Synthesis of (1*S**,2*S**,3*S**,4*S**,5*S**,6*S**,7*S**,8*S**)-1,2,7,8-Tetrachlorotricyclo-[4.2.0.0^{3,8}]octane-4,5-dicarboxylic Acid. Novel Entry into the C_2-Bissecocubane System

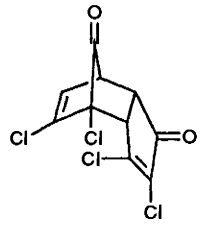
Colin J. Baker, Gordon I. Fray,* Graham R. Geen and Keith Ryan
School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK

Photocaging of the known Diels–Alder dimer of 2,3-dichlorocyclopentadienone, compound **1**, followed by alkali-induced double ring-cleavage of the resulting caged diketone *rac*-**2** or its dihydrate *rac*-**3**, led to the title tetrachloro dicarboxylic acid *rac*-**5**, thus affording a novel entry into the inherently chiral tricyclo[4.2.0.0^{3,8}]octane (C_2-bissecocubane) system. Electrolysis of the disodium salt of *rac*-**5** gave the tetrachloro alkene *rac*-**14**, from which other derivatives were obtained by standard methods.

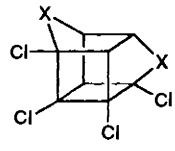
2,3-Dichlorocyclopentadienone spontaneously forms a Diels–Alder dimer which has been shown to possess structure *rac*-**1**.[1] Although earlier attempts to effect intramolecular [2 + 2] photocycloaddition of the olefinic bonds in dimer **1** failed,[1] it was later found[2] that the photoreaction proceeded satisfactorily in methanol (*cf.* ref. 3), and the caged diketone *rac*-**2** could be obtained by vacuum sublimation of the crude photoproduct (presumably a mixture of bis-hemiketal stereoisomers). This photocaging reaction thus provided confirmatory evidence for the *endo* configuration of *rac*-**1**. The tetrachloro dione *rac*-**2** was readily hydrated (even in moist air), and purification of the crude photoproduct was most conveniently accomplished by its conversion into the dihydrate *rac*-**3** and subsequent recrystallisation.

An investigation of the reaction of the diketone *rac*-**2** with alkali was originally undertaken as a possible route to the dichlorocubanedicarboxylic acid *rac*-**4** by double ring-contraction (*cf.* refs. 3–5). In the event, however, treatment of the diketone *rac*-**2** or its dihydrate *rac*-**3** with refluxing 10% aq. sodium hydroxide, or (better) with powdered sodium hydroxide in tetrahydrofuran (THF) at room temperature, effected a double ring-cleavage (for which there are also precedents[6–10]) with the formation of a tetrachloro dicarboxylic acid, $C_{10}H_8Cl_4O_4$, m.p. ~280 °C (decomp.) (dimethyl ester, m.p. 114–114.5 °C). Structure *rac*-**5**† was assigned to this dicarboxylic acid on the basis of the spectroscopic evidence and by analogy with, *e.g.*, the alkali-induced ring-opening reactions **6** ⟶ *rac*-**7**[9] and **8** ⟶ rac-**9**.[10] It should be noted that these reactions are known to occur with retention of stereochemical integrity, and may involve a chlorocarbanion which undergoes rapid intramolecular protonation. Thus the double ring-cleavage which results in diacid *rac*-**5** may be represented as shown in Scheme 1 (each bridge-opening being unidirectional to afford a chlorine-stabilised carbanion).

