A Synthetic Approach to Cyclo-octa-2,5,7-triene-1,4-dione

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Cyclo-octa-2,5,7-triene-1,4-dione bisethylene acetal [(13) or (14)] has been prepared by bromination of cyclo-octane-1,4-dione bisethylene acetal (11) to give the tribromo-compound (12), and subsequent dehydrobromination. The dibromo-*trans*-cyclo-octene bisacetal (17) is an intermediate in the dehydrobromination reaction, but it was not possible to distinguish spectroscopically between structures (13) and (14) for the triene bisacetal. The triene bisacetal could not be converted into cyclo-octa-2,5,7-triene-1,4-dione (3).

THE use of n.m.r. techniques has firmly established that [$4n + 2$]annulenes are diatropic.[1] The [$4n$]annulenediones are also potentially diatropic. For example, cyclobutenedione (1) [2] and some derivatives [3] have been prepared, and these exhibit chemical stability and dia-

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[1] R. C. Haddon, V. R. Haddon, and L. M. Jackman, *Topics Current Chem.*, 1971, **16**, 103; F. Sondheimer, *Accounts Chem. Research*, 1972, **5**, 81.

[2] J. C. Hinshaw, *Chem. Comm.*, 1971, 630.

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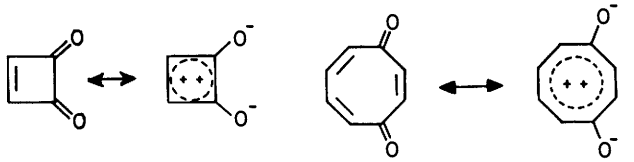
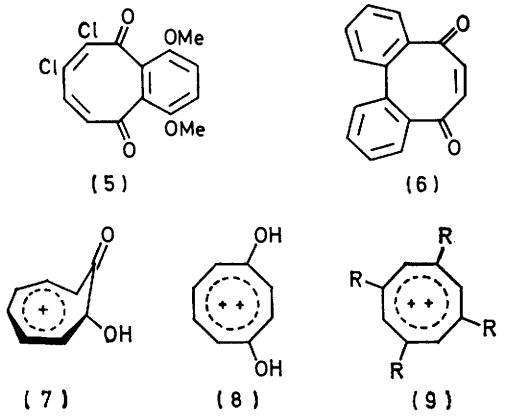
tropic properties attributable to a significant contribution from canonical form (2).



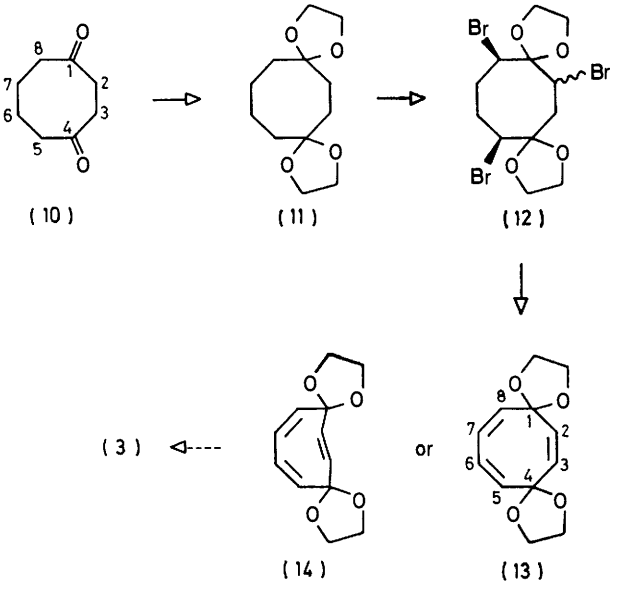
(1) (2) (3) (4)

[8]Annulene-1,4-dione (3) has also attracted wide interest. Early attempts [4] at synthesis in the benzannelated series were unsuccessful, but recently the preparations of the benzo-compound (5) [5] and the dibenzo-compound (6) [6] have been reported, although neither appears diatropic. Clearly, the non-benzannelated series can be expected to be more interesting. In addition to the contribution from canonical form (4) the monoprotonated species (7) could exhibit homoaromaticity, and the doubly protonated derivative (8) could be planar, especially since the cyclo-octatetraenediylium ions (9; R = Me or Ph) have been shown to be planar and aromatic.[7] Double protonation of [16]-annulene-1,4-dione yields a strongly diatropic dication.[8] The successful synthesis of the dione (3) was reported [9] during the course of the present work,[10] but the question of planarity of the doubly protonated species (8) remains unanswered since compound (3) decomposed in trifluoroacetic acid.



