92 ppm in the NMR spectrum. These NMR signals can only be reconciled with structure **7** since only migration of the C_4—C_7 bond or the equivalent C_3—C_4 bond in **2** will lead to a bishomocubane derivative in which the two Me groups are non-equivalent. The alternative mode of 1,2-bond shift, *viz*, of the central C_4—C_5 bond, would have given a 1,4-bishomocubane in which the two Me groups are identical.

The NMR spectrum of chloride **5** (yield 27%) also displays two singlets for the Me groups at δ 0·75 and δ 0·94, and in addition a symmetrical multiplet for the ethylene ketal function* at δ 3·80–4·40, a multiplet at δ 3·00–3·25 for the cage protons at $C_{2,3,4,8}$ and a multiplet at δ 2·40–2·65 ppm for the cage protons at C_1 and C_7. Treatment of **2** with HBr aq similarly gave dibromide **6** and alcohol **7**. Under these conditions ketalized alcohol **8** could not be obtained. Apparently hydrolysis of the ketal function takes place readily, presumably, because **8** is quite soluble in aqueous acid. The halides **5** and **6**, on the other hand, are almost insoluble in aqueous acid, and consequently, hydrolysis to the corresponding haloketones will not take place that easy. However, ketal alcohol **8** could be obtained in 40% yield by treatment of the carbinol **2** with $SOCl_2$. This reaction leads to a mixture of chloride **5** and ketal alcohol **8**. Of course, ketalization of ketone alcohol **7** with $HOCH_2CH_2OH$/TosOH also provided ketal alcohol **8**. Treatment of **2** with PBr_3 gave a mixture of dibromide **6** and alcohol **8** (contaminated with some of its phosphite ester). Interestingly, neither the reaction of **2** with $SOCl_2$ nor that with PBr_3 leads to simple halide formation, only rearranged products were obtained. Even the application of these reagents in the presence of pyridine did not change the reaction course. An attempt to prepare unrearranged 4-homocubane

*When a symmetrical absorption is observed, it does not necessarily imply that the ketal containing compound has a plane of symmetry.[5]



SCHEME 1

isopropylbromide by treatment of **2** with Ph_3P/Br_2 in DMF* only resulted in the isolation of rearranged formate **9** in 68% yield. The latter product gave upon transesterification ketal alcohol **8** in quantitative yield.

Although mass spectral data can not differentiate between 1,3 and 1,4-bishomocubanes, these types of cage compounds do show a characteristic cracking pattern, *viz* cleavage of the cage system in half.[7] Indeed intense peaks were observed at *m/e* 128, 130 ($C_7H_9Cl^+$) for chloride **5**, at *m/e* 172, 174 ($C_7H_9Br^+$) for bromide **6** and at *m/e* 110 ($C_7H_{10}O^+$) for alcohol **8**.

Carbinol **4**, when treated with $SOCl_2$, afforded chloride **10** and alcohol **11** in 30% and 45% yield,

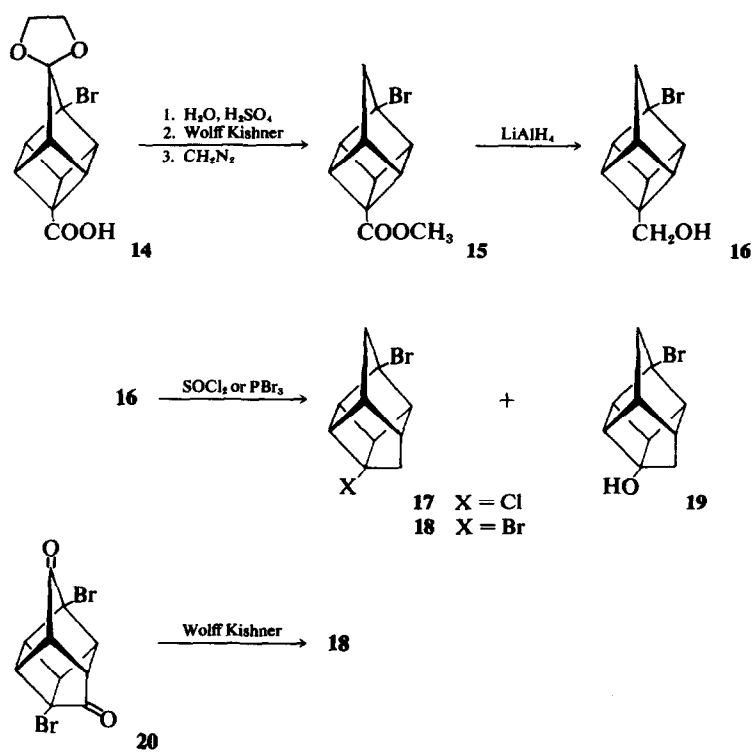
*Triphenylphosphine dibromide in DMF is known for its ability to give bromination without rearrangement.[6]