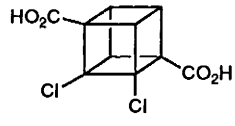
Unexpectedly, reaction of the caged diketone *rac*-**2** or its dihydrate *rac*-**3** with more concentrated (20%) aq. sodium hydroxide resulted in the formation (in moderate yield) of an isomer of *rac*-**5**. This second dicarboxylic acid (which was characterised as its dimethyl ester, m.p. 149.5–150 °C) showed spectral details which closely resembled those of *rac*-**5**, and it could be produced from the latter by treatment with 20% aq. alkali; it was therefore formulated as *rac*-**10**. The congruent conversion of the dimethyl ester of *rac*-**5** into that of *rac*-**10** could be effected by sodium methoxide in refluxing methanol, and confirmation of the proposed structures was obtained by analysis of the (second-order) ^{1}H NMR spectra of these diesters. In each case 2-H and 7-H gave rise to a singlet signal (dihedral-angle effect) while 3-, 6-, 4- and 5-H formed an ABB′A′ system. The estimated coupling constants, the values of which were obtained by computer simulation of the spectra, are given in Table 1. The spectrum of the diester derived from *rac*-**5** showed



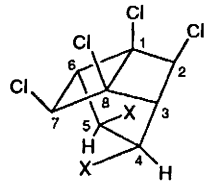
1



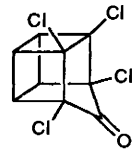
2 X = CO
3 X = C(OH)$_2$



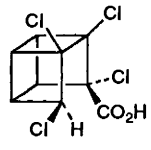
4



5 X = CO_2H



6

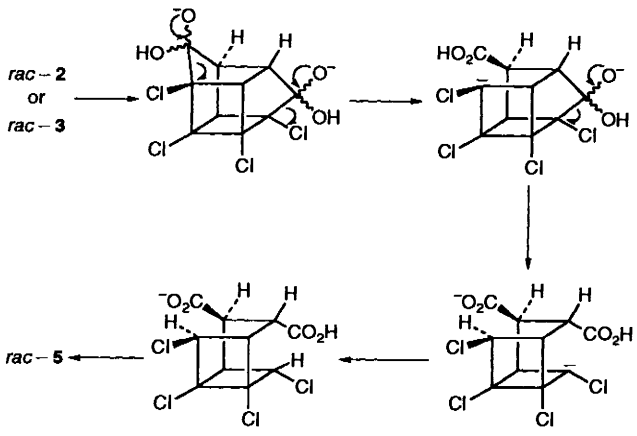


7

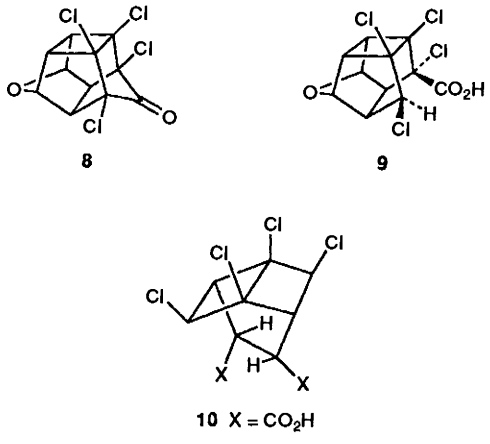
Table 1 ^{1}H NMR coupling constants (Hz)

	Dimethyl ester of *rac*-**5**	Dimethyl ester of *rac*-**10**
$J_{3,4}(=J_{5,6})$	2.5	2.3
$J_{3,5}(=J_{4,6})$	0.7	0.0
$J_{3,6}$	0.0	0.0
$J_{4,5}$	1.1	9.4

† In the naming of this compound it is essential to indicate the configuration of C-4 and C-5 relative to the other six chiral centres in order to distinguish *rac*-**5** from its diastereoisomer *rac*-**10**, which is the (1*S**,2*S**,3*S**,4*R**,5*R**,6*S**,7*S**,8*S**)-compound.