(5) (6) (7) (8) (9)

Our synthetic plan (Scheme) involved a simple bromination–dehydrobromination approach to the cyclo-octatrienedione (3). Oxidation of 4-hydroxycyclo-octanone gave cyclo-octane-1,4-dione (10),[11] acetalisation of which proved difficult. Under the usual conditions the intramolecular aldol product (15) [12] was produced, together with *ca.* 20% of the bisacetal (11). Various reagents and catalysts [13-18] were investigated without success. However, the use of ethylene glycol and oxalic acid in acetonitrile at room temperature [19] gave the monoacetal (16) in high yield. This compound could not be converted into the bisacetal by conventional methods, but treatment of the dione (10) with ethylene



(10) (11) (12) (3) (14) or (13)

SCHEME

glycol in acetonitrile in the presence of anhydrous oxalic acid and trimethyl orthoformate at room temperature for 12 h gave the bisacetal (11) in quantitative (spectroscopic) yield, and in 50% yield as the isolated crystalline compound. The crystalline compound is stable at 0 °C under an inert atmosphere but it decomposes upon distillation and in chloroform solution at room temperature. The acetalisation reaction is extremely sensitive to traces of mineral acid and metal ions, and it was found advantageous to clean glassware in decontaminating detergent before use.

Bromination of the bisacetal (11) by a modification of Garbisch's procedure,[20] using 3 equiv. of bromine in

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[5] J. Tsunetsugu, M. Sato, and S. Ebine, *J.C.S. Chem. Comm.*, 1973, 363.

[6] E. Ghera, Y. Gaoni, and S. Shoua, *J. Amer. Chem. Soc.*, 1976, **98**, 3627.

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[8] L. Lombardo and F. Sondheimer, *Tetrahedron Letters*, 1976, 3841.

[9] M. Oda, Y. Kayama, H. Miyazaki, and Y. Kitahara, *Angew. Chem.*, 1975, **87**, 414; *Angew. Chem. Internat. Edn.*, 1975, **14**, 418.

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[11] A. C. Cope, A. H. Keough, P. E. Peterson, H. E. Simmons, and G. W. Wood, *J. Amer. Chem. Soc.*, 1957, **79**, 3900.

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[16] H. J. Dauben, B. Löken, and H. J. Ringold, *J. Amer. Chem. Soc.*, 1954, **76**, 1359.

[17] H. Vorbrueggen, *Steroids*, 1963, **1**, 45.

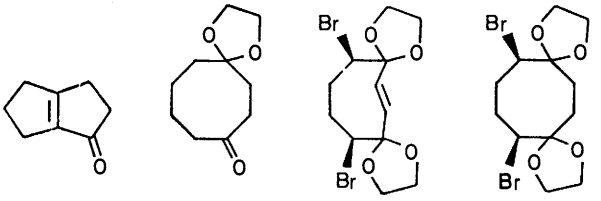
[18] F. Nerdel, J. Buddrus, G. Scherowsky, D. Klamann, and M. Fligge, *Annalen*, 1967, **710**, 85.

[19] N. H. Andersen and H.-S. Uh, *Synth. Comm.*, 1973, **3**, 125.

[20] E. W. Garbisch, *J. Org. Chem.*, 1965, **30**, 2109.

ether in the presence of anhydrous potassium carbonate, gave a crystalline tribromo-bisacetal (12) in 30% yield. The other products were not characterised. Although the relative stereochemistry of the bromine atoms in the crystalline tribomide (12) is not known, it can be inferred from the structure of a monodehydrobromination product (17) that the substituents at positions 5 and 8 are *cis*.