respectively (Scheme I). In contrast to dimethylcarbinol **2**, carbinol **4** could be converted into unrearranged homocubane methylchloride **12** or methylbromide **13** by treatment with $SOCl_2$ in the presence of pyridine or by treatment with PBr_3 in ether at −25°, respectively. In both cases only a small amount of rearranged products was isolated. It should be noted that **12** and **13** could be obtained in high yields, free from rearranged products, by a S_N2 displacement reaction of the tosylate of **4** with LiCl or LiBr in acetone.

Diphenylcarbinol **3** showed a different behaviour. Upon treatment with HCl aq or $SOCl_2$, no bridgehead bishomocubane alcohol was formed, but instead, a high melting solid (m.p. 281–288°) was isolated which was insoluble in most organic solvents. Thusfar, no structure could be assigned to this compound on account of the available spectroscopic and chemical data.

Carbinol **16** gave upon treatment with $SOCl_2$ a mixture of chloride **17** and alcohol **19** in 30% and 67% yield, respectively (Scheme II). The NMR spectrum of **17** as well as of **19** displays two unsymmetrical doublets for the methylene protons at C_6 and at C_{10}, which is unambiguous evidence for the asymmetric structure of the proposed bishomocubane products. The mass spectra of **17** and **19** exhibit intense peaks arising from cleavage of the bishomocubane skeleton in half, at *m/e* 100, 102 ($C_5H_5Cl^+$) and 144, 146 ($C_5H_5Br^+$) for the chloride **17**, and at *m/e* 82 ($C_5H_6O^+$) and 65 ($C_5H_5Br^+$-Br) for the alcohol **19**. The carbinol **16** gave, upon treatment with PBr_3, a mixture of dibromide **18** and alcohol **19** (together with some of its phosphite ester). The same dibromide **18** could be prepared from 1,3-bishomocubane dione **20**[4] by a Wolff Kishner reduction, and hence confirming the proposed structure.

In conclusion it may be pointed out that the cationic rearrangement of homocubane carbinols provides an attractive route for the synthesis of bridgehead 1,3-bishomocubane alcohols. These compounds are not easily accessible by other routes. The driving force in this stereospecific cationic rearrangement most likely is relief of ring strain leading to the 1,3-bishomocubane cage system by exclusive migration of the C_4—C_7 bond (or the equivalent C_3—C_4 bond) in the homocubane skeleton. 1,4-Bishomocubane derivatives arising from a 1,2 shift of the central C_4—C_5 bond were not observed. The present results are in line with the previous observation of exclusive cleavage of the C_4—C_7 bond (or the equivalent C_3—C_4 bond) during the homoketonization reaction of a bridgehead homocubane alcohol with an OH at the 4-position.[2] Apparently in both cases relief of cage strain is higher by cleavage of the C_4—C_7 (or C_3—C_4) bond than of the C_4—C_5 bond. This energy difference is responsible for the high selective bond migration.