Scheme 1

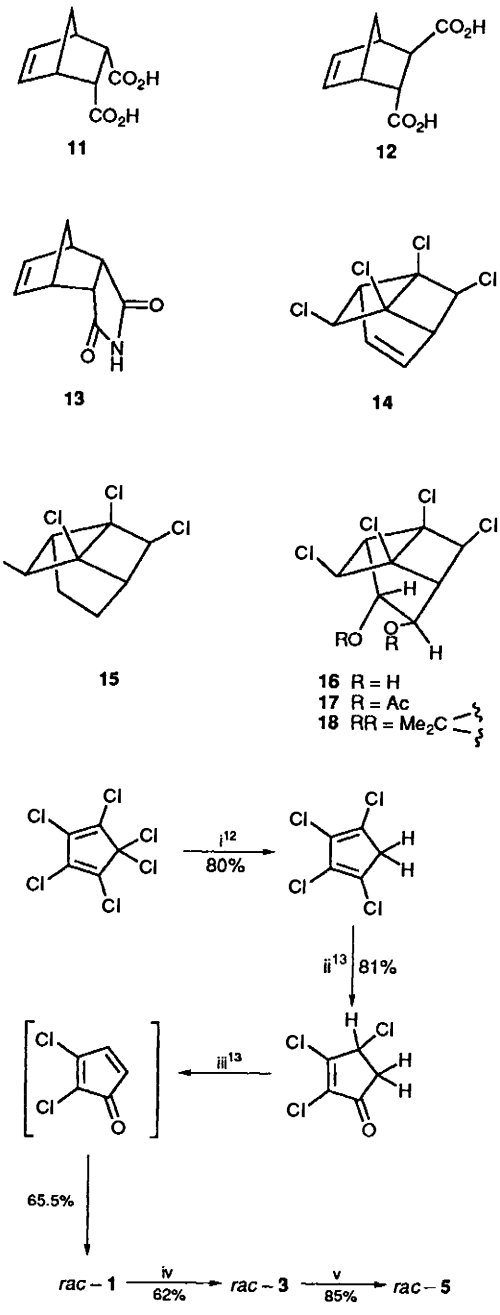


10 X = CO_2H

a low value for $J_{4,5}$, and W-couplings between the pairs 3-H and 5-H, and 4-H and 6-H. In contrast, for the diester of *rac*-**10**, $J_{4,5}$ was large and $J_{3,5}$ and $J_{4,6}$ were zero. These results were consistent with the structures assigned to diacids *rac*-**5** and *rac*-**10**.

While base-catalysed inversion of stereochemistry is unexceptional for an ester, the corresponding process for a carboxylate salt might be thought unusual in 20% aq. alkali. Nevertheless, a similar transformation (involving a single inversion) was found in the conversion of the *cis-endo*-dicarboxylic acid **11** into the thermodynamically more stable *trans*-isomer *rac*-**12** by the action of 20% aq. sodium hydroxide.* The (faster) double inversion occurring in the isomerisation *rac*-**5** ⟶ *rac*-**10** would seem to result from the relief of steric congestion in which the carboxy groups and the hydrogen atoms 2-H and 7-H are implicated.

The reaction sequence leading to the dicarboxylic acid *rac*-**5** consists of five easy steps from hexachlorocyclopentadiene (Scheme 2), and represents a novel formation of the tricyclo[4.2.0.0^{3,8}]octane system,† the basic carbon skeleton of which is intrinsically chiral but possesses C_2 symmetry.‡ (For



Scheme 2 *Reagents:* i, Zn, AcOH; ii, conc. H_2SO_4; iii, NaOAc, AcOH; iv, *hv*, MeOH, followed by aq. HCl; v, NaOH, THF; followed by aq. HCl

previous preparations of this tricyclic system see refs. 16–22). Modification of the functionality of the dicarboxylic acid *rac*-**5** was investigated briefly, as follows. Removal of the carboxy groups was effected by anodic bis-decarboxylation. In the previously recommended general procedure[23] a solution of the 1,2-dicarboxylic acid (or its cyclic anhydride) in aq. pyridine containing triethylamine is electrolysed using smooth platinum electrodes.§ In contrast, the Kolbe electrolytic coupling reaction is normally carried out in methanol containing a little sodium methoxide,[23,26] and in at least one example[27] similar conditions have been used successfully for the preparation of a cycloalkene from a cycloalkane-1,2-dicarboxylic acid. In the present case it was found that a modification of the latter conditions, using methanol containing sufficient sodium methoxide to ensure the complete conversion of the dicarboxylic acid *rac*-**5** into its disodium salt, resulted in a much