Dehydrobromination of the tribromo-bisacetal (12) using an excess of potassium t-butoxide in refluxing t-butyl alcohol for 7 days gave the triene bisacetal (13) or (14), m.p. 69—72°, in 68% yield. The triene bisacetal could be catalytically reduced to the saturated compound (11), confirming its monocyclic nature. The action of potassium t-butoxide in refluxing ether upon (12) for 36 h gave a monodehydrobromination product (17) (63%) plus the triene bisacetal (13) or (14) (13%). The monodehydrobromination product (17) could be converted into the triene bisacetal by further treatment with potassium t-butoxide in refluxing t-butyl alcohol. The use of 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) with (12) led to a mixture of (13) or (14) and (17).



(15) (16) (17) (18)

Catalytic hydrogenation of the monodehydrobromination product (17) (uptake of 1 mol equiv.) gave (18). The presence of an AB quartet (J 16 Hz) at δ 6.38 and 5.84 with no further vicinal coupling in the n.m.r. spectrum of a solution of (17) in deuteriochloroform indicated that the double bond possessed the *trans*-configuration and that it was located between atoms 2 and 3. This was confirmed by X-ray crystallography, which showed that the molecule adopts a twist-crown conformation having the bromine substituents *cis*, and a considerably twisted *trans*-double bond involving a mean torsion angle of 144°.[21]

It is interesting that the single dehydrobromination of the tribromo-compound (12) gives a *trans*-cyclo-octene (17) in high yield. The stereochemical course of elimination reactions in medium-ring compounds has been studied by Sicher.[22] *trans*-Cyclo-octene arises from synperiplanar elimination in bromo-cyclo-octane, and *syn*-elimination is more favourable in non-polar solvents such as benzene and t-butyl alcohol where ion pair formation is implicated. However it is most unusual to have predominantly a *trans*-cyclo-octene product (17) in a dehydrobromination reaction. The relative stereochemistry of the bromine atoms in (17) indicates that the precursor (12) must be either the all-*cis*-2,5,8-tribromo- or the *trans*-2-bromo-*cis*-5,8-dibromo-compound. No firm conclusion can be drawn; CPK models indicate that both diastereoisomers exhibit a favourable synperiplanar relationship between a hydrogen atom on C-3 and the bromine on C-2.

The triene bisacetal (13) or (14) is obtained from both the tribromide (12) and the dibromo-compound (17), which suggests that (17) is an intermediate in the formation of the triene bisacetal. It is therefore chemically more reasonable for structure (14) to represent the triene bisacetal, but the spectroscopic data do not allow a distinction to be drawn between (13) and (14). The u.v. spectrum shows $\lambda_{max.}$ 244 nm (ε 6 700), while 5,7-dibromocyclo-octa-1,3-diene shows $\lambda_{max.}$ 238 nm (5 670) and 5,8-dibromocyclo-octa-1,3-diene shows $\lambda_{max.}$ 240 nm (6 310).[23] Although the triene bisacetal exhibits an i.r. band at 980 cm^{-1}, which is considered diagnostic for *trans*-cyclo-octenes,[24] the precursor (17) shows no such band, casting doubt on the reliability of this method.

The proton n.m.r. spectrum (see Table 1) offered no distinction between (13) and (14) since the protons on the isolated double bond in both structures are equivalent. In principle, examination of the ^{13}C satellite proton resonances of the isolated double bond ($J_{C,H}$ 152 Hz; see Table 2) should enable one to distinguish (13) from (14), but in practice this proved impossible. Although the *trans*-compound (14) is chiral, the use of a chiral shift reagent tris[3-(2,2,2-trifluoro-1-hydroxyethylidene)-(+)-camphorato]europium(III) did not cause any separation of the proton resonance of the isolated double bond, but this may have been due to weak binding with shift reagent (see Table 1) rather than the absence of a *trans*-double bond. The ^{13}C Fourier transform n.m.r. spectrum (see Table 2) was also unhelpful in distinguishing (13) from (14). The fully coupled ^{13}C spectrum revealed a difference in $J_{C,H}$ for the isolated (152 Hz) and conjugated (159 and 162.5 Hz) double bonds. *trans*-Cyclo-octene [25] has $J_{C,H}$ 151 Hz, whereas *cis*-cyclo-octene has $J_{C,H}$ 154 Hz, but it would be unreasonable to rely on such a small difference to distinguish between structures (13) and (14).

There exist various reagents which react selectively with *trans*-cyclo-octene in the presence of the *cis*-isomer,[24,26] but a selection of these methods has not resolved the problem in the present work, and the question must remain unanswered until crystals suitable for X-ray analysis can be obtained.

Whether the triene bisacetal possesses structure (13) or (14), the desired cyclo-octatriene-1,4-dione (3) or a double bond isomer should be produced by removing the acetal

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groups. However all attempts have been uniformly unsuccessful. No characterisable products were obtained using aqueous sulphuric acid,[27] aqueous acetic acid,[28] tartaric acid,[29] magnesium sulphate in wet tetrafluoroborate, which is regarded as a relatively mild and 'neutral' reagent for acetal cleavage,[35] caused decomposition of the triene bisacetal (13) or (14), and no diketone (3) was detected.

TABLE 1

^{1}H N.m.r. spectra

Compound	Solvent	δ H-2	H-3	H-5	H-8	H-6	H-7	Acetal protons
(10)	$CDCl_3$	2.68 (4 H, s)		2.41 (4 H, m)		1.86 (4 H, m)		
(11)	CCl_4	1.72—1.64				(12 H br, d)		3.79 (8 H, fine d)
(12)	$CDCl_3$	5.10 [b] (1 H, m)	2.76 (2 H, m)	4.70 [b] 4.06 [b]	(1 H, m and 1 H of 5 H, m)	2.40 (4 H, m)		4.30 (4 H, s) and 4.06 (4 H of 5 H, m)
(13) or (14)	CCl_4	6.30 (2 H, s)		5.62 (4 H, s)				3.90 (8 H, m)
(13) or (14)	C_6D_6	6.82 (2 H, s)		5.84 (2 H, m) (AA'BB'm, J 12 Hz)		5.46 (2 H, m)		3.52 (8 H, s)
(13) or (14)	C_6D_6 [a]	8.03 (2 H, s)		6.79 (2 H, m) (AA'BB'm, J 12 Hz)		5.70 (2 H, m)		4.40 (4 H, m) and 4.20 (4 H, m)
(16)	$CDCl_3$	2.20 (2 H, m)	2.50 (4 H, m)		1.16 (6 H, m)			3.88 (4 H, s)
(17)	$CDCl_3$	6.38 and 5.84 (ABq, J 16 Hz)		4.05 (2 H of 6 H, m)		2.29 (2 H, m) and 1.87 (2 H, m)		4.20 (4 H, m) and 4.05 (4 H of 6 H, m)
(18)	$CDCl_3$	2.32 (4 H, m)		4.38 (2 H, m)		1.80 (4 H, m)		4.05 (8 H, m)

[a] 1.1 mol equiv. $Eu(fod)_3$ added. [b] Tentative assignment.

TABLE 2

^{13}C N.m.r. spectra

Compound	δ ($CDCl_3$) C-1	C-4	C-2	C-3	C-5	C-8	C-6	C-7	Acetal carbons
(11)	111.47			33.25 and 31.77			21.33		64.25
(12)				52.24, 44.20, 55.75, and 56.60			33.33 and 32.17		68.23, 65.96, and 65.48
(13) or (14)	118.4		142.1 ($J_{C,H}$ 152, $J_{C,C,H}$ 3.5 Hz)		155.51 and 151.74 ($J_{C,H}$ 159, 162.5 Hz)				78.38 and 78.13 ($J_{C,H}$ 150, $J_{C,C,H}$ 1.7 Hz)
(16)	111.42	176.17	22.61 [a]	40.03 and 39.88		29.09,[a] 31.85,[a] and 34.71 [a]			64.30
(17)	109.35 and 109.95		130.78 and 132.03		61.07 and 61.05		34.34 and 33.86		66.38, 65.78, 65.56, and 65.39
(18)	109.42		32.71 [a]		58.00		30.39 [a]		65.83 and 65 41

[a] These assignments are tentative.

benzene,[14] acetone–toluene-*p*-sulphonic acid,[30] boron trifluoride–ether,[31] boron trichloride,[32] or formic acid.[33] Reactions using levulinic acid,[34] boric acid, and moist silica gel led to the recovery of starting material. The failure to isolate cyclo-octatrienedione (3) under these conditions may be due to its instability in protic and acidic solvents.[9] However, even the use of trityl

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[28] R. Antonucci, S. Bernstein, R. Littell, K. J. Sax, and J. H. Williams, *J. Org. Chem.*, 1952, **17**, 1341.
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[30] G. Rosenkranz, J. Pataki, and C. Djerassi, *J. Org. Chem.*, 1952, **17**, 290.
[31] A. Bowers, L. C. Ibáñez, and H. J. Ringold, *Tetrahedron*, 1959, **7**, 138.

EXPERIMENTAL

Apparatus and equipment have been described in a previous publication.[36]

Cyclo-octane-1,4-dione (10).—A solution of chromium trioxide (48.5 g, 0.5 mol) in glacial acetic acid (115 ml) and water (30 ml) was added dropwise to a stirred solution of 4-hydroxycyclo-octanone (71 g, 0.5 mol; B.A.S.F., Ludwigshafen) in acetic acid (200 ml) at such a rate that the temperature remained below 35 °C. The mixture was then poured

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[33] A. Gorgues, *Comptes rend.*, 1967, **265C**, 1130.
[34] C. H. DePuy and B. W. Ponder, *J. Amer. Chem. Soc.*, 1959, **81**, 4629.
[35] D. H. R. Barton, P. D. Magnus, G. Smith, G. Streckert, and D. Zurr, *J.C.S. Perkin I*, 1972, 542.
[36] P. A. Chaloner and A. B. Holmes, *J.C.S. Perkin I*, 1976, 1838.

into water (2 l). The product was extracted with chloroform (6 × 150 ml), and the combined organic layers were washed with water, followed by saturated sodium hydrogen carbonate solution, until the washings were colourless. After drying (Na_2SO_4), the chloroform solution was concentrated at reduced pressure to a pale yellow oil, which was distilled to give cyclo-octane-1,4-dione (10) (41 g, 66%), b.p. 60—62 °C at 0.2 mmHg (lit.,[11] 73—76 °C at 1 mmHg); $\nu_{max.}$(CCl_4) 1 715s cm^{-1}.

Cyclo-octane-1,4-*dione Bisethylene Acetal* (11).—A solution of cyclo-octane-1,4-dione (10) (10 g, 0.071 mol) in a mixture of ethylene glycol (37 g, 0.6 mol), anhydrous oxalic acid (5 g), trimethyl orthoformate (27 g, 0.24 mol), and anhydrous acetonitrile (300 ml) was stirred at room temperature for 12 h in a vessel which had previously been cleaned with ' Decon 90 ' decontaminating detergent. The mixture was then poured into water (300 ml) and the resulting solution was neutralised with an excess of solid sodium hydrogen carbonate. Extraction of the aqueous solution with ether (3 × 150 ml) and washing of the combined organic phases with saturated sodium hydrogen carbonate solution (100 ml) and saturated aqueous sodium chloride solution (2 × 150 ml), followed by drying (Na_2SO_4) and evaporation, gave a dark yellow oil (13.5 g). Crystallisation from hexane at −15 °C and filtration from the mother liquors at 0 °C gave the *bisacetal* (11) (7.5 g, 50%) as crystals, m.p. 40—43 °C; $\nu_{max.}$(CCl_4) 2 870s, 1 135s, 1 120s, 1 095s, and 1 050 cm^{-1}; *m/e* 228 (M^+, 10%), 185 (64), 183 (32), and 166 (100) (Found: C, 62.9; H, 8.6. $C_{12}H_{20}O_4$ requires C, 63.15; H, 8.7%). Attempted acetalisation of cyclo-octane-1,4-dione (10) (31 g, 0.21 mol) using ethylene glycol (34 g, 0.55 mol) and toluene-*p*-sulphonic acid (0.5 g) in refluxing benzene (500 ml) with azeotropic removal of water gave, after standard work-up, a dark yellow oil (39 g) which was distilled: fraction 1 (3.2 g), b.p. 50 °C at 0.1 mmHg, was identified as bicyclo[3.3.0]oct-1(5)-en-2-one (15) (lit.,[12] b.p. 62 °C at 0.9 mmHg); fraction 2 (10.7 g), b.p. 60—85 °C at 0.1 mmHg, was a mixture of (11), (15), and (16); fraction 3 (14.1 g), b.p. 85—97 °C at 0.1 mmHg, was redistilled to give the bisacetal (11) (4.5 g, 20%), b.p. 90—100 °C at 0.1 mmHg, but these samples always exhibited i.r. bands at 1 715 cm^{-1}. A pure sample could be obtained by crystallisation from hexane at −15 °C or by g.l.c. on a Carbowax column (1 m × 1 mm) at 185 °C.

Cyclo-octane-1,4-*dione Monoethylene Acetal* (16).—A solution of cyclo-octane-1,4-dione (10) (5 g, 95.7 mmol), ethylene glycol (20 g, 300 mmol), and anhydrous oxalic acid (5 g, 55.5 mmol) in acetonitrile (300 ml) was stirred at room temperature for 18 h.[19] The solution was poured into water (300 ml), and neutralised with an excess of solid sodium hydrogen carbonate. The aqueous solution was extracted with ether (3 × 150 ml) and the combined organic extracts were washed with saturated sodium chloride solution, dried (Na_2SO_4), and evaporated to give a pale yellow oil (5.7 g), which was triturated with ice-cold hexane to yield a white solid. Recrystallisation from hexane at 0 °C gave the monoacetal (16) (4.3 g, 65%) as needles, m.p. 49—51 °C; $\nu_{max.}$ ($CHCl_3$) 2 890m, 1 700s, 1 140s, 1 100s, 1 090s, and 1 040s cm^{-1}; *m/e* 184 (M^+, 65%), 155 (80), 142 (20), 141 (18), and 112 (100) (Found: C, 65.1; H, 8.5. $C_{10}H_{16}O_3$ requires C, 65.2; H, 8.7%).

2,5,8-*Tribromocyclo-octane*-1,4-*dione Bisethylene Acetal* (12).—To a stirred solution of cyclo-octane-1,4-dione bisethylene acetal (11) (4.25 g, 0.02 mol) in ether (200 ml) was added bromine (10 8 g, 0.06 mol) at room temperature over 3/4 h. The mixture was stirred for 1 h, and then anhydrous potassium carbonate (20 g) and methylene chloride (200 ml) were added. After stirring for 1/2 h, the mixture was filtered and the solid was washed with methylene chloride (100 ml). The combined filtrate and washings were concentrated to give a semisolid (12.7 g). This was triturated with ice-cold methanol, after which filtration gave a cream solid (4. 7 g), m.p. *ca.* 165 °C. Crystallisation from chloroform–methanol gave the *tribromo-compound* (12) (2.7 g, 30%), m.p. 184—186 °C (decomp.); $\nu_{max.}$ (CCl_4) 2 900m, 1 115s, and 1 060s cm^{-1}; *m/e* 468, 466, 464, 462 (M^+ <1%), 376, 374, 372 (60%), 284, and 282 (100) (Found: C, 30.95; H, 3.9. $C_{12}H_{17}Br_3O_4$ requires C, 30.8; H, 3.7%).

Cyclo-octa-2,5,7-*triene*-1,4-*dione Bisethylene Acetal* (13) *or* (14).—A solution of the tribromo-compound (12) (2.5 g, 5.37 mmol) and potassium t-butoxide[37] (2.5 g, 22.3 mmol) in t-butyl alcohol (700 ml) was heated under reflux in an argon atmosphere for 7 days. It was then cooled and poured into water, and the aqueous mixture was extracted with ether (3 × 300 ml). The combined extracts were washed with saturated aqueous sodium chloride solution (2 × 300 ml), dried (Na_2SO_4), and concentrated to give a pale yellow semicrystalline oil (1.3 g). Preparative layer chromatography on kieselgel developed in methylene chloride gave a band, R_F 0.35 which, upon extraction yielded the *triene bisacetal* (13) or (14) (0.815 g, 68%). Recrystallisation from hexane at −20 °C gave needles, m.p. 69—72 °C; $\nu_{max.}$ (CCl_4) 2 890s, 1 615w, 1 165s, 1 150s, 1 120s, 1 015s, 980s, 947s, 890m, and 700w cm^{-1}; $\lambda_{max.}$ (EtOH) 244 nm (ε 6 700); *m/e* 222 (M^+, 6%), 221 (5), 149 (30), 137 (40), and 136 (100) (Found: C, 64.5; H, 6.1%; M^+, 222.089 8. $C_{12}H_{14}O_4$ requires C, 64.9; H, 6.3%; *M*, 222.089 1). Catalytic reduction of the triene bisacetal (13) or (14) (10 mg, 0.05 mmol) in hexane (5 ml) over platinum (prereduced from 1 mg of PtO_2) at room temperature resulted in the uptake of 3 mol. equiv. of hydrogen at atmospheric pressure. Removal of the solvent and the catalyst gave cyclo-octane-1,4-dione bisethylene acetal (11) (9 mg), identical with that prepared from cyclo-octane-1,4-dione by the previously described method.

cis-5,8-*Dibromo*-trans-*cyclo-oct*-2-*ene*-1,4-*dione Bisethylene Acetal* (17).—A solution of the tribromo-compound (12) (1 g, 21.4 mmol) and potassium t-butoxide (1 g, 96.6 mmol) in anhydrous ether (250 ml) was heated under reflux in a nitrogen atmosphere for 36 h. The solution was cooled and poured into ice-cold saturated aqueous sodium chloride. The organic phase was separated from the aqueous phase, which was further extracted with ether (3 × 75 ml). The combined organic layers were washed with saturated aqueous sodium chloride solution (2 × 100 ml), dried (Na_2SO_4), and evaporated to give a yellow oil (0.778 g). This was triturated with ice-cold hexane to give a white solid (0.521 g, 63%), which was recrystallised from methylene chloride–hexane to give the *dibromo-compound* (17) as needles, m.p. 143—144 °C; $\nu_{max.}$ ($CHCl_3$) 2 890m, 1 150s, 1 010s, 955s, and 930m cm^{-1}; *m/e* 386, 384, 382 (M^+, 1%), 305, 303 (1), and 223 (100) (Found: C, 37.5; H, 4.2; Br, 40.9. $C_{12}H_{16}Br_2O_4$ requires C, 37.5; H, 4.2; Br, 41.6%). Concentration of the hexane filtrate from the trituration and preparative layer chromatography of the concentrate gave the triene bisacetal (13) or (14) (64.7 mg, 13.5%).

[37] L. Skattebøl and S. Soloman, *Org. Synth.*, Coll. Vol. V, 1973, p. 306.

Dehydrobromination of the Dibromo-compound (17).—The dibromo-compound (17) (100 mg, 0.26 mmol) and potassium t-butoxide (90 mg, 0.8 mmol) were heated in refluxing t-butyl alcohol (65 ml) for 7 days. After the usual work-up and chromatography the triene bisacetal (13) or (14) was isolated (23 mg, 40%).

Dehydrobromination of the Tribromo-compound (12) *with 1,5-Diazabicyclo*[5.4.0]*undec-5-ene*.—The tribromo-compound (12) (0.5 g, 1 mmol) was heated in 1,5-diazabicyclo-[5.4.0]undec-5-ene (2 ml; Ralph N. Emanuel) at 85 °C for 12 h. The cooled mixture was poured into water (10 ml) and the product was isolated by extraction with ether (3 × 10 ml) as described above. Concentration of the washed and dried extract gave an oil (202 mg), which was purified by layer chromatography to give the triene bisacetal (13) or (14) (50.5 mg, 20%).

cis-5,8-*Dibromocyclo-octane*-1,4-*dione Bisethylene Acetal* (18).—The dibromo-compound (17) (200 mg, 0.52 mmol) in ethyl acetate (20 ml) containing platinum (prereduced from 20 mg of PtO_2) was hydrogenated at atmospheric pressure for 12 h. Removal of the catalyst and the solvent gave a solid (176 mg, 88%), which was recrystallised from ether–petroleum (b.p. 30—40 °C) to give the saturated *dibromo-bisacetal* (18) (120 mg, 60%) as needles, m.p. 154—155°; $\nu_{max.}$ ($CHCl_3$) 2 890m, 1 150s, 1 120s, 1 055s, 1 035s, 1 010m, 980s, 950s, and 900m cm^{-1}; *m/e* 388, 386, 384 (M^+, 1%), 303, 305 (100), 289, 287, 285 (50), and 225 (25) (Found: C, 37.3; H, 4.7; Br, 41.35. $C_{12}H_{18}Br_2O_4$ requires C, 37.3; H, 4.7; Br, 41.4%).

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