SCHEME 2

EXPERIMENTAL

IR spectra were taken on a Perkin-Elmer 125 grating spectrometer. NMR spectra were recorded on a Varian A60 spectrometer, using TMS as internal standard. All m.ps are uncorrected and determined on a Kofler hot stage. Elemental analyses were carried out in duplicate (their average values are reported), in the microanalytical department of the University at Groningen under supervision of Mr. W. M. Hazenberg.

Methyl 1-*bromopentacyclo*[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]*nonan*-9-*one ethylene ketal* 4-*carboxylate* (**1**)

Carboxylic acid **14**, prepared as described by Key[4,8] was esterified with CH_2N_2 to give **1** (97%), m.p. 107–109° (lit.[4] m.p. 106–108°).

Dimethyl 4-(1-*bromopentacyclo*[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]*nonyl*-9-*one ethylene ketal*) *carbinol* (**2**)

A soln of **1** (0·5 g, 1·6 mmole) in anhyd ether (25 ml) was added to a soln of MeMgI in ether. After stirring overnight, the mixture was diluted with water and extracted with ether. The ether layer was dried ($MgSO_4$) and concentrated to give crude **2** (0·5 g, 95%). Recrystallization from hexane gave a pure sample: m.p. 114–115°; IR ν_{max}^{KBr} 3500, 3440 (O—H) cm^{-1}; NMR ($CDCl_3$): δ 3·78–4·38 (sym.m, 4H, ketal group), 3·3–3·5 (m, 5H), 2·55–2·85 (m, 1H, proton at C_8), 1·27 (s, 1H, OH), 1·10 (s, 6H, Me); *m/e* 254 (M^+—C_3H_6OH, 1Br). (Found: C, 54·10; H, 5·61; Br, 25·70; Calc. for $C_{14}H_{17}BrO_3$: C, 53·69; H, 5·47; Br, 25·52%).

Diphenyl 4-(1-*bromopentacyclo*[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]*nonyl*-9-*one ethylene ketal*) *carbinol* (**3**)

This was prepared as described above using PhMgBr instead of MeMgI. Ester **1** gave **3** in 87% yield, m.p. 162·5–164·5° (recrystallized from hexane); IR ν_{max}^{KBr} 3600 (O—H), 1600 (phenyl) cm^{-1}; NMR ($CDCl_3$) δ 7·26 (m, 10H, phenyl), 3·75–4·35 (sym.m, 4H, ketal group), 3·45–3·75 (m, 5H), 2·15–2·45 (m, 1H, proton at C_8), UV (EtOH) λ_{max} in nm (ε) 251 (496); 258 (564); 264 (449). (Found: C, 65·52; H, 4·63; Br, 18·27; Calc. for $C_{24}H_{21}BrO_3$: C, 65·91; H, 4·84; Br, 18·27%).

4-(1-*Bromopentacyclo*[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]*nonyl*-9-*one ethylene ketal*) *carbinol* (**4**)

This was prepared as described above using excess LAH. Ester **1** gave **4** in almost quantitative yield, m.p. 84–87° (recrystallized from hexane) (lit.[8] m.p. 80–84°); IR ν_{max}^{KBr} 3450 (O—H) cm^{-1}; NMR ($CDCl_3$) δ 3·75–4·40 (sym.m, 4H, ketal group), 3·25–3·60 (m, 5H), 3·67 (s, 2H, —CH_2—O—), 2·65–3·00 (m, 1H, proton at C_8), 1·77 (s, 1H, OH); *m/e* 285 (M^+, 1Br).