* Alkaline hydrolysis (conditions not specified) of the cyclic imide **13** resulted in the *trans*-dicarboxylic acid *rac*-**12**.[11]

† Also dubbed 'C_2-bissecocubane', '9-nortwistbrendane', 'bisnortwistane', and [O]triblattane.[14]

‡ Such systems have been designated 'gyrochiral',[15] but this term has apparently not been accepted.[14]

§ Numerous examples of the application of this procedure are quoted in refs. 23 and 24. The usually modest yields obtainable by this method have been improved in one case[25] by the replacement of most of the pyridine by acetonitrile and the addition of a polymerisation inhibitor.

cleaner reaction than that in pyridine, and led to the tetrachloroalkene *rac*-**14** in 54% yield (after recrystallisation); catalytic hydrogenation then produced the saturated tetrachloro compound *rac*-**15**. Bishydroxylation of the double bond in alkene *rac*-**14** with osmium tetraoxide in the presence of *N*-methylmorpholine *N*-oxide[28] afforded the *cis*-1,2-diol *rac*-**16**,* which formed the diacetyl derivative *rac*-**17** and the acetonide *rac*-**18**.

Experimental

IR spectra were determined for Nujol mulls using a Perkin-Elmer 881 spectrophotometer. NMR spectra were measured using JEOL PS100, FS90Q, FX200 or GX270 instruments (solutions in $CDCl_3$ unless stated otherwise, with Me_4Si as internal standard); coupling constants (J) are given in Hz. Electron-impact mass spectra were recorded with an AEI MS902 spectrometer; the reported chlorinated ions had correct $^{35}Cl/^{37}Cl$ isotopic abundance ratios.

4,5,7,8-*Tetrachlorotricyclo*[5.2.1.$0^{2,6}$]*deca*-4,8-*diene*-3,10-*dione* rac-**1**.—An improved preparation of the dimer *rac*-**1** resulted from the following modification of the originally described procedure.[13] To a vigorously stirred solution of 2,3,4-trichlorocyclopent-2-enone[13] (80.0 g, 431 mmol) in glacial acetic acid (400 cm^3) at room temperature was gradually added anhydrous sodium acetate (100 g, 1.2 mol). After the mixture had been stirred for 48 h, water (1000 cm^3) was added and the mixture was left for a further 24 h. The crystalline product was filtered off, washed well with water, dried ($MgSO_4$) and recrystallised from acetone–diethyl ether to give the dimer *rac*-**1** (42.1 g, 65.5%), m.p. 187–188 °C (lit.,[13] 184–185 °C).

3,4,5,9-*Tetrachloropentacyclo*[5.3.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]*decane*-6,10-*dione* rac-**2**.—The dimer *rac*-**1** (23.9 g, 80.2 mmol) was dissolved in warm methanol (900 cm^3), and the solution was irradiated at room temperature for 6 days in a Hanovia Photoreactor (125 W medium-pressure mercury arc, surrounded by a quartz water-jacket). Most of the solvent was then removed under reduced pressure, and the residual solution was transferred to a vacuum sublimation apparatus. After evaporation of the remaining solvent under reduced pressure, the gummy product was covered with a layer of sand, heated to *ca.* 140 °C under high vacuum, and finally sublimed at 160–180 °C/0.1 mmHg to give the caged *diketone* rac-**2** (14.5 g, 61%). Repeated sublimation gave a pure analytical sample, m.p. 220–222 °C (Found: C, 40.5; H, 1.4; Cl, 47.3. $C_{10}H_4Cl_4O_2$ requires C, 40.31; H, 1.35; Cl, 47.60%); ν_{max}/cm^{-1} 1810 and 1775; δ_H[100 MHz; $(CD_3)_2SO$] 4.25–4.1 (2 H, symmetrical m) and 3.55–3.4 (2 H, symmetrical m) (ABB'A' system); *m*/*z* 296 (M^+, 5%) and 233 (100).

In moist air the diketone *rac*-**2** was gradually converted into its dihydrate *rac*-**3**, and it was more convenient to isolate and purify the photoproduct as this derivative, as follows.

3,4,5,9-*Tetrachloropentacyclo*[5.3.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]*decane*-6,6,10,10-*tetraol* rac-**3**.—The crude photoproduct, prepared from the dimer *rac*-**1** (23.6 g, 79.2 mmol) as described above, was taken up in acetone (30 cm^3); water (5 cm^3) and conc. hydrochloric acid (5 cm^3) were added, and the mixture was left overnight at room temperature. The solution was then evaporated under reduced pressure, and several portions of acetone were distilled from the residue, which was finally crystallised (several crops) from acetone–dichloromethane at −15 °C to afford the *tetraol* rac-**3** (16.3 g, 62%), m.p. 220.5–222.5 °C (slow heating) (Found: C, 35.85; H, 2.5; Cl, 42.3. $C_{10}H_8Cl_4O_4$ requires C, 35.96; H, 2.41; Cl, 42.46%); ν_{max}/cm^{-1} 3649, 3520, 3408 and 3340–3180 br sh; δ_H[90 MHz; $(CD_3)_2CO$] 5.67 (2 H, s), 5.62 (2 H, s), 3.4–3.25 (2 H, symmetrical m) and 2.95–2.85 (2 H, symmetrical m) (ABB'A' system); δ_C[68 MHz; $(CD_3)_2CO$] 106.2, 75.6, 70.7, 58.0 and 49.9; *m*/*z* 296 (M^+ − $2H_2O$, 6%) and 233 (100).

(1S*,2S*,3S*,4S*,5S*,6S*,7S*,8S*)-1,2,7,8-*Tetrachlorotricyclo*[4.2.0.$0^{3,8}$]*octane*-4,5-*dicarboxylic Acid* rac-**5**.—To a vigorously stirred mixture of finely ground sodium hydroxide (28.0 g, 700 mmol) and peroxide-free THF (350 cm^3) was added, during 15 min, a solution of the tetraol *rac*-**3** (28.0 g, 83.8 mmol) in the same solvent (250 cm^3). Continued stirring of the mixture at room temperature resulted in the formation of a gel which rendered the stirrer inoperative, but, after the addition of more THF (50 cm^3), stirring was resumed and was continued for 4 days. Ice was added to the resulting suspension, and the mixture was acidified with conc. hydrochloric acid (75 cm^3). The upper layer was separated, and the lower layer was extracted with diethyl ether (2 × 100 cm^3), the ethereal extracts being combined with the original organic layer. The combined solutions were washed with water, dried ($MgSO_4$) and evaporated under reduced pressure. Recrystallisation of the residue from acetone–chloroform (several crops) gave the *dicarboxylic acid* rac-**5** (23.9 g, 85%), m.p. ~280 °C (decomp.) (Found: C, 35.8; H, 2.5; Cl, 42.3. $C_{10}H_8Cl_4O_4$ requires C, 35.96; H, 2.41; Cl, 42.46%); ν_{max}/cm^{-1} 1707 br; δ_H[90 MHz; $(CD_3)_2SO$] 13.35 (2 H, v br s), 4.22 (2 H, s), 3.86 (2 H, apparent s) and 3.49 (2 H, apparent s); δ_C[22.5 MHz; $(CD_3)_2SO$] 172.9, 72.4, 62.0, 57.1 and 44.8; *m*/*z* 278 (M^+ − HCl − H_2O, 1%) and 36 (HCl, 100).

The *dimethyl ester* (prepared with methanolic sulfuric acid) had m.p. 114–114.5 °C (from MeOH at 0 °C) (Found: C, 40.0; H, 3.5; Cl, 39.35. $C_{12}H_{12}Cl_4O_4$ requires C, 39.81; H, 3.34; Cl, 39.17%); ν_{max}/cm^{-1} 1731 br; δ_H(200 MHz) 4.14 (2 H, s), 3.91–3.88 (2 H, symmetrical m), 3.83 (6 H, s) and 3.67–3.64 (2 H, symmetrical m) (ABB'A' system; for *J*-values see Table 1); δ_C(22.5 MHz) 171.6, 72.3, 61.2, 56.9, 53.4 and 45.0; *m*/*z* 325 (M^+ − Cl, 26%) and 59 ($MeOCO^+$, 100).

(1S*,2S*,3S*,4R*,5R*,6S*,7S*,8S*)-1,2,7,8-*Tetrachlorotricyclo*[4.2.0.$0^{3,8}$]*octane*-4,5-*dicarboxylic Acid* rac-**10**.—A solution of the diketone *rac*-**2** (1.30 g, 4.36 mmol) in 20% aq. sodium hydroxide (10 cm^3) was heated under reflux for 3 h. The resulting dark mixture was washed with diethyl ether and then poured into an excess of ice-cold dil. hydrochloric acid. The product was collected in diethyl ether, and the ethereal solution was washed with water, dried ($MgSO_4$) and evaporated. Crystallisation of the residue from benzene yielded the crude (discoloured) *dicarboxylic acid* rac-**10** (0.72 g, 49%), which was purified further by repeated recrystallisations from acetone–chloroform; the m.p. (~215 °C) was diffuse and variable, and depended on the rate of heating (Found: C, 35.4; H, 2.3; Cl, 42.0. $C_{10}H_8Cl_4O_4$ requires C, 35.96; H, 2.41; Cl, 42.46%); ν_{max}/cm^{-1} 1730 sh and 1714; δ_H[100 MHz; $(CD_3)_2CO$] 4.88 (2 H, s), 4.07 (2 H, apparent s) and 3.52 (2 H, apparent s); δ_C[68 MHz; $(CD_3)_2CO$] 171.3, 72.4, 61.1, 57.4 and 42.3; *m*/*z* 314 (M^+ − H_2O, 2%) and 251 (100).

Similar treatment of the dihydrate *rac*-**3** or the dicarboxylic acid *rac*-**5** afforded the same product *rac*-**10** (comparison of IR and NMR spectra).

The *dimethyl ester* (prepared with methanolic sulfuric acid) had m.p. 149.5–150 °C (from MeOH at 0 °C) (Found: C, 40.2; H, 3.4; Cl, 39.0. $C_{12}H_{12}Cl_4O_4$ requires C, 39.81; H, 3.34; Cl, 39.17%); ν_{max}/cm^{-1} 1735 br sh and 1720; δ_H(200 MHz) 4.46 (2 H, s), 3.80 (6 H, s), 3.72–3.71 (2 H, symmetrical m) and 3.46–3.45 (2 H, symmetrical m) (ABB'A' system; for *J*-values

* It may be noted that there is no C_2 axis of symmetry in this structure.

see Table 1); δ_C(22.5 MHz) 170.4, 71.8, 60.0, 56.2, 53.2 and 42.2; *m/z* 329 ($M^+ - OMe$, 11%) and 59 ($MeOCO^+$ 100). This product was also formed from the dimethyl ester of diacid *rac*-**5**, by treatment with sodium methoxide (3.5 mol equiv.) in refluxing methanol for 19 h, followed by acidification.

Treatment of Bicyclo[2.2.1]*hept*-5-*ene*-2,3-cis-endo-*dicarboxylic Acid* **11** *with Aqueous Alkali*.—A solution of the *cis-endo*-dicarboxylic acid **11** (1.00 g, 5.49 mmol) in 20% aq. sodium hydroxide (20 cm^3) was heated under reflux for 18 h, and was then cooled, and acidified with conc. hydrochloric acid. The mixture was extracted repeatedly with diethyl ether, and the ethereal solution was dried ($MgSO_4$) and evaporated. The ^1H NMR spectrum [90 MHz; $(CD_3)_2SO$] of the residue (0.71 g, 71%) was virtually identical with that of an authentic sample of bicyclo[2.2.1]hept-5-ene-2,3-*trans*-dicarboxylic acid **12**.

(1S*,2S*,3S*,6S*,7S*,8S*)-1,2,7,8-*Tetrachlorotricyclo*-[4.2.0.$0^{3,8}$]*oct*-4-*ene* rac-**14**.—A stirred solution of the dicarboxylic acid *rac*-**5** (10.0 g, 29.9 mmol) in methanol (250 cm^3) containing sodium methoxide (3.50 g, 64.8 mmol) was electrolysed under reflux by using smooth platinum foil electrodes (3 × 3 cm; positioned 7–8 mm apart) and a 100 W DC power supply, the circuit incorporating a rheostat, an ammeter, and a polarity-reversing switch. After 24 h at 1.0–0.8 A, the solution was concentrated (to ~ 50 cm^3) and poured into water. The resulting precipitate was filtered off, washed thoroughly with water, and dried. Recrystallisation of the crude product from methanol at −15 °C gave the *tetrachloroalkene* rac-**14** (3.93 g, 54%), m.p. 143–144 °C (sublimation) (Found: C, 39.2; H, 2.7; Cl, 58.0. $C_8H_6Cl_4$ requires C, 39.39; H, 2.48; Cl, 58.13%); δ_H(270 MHz) 6.37 (2 H, symmetrical m), 3.94 (2 H, s) and 3.51 (2 H, symmetrical m) (the estimated coupling constants of the AXX'A' system were as follows: $J_{3,4} = J_{5,6} = 5.5$, $J_{3,5} = J_{4,6} = 2.2$, $J_{3,6} = 0.0$, and $J_{4,5} = 7.3$); δ_C(68 MHz) 130.6, 72.2, 66.5 and 57.3; *m/z* ($M^+ - Cl$, 30%) and 171 (100).

(1S*,2S*,3S*,6S*,7S*,8S*)-1,2,7,8-*Tetrachlorotricyclo*-[4.2.0.$0^{3,8}$]*octane* rac-**15**.—Hydrogenation of the tetrachloroalkene *rac*-**14** at room temperature and atmospheric pressure in the presence of 10% Pd–C in ethanol gave a quantitative yield of the *dihydro derivative* rac-**15**, m.p. 181–182 °C (from MeOH at 0 °C) (Found: C, 38.9; H, 3.4; Cl, 57.5. $C_8H_8Cl_4$ requires C, 39.06; H, 3.28; Cl, 57.66%); δ_H(270 MHz) 4.32 (2 H, s), 3.19 (2 H, br s) and 2.3–2.0 (4 H, m); δ_C(68 MHz) 72.1, 62.5, 56.2 and 23.1; *m/z* 209 ($M^+ - Cl$, 6%) and 122 (100).

(1S*,2S*,3S*,4R*,5S*,6S*,7S*,8S*)-1,2,7,8-*Tetrachlorotricyclo*[4.2.0.$0^{3,8}$]*octane*-4,5-*diol* rac-**16**.—A solution of the tetrachloroalkene *rac*-**14** (3.20 g, 13.1 mmol) in acetone (20 cm^3) was added to a mixture of *N*-methylmorpholine *N*-oxide (1.70 g, 14.5 mmol) in water (5 cm^3) and a 1% solution of osmium tetraoxide in *tert*-butyl alcohol (3.5 cm^3). After the mixture had been stirred for 22 h at room temperature, it was treated with aq. sodium dithionite (0.5 g in 10 cm^3), neutralised with 2% aq. sulfuric acid, concentrated under reduced pressure, and finally acidified (to pH 2) with dil. aq. sulfuric acid and extracted with diethyl ether. The ethereal solution was washed with brine, dried ($MgSO_4$) and evaporated. Crystallisation of the residue from chloroform then afforded the *diol* rac-**16** (2.62 g, 72%), m.p. 130.5–131.5 °C (Found: C, 34.5; H, 2.9; Cl, 51.3. $C_8H_8Cl_4O_2$ requires C, 34.56; H, 2.90; Cl, 51.02%); ν_{max}/cm^{-1} 3440 and 3319; δ_H[270 MHz; $(CD_3)_2CO + D_2O$] 5.22 (1 H, s), 4.70 (1 H, dd, *J* 6.2 and 3.2), 4.67 (1 H, s), 4.45 (1 H, ddd, *J* 6.2, 3.6 and 1.2), 3.34 (1 H, d, *J* 3.6) and 3.20 (1 H, dd, *J* 3.2 and 1.2); δ_C[68 MHz; $(CD_3)_2CO$] 73.9, 72.5, 69.1, 68.3, 62.1, 61.5, 61.2 and 59.9; *m/z* 241 ($M^+ - Cl$, 1%) and 60 (100).

The *diacetate* rac-**17**, prepared by reaction with acetic anhydride in triethylamine, catalysed by 4-(dimethylamino)-pyridine,[29] had m.p. 249–250 °C (sublimation) (from Me_2CO–MeOH) (Found: C, 39.7; H, 3.4; Cl, 39.15. $C_{12}H_{12}Cl_4O_4$ requires C, 39.81; H, 3.34; Cl, 39.17%); ν_{max}/cm^{-1} 1752 and 1735; δ_H(270 MHz) 5.63 (1 H, ddd, *J* 6.6, 3.2 and 1.2), 5.57 (1 H, dd, *J* 6.6 and 3.1), 4.91 (1 H, s), 4.36 (1 H, s), 3.40 (1 H, d, *J* 3.2), 3.31 (1 H, dd, *J* 3.1 and 1.2), 2.15 (3 H, s) and 2.09 (3 H, s); δ_C(68 MHz) 169.1, 169.0, 71.6, 70.8, 67.7, 67.6, 59.3, 58.0, 57.7, 57.2, 20.7 and 20.4; *m/z* 325 ($M^+ - Cl$, 52%) and 187 (100).

The *acetonide* rac-**18**, prepared by reaction of the diol *rac*-**16** with dry acetone in the presence of molecular sieves (5 Å) and a catalytic quantity of trifluoroacetic acid, had m.p. 181–182 °C (from MeOH) (Found: C, 41.5; H, 3.9; Cl, 44.5. $C_{11}H_{12}Cl_4O_2$ requires C, 41.54; H, 3.79; Cl, 44.59%); δ_H(270 MHz) 4.91 (1 H, s), 4.86 (1 H, dd, *J* 6.6 and 4.4), 4.75 (1 H, ddd, *J* 6.6, 3.3 and 1), 4.21 (1 H, s), 3.47 (1 H, d, *J* 3.3), 3.34 (1 H, dd, *J* 4.4 and 1), 1.57 (3 H, s) and 1.39 (3 H, s); δ_C(68 MHz) 113.2, 76.6, 75.0, 71.9, 70.8, 60.0, 59.4, 58.5, 56.0, 25.7 and 24.1; *m/z* 301 ($M^+ - CH_3$, 9%) and 43 (100).

Acknowledgements

Thanks are due to the SERC for a Studentship (to G. R. G.), to Dr. M. Murray for the computer-simulated NMR spectra, and to the following undergraduate students for experimental assistance: Anne W. Gladwyn, Michael G. Lee, Andrew J. Milling and James L. Croft.

References

1 M. Akhtar, J. C. Chadwick, S. A. Francis and G. I. Fray, *Tetrahedron*, 1975, **31**, 601.
2 G. R. Geen, Ph.D. Thesis, University of Bristol, 1978.
3 P. E. Eaton and T. W. Cole, *J. Am. Chem. Soc.*, 1964, **86**, 962.
4 P. E. Eaton and T. W. Cole, *J. Am. Chem. Soc.*, 1964, **86**, 3157.
5 J. C. Barborak, L. Watts and R. Pettit, *J. Am. Chem. Soc.*, 1966, **88**, 1328.
6 G. L. Dunn, V. J. DiPasquo and J. R. E. Hoover, *J. Org. Chem.*, 1968, **33**, 1454.
7 C. L. Perrin and M.-T. Hsia, *Tetrahedron Lett.*, 1975, 751.
8 R. N. McDonald and C. A. Curi, *Tetrahedron Lett.*, 1976, 1423.
9 W. G. Dauben and L. N. Reitman, *J. Org. Chem.*, 1975, **40**, 841.
10 A. P. