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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 C₄—C₇ (or the equivalent C₃—C₄ 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 1⁴ (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 C₄—C₇ bond or the equivalent C₃—C₄ 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 C₄—C₅ 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 C₁ and C₇. 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 SOCl₂. This reaction leads to a mixture of chloride 5 and ketal alcohol 8. Of course, ketalization of ketone alcohol 7 with HOCH₂CH₂OH/TosOH also provided ketal alcohol 8. Treatment of 2 with PBr₃ gave a mixture of dibromide 6 and alcohol 8 (contaminated with some of its phosphite ester). Interestingly, neither the reaction of 2 with SOCl₂ nor that with PBr₃ 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 $\text{Ph}_3\text{P}/\text{Br}_2$ 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 ($\text{C}_7\text{H}_9\text{Cl}^+$) for chloride 5, at m/e 172, 174 ($\text{C}_7\text{H}_9\text{Br}^+$) for bromide 6 and at m/e 110 ($\text{C}_7\text{H}_{10}\text{O}^+$) 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.⁸

respectively (Scheme I). In contrast to dimethylcarbinol 2, carbinol 4 could be converted into un-rearranged 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 $\text{S}_\text{N}2$ 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. $281\text{--}288^\circ$) 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 ($\text{C}_5\text{H}_5\text{Cl}^+$) and 144, 146 ($\text{C}_5\text{H}_5\text{Br}^+$) for the chloride

17, and at m/e 82 ($\text{C}_5\text{H}_5\text{O}^+$) and 65 ($\text{C}_5\text{H}_5\text{Br}^+-\text{Br}$) 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 20⁴ 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 $\text{C}_4\text{--C}_7$ bond (or the equivalent $\text{C}_3\text{--C}_4$ bond) in the homocubane skeleton. 1,4-Bishomocubane derivatives arising from a 1,2 shift of the central $\text{C}_4\text{--C}_5$ bond were not observed. The present results are in line with the previous observation of exclusive cleavage of the $\text{C}_4\text{--C}_7$ bond (or the equivalent $\text{C}_3\text{--C}_4$ 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 $\text{C}_4\text{--C}_7$ (or $\text{C}_3\text{--C}_4$) bond than of the $\text{C}_4\text{--C}_5$ 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 Koffler 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 CH₂N₂ 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 (MgSO₄) and concentrated to give crude 2 (0.5 g, 95%). Recrystallization from hexane gave a pure sample: m.p. 114–115°; IR $\nu_{\text{max}}^{\text{KBr}}$ 3500, 3440 (O—H) cm⁻¹; NMR (CDCl₃) δ 3.78–4.38 (sym.m, 4H, ketal group), 3.3–3.5 (m, 5H), 2.55–2.85 (m, 1H, proton at C₈), 1.27 (s, 1H, OH), 1.10 (s, 6H, Me); *m/e* 254 (M⁺—C₇H₈OH, 1Br). (Found: C, 54.10; H, 5.61; Br, 25.70; Calc. for C₁₄H₁₇BrO₃: 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 $\nu_{\text{max}}^{\text{KBr}}$ 3600 (O—H), 1600 (phenyl) cm⁻¹; NMR (CDCl₃) 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 C₈), 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 C₂₄H₂₁BrO₃: 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 $\nu_{\text{max}}^{\text{KBr}}$ 3450 (O—H) cm⁻¹; NMR (CDCl₃) δ 3.75–4.40 (sym.m, 4H, ketal group), 3.25–3.60 (m, 5H), 3.67 (s, 2H, —CH₂—O—), 2.65–3.00 (m, 1H, proton at C₈), 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 NaHCO₃ aq (5%) and dried (MgSO₄). 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 $\nu_{\text{max}}^{\text{KBr}}$ 1310, 1045, 990 cm⁻¹; NMR (CDCl₃) δ 3.80–4.40 (sym.m, 4H, ketal group), 3.00–3.25 (m, 4H), 2.40–2.65 (m, 2H, protons at C₁ and C₇), 0.94 (s, 3H, Me), 0.75 (s, 3H, Me); *m/e* 331 (M⁺, 1Br, 1Cl), 128 (C₇H₈Cl⁺). (Found: C, 50.61; H, 4.96; Br, 24.17; Cl, 10.83; Calc. for C₁₄H₁₆BrClO₂: 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 (CDCl₃) 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 $\nu_{\text{max}}^{\text{KBr}}$ 1305, 1040, 980 cm⁻¹; NMR (CDCl₃) δ 3.75–4.40 (sym.m, 4H, ketal group), 3.00–3.30 (m, 4H), 2.35–2.75 (m, 2H, protons at C₁ and C₇), 0.93 (s, 3H, methyl), 0.75 (s, 3H, Me); *m/e* 376 (M⁺, 2Br), 173 (C₇H₈Br⁺). (Found: C, 45.09; H, 4.34; Br, 42.14; Calc. for C₁₄H₁₆Br₂O₂: C, 44.71; H, 4.29; Br, 42.49%). Further elution with ether gave alcohol 7 (70%).

Rearrangement of 2 with SOCl₂. A soln of carbinol 2 (1.0 g, 3.2 mmole) in SOCl₂ (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 NaHCO₃ aq (5%) and dried (MgSO₄). 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 $\nu_{\text{max}}^{\text{KBr}}$ 3320 (OH), 1320 cm⁻¹; NMR (CDCl₃) δ 3.75–4.40 (sym.m, 4H, ketal group), 2.75–3.15 (m, 4H), 2.25–2.55 (m, 2H, protons at C₁ and C₇), 1.60 (s, 1H, OH), 0.87 (s, 3H, Me), 0.70 (s, 3H, methyl); *m/e* 313 (M⁺, 1Br), 110 (C₇H₁₀O⁺). (Found: C, 53.74; H, 5.53; Br, 25.55; Calc. for C₁₄H₁₇BrO₃: C, 53.69; H, 5.47; Br, 25.51%).

Rearrangement of 2 with PBr₃. The same procedure as in the rearrangement of 2 with SOCl₂ 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 (MgSO₄) 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 $\nu_{\text{max}}^{\text{KBr}}$ 1730 (C=O), 1175 (ester) cm⁻¹; NMR (CDCl₃) 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 C₁ and C₇), 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 C₁₅H₁₇BrO₄: 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 SOCl₂. A soln of carbinol 4 (1.0 g, 3.5 mmole) in SOCl₂ (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 $\nu_{\text{max}}^{\text{KBr}}$ 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 $\text{C}_{12}\text{H}_{12}\text{BrClO}_2$: 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 $\nu_{\text{max}}^{\text{KBr}}$ 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_6); m/e 285 (M^+ , 1Br), 82 ($\text{C}_5\text{H}_5\text{O}^+$). (Found: C, 50.10; H, 4.69; Br, 28.00; Calc. for $\text{C}_{12}\text{H}_{13}\text{BrO}_3$: 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 $\nu_{\text{max}}^{\text{KBr}}$ 1295, 1040, 840 cm^{-1} ; NMR (CDCl_3) δ 3.85–4.40 (sym.m, 4H, ketal group), 3.64 (s, 2H, $-\text{CH}_2\text{Cl}$), 3.4–3.6 (m, 5H), 2.7–3.1 (m, 1H, proton at C_6).

(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 $\nu_{\text{max}}^{\text{KBr}}$ 1290, 1080, 835 cm^{-1} ; NMR (CDCl_3) δ 3.75–4.40 (sym.m, 4H, ketal group), 3.52 (s, 2H, $-\text{CH}_2\text{Br}$), 3.30–3.70 (m, 5H), 2.70–3.05 (m, 1H, proton at C_6); m/e 348 (M^+ , 2Br). (Found: C, 41.63; H, 3.58; Br, 45.44; Calc. for $\text{C}_{12}\text{H}_{12}\text{Br}_2\text{O}_2$: 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 $\nu_{\text{max}}^{\text{KBr}}$ 1720 ($\text{C}=\text{O}$); 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_6); m/e 255 (M^+ , 1 Br). (Found: C, 52.07; H, 4.32; Br, 31.37; Calc. for $\text{C}_{11}\text{H}_{11}\text{BrO}_2$: 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 $\nu_{\text{max}}^{\text{KBr}}$ 3350 (OH) cm^{-1} ; NMR (CDCl_3) δ 3.64 (s, 2H, $-\text{CH}_2\text{O}-$), 2.9–3.4 (m, 6H), 2.14 (d, $J = 1.5$ Hz, 2H, protons at C_6), 1.43 (s, 1H, OH) m/e 196 ($\text{M}^+ - \text{CH}_2\text{OH}$). (Found: C, 52.80; H, 4.91; Br, 35.12; Calc. for $\text{C}_{10}\text{H}_{11}\text{BrO}$: 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 $\nu_{\text{max}}^{\text{KBr}}$ 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_6 and C_{10}); n/e 145 ($\text{C}_5\text{H}_5\text{Br}^+$), 100 ($\text{C}_5\text{H}_5\text{Cl}^+$). (Found: C, 48.81; H, 4.20; Br, 32.18; Cl, 14.39; Calc. for $\text{C}_{10}\text{H}_{10}\text{BrCl}$: 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 $\nu_{\text{max}}^{\text{KBr}}$ 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 ($\text{C}_5\text{H}_6\text{O}^+$) (Found: C, 52.96; H, 4.88; Br, 34.92; Calc. for $\text{C}_{10}\text{H}_{11}\text{BrO}$: 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 $\nu_{\text{max}}^{\text{KBr}}$ 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_6 and C_{10}); m/e 145 ($\text{C}_5\text{H}_5\text{Br}^+$) (Found: C, 41.49; H, 3.63; Br, 55.32; Calc. for $\text{C}_{10}\text{H}_{10}\text{Br}_2$: 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[5.3.0.2⁵.0^{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 Key⁸ during the tosylation of **4**.

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