Rearrangement of **2** *with* HCl. A slurry of **2** (0·3 g, 1 mmole) in HCl aq (5 ml) was stirred overnight. Then water was added and the mixture extracted with ether. The extracts were washed with $NaHCO_3$ aq (5%) and dried ($MgSO_4$). Solvent was evaporated yielding an oil which was dissolved in benzene and chromatographed over silica. Elution with benzene furnished **5** (0·09 g, 27%). Recrystallization from hexane and subsequent sublimation (100°/12 mm) gave a pure sample, m.p. 117–122°; IR ν_{max}^{KBr} 1310, 1045, 990 cm^{-1}; NMR ($CDCl_3$) δ 3·80–4·40 (sym.m, 4H, ketal group), 3·00–3·25 (m, 4H), 2·40–2·65 (m, 2H, protons at C_1 and C_7), 0·94 (s, 3H, Me), 0·75 (s, 3H, Me); *m/e* 331 (M^+, 1Br, 1Cl), 128 ($C_7H_9Cl^+$). (Found: C, 50·61; H, 4·96; Br, 24·17; Cl, 10·83; Calc. for $C_{14}H_{16}BrClO_2$: C, 50·70; H, 4·86; Br, 24·10; Cl, 10·69%). Further elution with ether gave **7** as an oil; (0·19 g, 57%). IR ν_{max} 3400 (broad OH), 1775 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 3·47–2·20 (m, 6H), 2·28 (s, 1H, OH), 0·78 (s, 3H, Me), 0·92 (s, 3H, Me). The alcohol could not be obtained analytically pure; it was characterized by its conversion into ketalized alcohol **8** (*vide infra*) by treatment with *p*-toluenesulfonic acid and ethylene glycol in benzene.

Rearrangement of **2** *with* HBr. The same procedure as for the reaction of **2** with HCl aq was used, giving a mixture of dibromide **6** and alcohol **7** which was separated by chromatography over silica. Elution with benzene furnished **6** (17%). Recrystallization from hexane gave an analytical sample, m.p. 128–131°; IR ν_{max}^{KBr} 1305, 1040, 980 cm^{-1}; NMR ($CDCl_3$) δ 3·75–4·40 (sym.m, 4H, ketal group), 3·00–3·30 (m, 4H), 2·35–2·75 (m, 2H, protons at C_1 and C_7), 0·93 (s, 3H, methyl), 0·75 (s, 3H, Me); *m/e* 376 (M^+, 2Br), 173 ($C_7H_9Br^+$). (Found: C, 45·09; H, 4·34; Br, 42·14; Calc. for $C_{14}H_{16}Br_2O_2$: C, 44·71; H, 4·29; Br, 42·49%). Further elution with ether gave alcohol **7** (70%).

Rearrangement of **2** *with* $SOCl_2$. A soln of carbinol **2** (1·0 g, 3·2 mmole) in $SOCl_2$ (15 ml) was stirred at room temp for 2 days. Then the mixture was poured into ice-water and extracted with ether. The extracts were washed with $NaHCO_3$ aq (5%) and dried ($MgSO_4$). Solvent was removed yielding a mixture of chloride **5** and alcohol **8**, which was separated by chromatography over silica. Elution with benzene afforded the chloride **5** (0·25 g, 23%). Further elution with ether gave alcohol **8** as an oil. Crystallization from hexane afforded pure alcohol **8** (0·4 g, 40%), m.p. 88·5–89·5° (after drying at 70°/12 mm for 24 hr); IR ν_{max}^{KBr} 3320 (OH), 1320 cm^{-1}; NMR ($CDCl_3$) δ 3·75–4·40 (sym.m, 4H, ketal group), 2·75–3·15 (m, 4H), 2·25–2·55 (m, 2H, protons at C_1 and C_7), 1·60 (s, 1H, OH), 0·87 (s, 3H, Me), 0·70 (s, 3H, methyl); *m/e* 313 (M^+, 1Br), 110 ($C_7H_{10}O^+$). (Found: C, 53·74; H, 5·53; Br, 25·55; Calc. for $C_{14}H_{17}BrO_3$: C, 53·69; H, 5·47; Br, 25·51%).

Rearrangement of **2** *with* PBr_3. The same procedure as in the rearrangement of **2** with $SOCl_2$ was used, giving a mixture of dibromide **6** and alcohol **8** (together with its phosphite ester) which was separated by chromatography over silica. Elution with benzene gave pure dibromide **6** (14%). Further elution with ether gave alcohol **8** (50%) contaminated with some of its phosphite ester.

6,6-*Dimethyl*-9-*bromopentacyclo*[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]*deca*-10-*one ethylene ketal* 5-*formate* (**9**)

To a stirred ice-cooled soln of carbinol **2** (0·2 g, 0·6 mmole) in DMF (3 ml) was added triphenylphosphine (0·2 g, 0·7 mmole). Then bromine (0·12 g, 0·7 mmole) was added at such a rate that the reaction temp could be kept below 55°. After stirring at room temp for 18 hr, the mixture was diluted with water and extracted with ether. The ether layer was dried ($MgSO_4$) and concentrated to give an oil which was chromatographed over silica. Elution with benzene furnished formate **9** (0·15 g, 68%). Recrystallization from hexane gave a pure sample, m.p. 107–109°; IR ν_{max}^{KBr} 1730 (C=O), 1175 (ester) cm^{-1}; NMR ($CDCl_3$) δ 8·08 (s, 1H, OC(=O)H), 3·75–4·35 (sym.m, 4H, ketal group), 3·00–3·35 (m, 4H), 2·30–2·55 (m, 2H, protons at C_1 and C_7), 0·93 (s, 3H, methyl), 0·78 (s, 3H, methyl). *m/e* 341 (M^+, 1Br). (Found: C, 52·91; H, 5·11; Br, 23·72; Calc. for $C_{15}H_{17}BrO_4$: C, 52·80; H, 5·03; Br, 24·43%). The formate **9** was converted into alcohol **8**, in quantitative yield, by refluxing in MeOH (10 ml) containing NaOMe (0·5 g), for 2 hr.

Rearrangement of **4** *with* $SOCl_2$. A soln of carbinol **4** (1·0 g, 3·5 mmole) in $SOCl_2$ (15 ml) was stirred at room

temp for 16 hr. The $SOCl_2$ was removed *in vacuo*, the residue diluted with water and ether extracted. The ether layer was dried ($MgSO_4$) and concentrated to give a dark brown oil which was chromatographed over silica. Elution with benzene afforded ketal **10** (0·38 g, 30%). Recrystallization from hexane and subsequent sublimation *in vacuo* gave a pure sample, m.p. 72–76°; IR ν_{max}^{KBr} 1310, 1050, 980 cm^{-1}; NMR ($CDCl_3$) δ 3·74–4·37 (sym.m, 4H, ketal group), 2·8–3·3 (m, 5H), 2·15–2·5 (m, 1H, proton at C_1), 1·96 (AB quartet, $J = 10$ Hz, 2H, protons at C_6); *m/e* 303 (M^+, 1Br, 1Cl). (Found: C, 47·35; H, 3·87; Br, 26·61; Cl, 12·22; Calc. for $C_{12}H_{12}BrClO_2$: C, 47·47; H, 3·98; Br, 26·32; Cl, 11·67%). Further elution with benzene/ether (1:1) gave ketal **11** (0·45 g, 45%). Crystallization from hexane gave an analytically pure sample, m.p. 114–120°; IR ν_{max}^{KBr} 3250 (OH) cm^{-1}; NMR ($CDCl_3$) δ 3·75–4·35 (sym.m, 4H, ketal group), 2·65–3·30 (m, 5H), 2·57 (s, 1H, OH), 2·17–2·45 (m, 1H, proton at C_1), 1·73 (AB quartet, 2H, protons at C_8); *m/e* 285 (M^+, 1Br), 82 ($C_5H_6O^+$). (Found: C, 50·10; H, 4·69; Br, 28·00; Calc. for $C_{12}H_{13}BrO_3$: C, 50·55; H, 4·60; Br, 28·03%).

1-*Bromopentacyclo*[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]*nonan*-9-*one ethylene ketal* 4-*methylchloride* **12**

(A) *From carbinol* **4**. $SOCl_2$ (1·5 g, 13 mmole) was added dropwise to a soln of **4** (0·2 g, 0·7 mmole) in pyridine (1·0 g, 13 mmole). After being stirred for 8 hr at 75°, the mixture was poured onto crushed ice and extracted with ether. The ether phase was dried ($MgSO_4$) and the solvent evaporated to give chloride **12** (0·15 g, 70%) as a crystalline solid. Recrystallization from hexane gave a pure sample, m.p. 86–89° (lit.* m.p. 87–89°); IR ν_{max}^{KBr} 1295, 1040, 840 cm^{-1}; NMR ($CDCl_3$) δ 3·85–4·40 (sym.m, 4H, ketal group), 3·64 (s, 2H, —CH_2Cl), 3·4–3·6 (m, 5H), 2·7–3·1 (m, 1H, proton at C_8).

(B) *From the tosylate of* **4**. A mixture of the tosylate of **4**, (0·25 g, 0·57 mmole) prepared in the usual way,[8] and anhyd LiCl (0·5 g, 12 mmole) in acetone, was heated under reflux for 8 hr. After cooling to room temp, water was added and the soln extracted with ether. The extracts were dried ($MgSO_4$) and concentrated to give chloride **12** (0·18 g, 100%), m.p. 80–84° (hexane).

1-*Bromopentacyclo*[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]*nonan*-9-*one ethylene ketal* 4-*methylbromide* **13**

(A) *From the carbinol* **4**. A soln of **4** (0·4 g, 1·3 mmole) in ether (20 ml) was cooled to −25°. PBr_3 (0·4 g, 1·5 mmole) was added dropwise. After stirring at room temp for 16 hr, the mixture was poured onto crushed ice and ether extracted. The ether phase was dried ($MgSO_4$) and concentrated to give the methylbromide **13** (0·14 g, 30%). Crystallization from hexane gave pure **13**, m.p. 76·5–79·0°; IR ν_{max}^{KBr} 1290, 1080, 835 cm^{-1}; NMR ($CDCl_3$) δ 3·75–4·40 (sym.m, 4H, ketal group), 3·52 (s, 2H, —CH_2Br), 3·30–3·70 (m, 5H), 2·70–3·05 (m, 1H, proton at C_8); *m/e* 348 (M^+, 2Br). (Found: C, 41·63; H, 3·58; Br, 45·44; Calc. for $C_{12}H_{12}Br_2O_2$: C, 41·41; H, 3·48; Br, 45·93%).

(B) *From the tosylate of* **4**. The same procedure as for chloride **12** was used, utilizing LiBr as reagent. A 90% yield of the methylbromide **13** was obtained.

Methyl 1-*bromopentacyclo*[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]*nonane* 4-*carboxylate* **15**

1-Bromopentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$] nonane 4-carboxylic acid, prepared as described previously,[3] was treated with ethereal CH_2N_2 to give ester **15** (93%), m.p. 46·5–47·5° (hexane); IR ν_{max}^{KBr} 1720 (C=O); NMR ($CDCl_3$) δ 3·68 (s, 3H, OCH_3), 3·1–3·9 (m, 6H), 2·16 (d, $J = 1·5$ Hz, 2H, protons at C_9); *m/e* 255 (M^+, 1 Br). (Found: C, 52·07; H, 4·32; Br, 31·37; Calc. for $C_{11}H_{11}BrO_2$: C, 51·79; H, 4·35; Br, 31·33%).

4-(1-*Bromopentacyclo*[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]*nonyl*) *carbinol* **16**

A soln of ester **15** (1·4 g, 5·5 mmole) in anhyd ether (20 ml) was added gradually to a slurry of LAH in ether. After stirring overnight, the mixture was diluted with water and extracted with ether. The ether layer was dried ($MgSO_4$) and concentrated to give crude carbinol **16**. (1·2 g, 95%). Crystallization from pentane gave an analytically pure sample, m.p. 44–46°; IR ν_{max}^{KBr} 3350 (OH) cm^{-1}; NMR ($CDCl_3$) δ 3·64 (s, 2H, —CH_2O—), 2·9–3·4 (m, 6H), 2·14 (d, $J = 1·5$ Hz, 2H, protons at C_9), 1·43 (s, 1H, OH) *m/e* 196 (M^+—CH_2OH). (Found: C, 52·80; H, 4·91; Br, 35·12; Calc. for $C_{10}H_{11}BrO$: C, 52·89; H, 4·88; Br, 35·19%).

Rearrangement of **16** *with* $SOCl_2$. The same procedure as for the rearrangement of carbinol **4** with $SOCl_2$ was used, giving a mixture of chloride **17** and alcohol **19** which was separated by chromatography over silica. Elution with hexane furnished **17** (30%). Crystallization from EtOH and subsequent sublimation (70°/12 mm) gave an analytically pure sample, m.p. 54–64°; IR ν_{max}^{KBr} 1090, 850 cm^{-1}; NMR ($CDCl_3$) δ 2·9–3·3 (m, 4H), 2·5–2·9 (m, 2H, protons at C_1 and C_7), 1·97 (complex AB pattern, 4H, protons at C_8 and C_{10}); *m/e* 145 ($C_5H_5Br^+$), 100 ($C_5H_5Cl^+$). (Found: C, 48·81; H, 4·20; Br, 32·18; Cl, 14·39; Calc. for $C_{10}H_{10}BrCl$: C, 48·90; H, 4·10; Br, 32·54; Cl, 14·43%).

Further elution with ether gave **19** (67%) as an oil, which solidified on standing, m.p. 73·5–84·5° (hexane); IR ν_{max}^{KBr} 3250 (OH) cm^{-1}; NMR ($CDCl_3$) δ 2·35–3·25 (m, 6H), 1·97 (AB quartet, $J = 10$ Hz, 2H, protons at C_{10}), 1·83 (s, 1H, OH), 1·70 (AB quartet, $J = 10$ Hz, 2H, protons at C_6); *m/e* 82 ($C_5H_6O^+$) (Found: C, 52·96; H, 4·88; Br, 34·92; Calc. for $C_{10}H_{11}BrO$: C, 52·89; H, 4·88, Br, 35·19%).

Rearrangement of **16** *with* PBr_3. The same procedure as for the rearrangement of **2** with $SOCl_2$ was used, giving mixture of dibromide **18** and alcohol **19** (contaminated with some of its phosphite ester) which was separated by chromatography over silica. Elution with hexane gave **18** (18%) as a crystalline solid, m.p. 81–82° (EtOH); IR ν_{max}^{KBr} 1090, 855 cm^{-1}; NMR ($CDCl_3$) δ 2·85–3·15 (m, 4H), 2·5–2·75 (m, 2H, protons at C_1 and C_7), 2·00 (AB quartet, $J = 11$ Hz, 4H, protons at C_8 and C_{10}); *m/e* 145 ($C_5H_5Br^+$) (Found: C, 41·49; H, 3·63; Br, 55·32; Calc. for $C_{10}H_{10}Br_2$: C, 41·41; H, 3·48; Br, 55·11%). Further elution with ether gave alcohol **19** together with a small amount of its phosphite ester.

5,9-*Dibromopentacyclo*[5.3.0.^{2,5}.$0^{3,9}$.$0^{4,8}$]*decane* **18** *from* 5,9-*dibromopentacyclo*[5.3.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]*deca*-6,10-*dione* **(20)**

A soln of di-ketone **20**[4] (1·0 g, 3·1 mmole) in hydrazine hydrate (30 ml, 100%) was refluxed for 4 hr. After cooling, diethylene glycol (70 ml) and KOH (4·5 g) were added. The apparatus was arranged for distillation and the mixture was slowly heated in an oil bath to 220° and which temp was maintained for 3 hr. The mixture was allowed to cool, poured into water and ether extracted. The ether extracts were washed with HCl aq and dried ($MgSO_4$). Solvent was evaporated giving dibromide **18** (0·4 g, 50%), as a crystalline solid, m.p. 81–82·5°.

*The same chloride **12** was found and characterized by Key[8] during the tosylation of **4**.

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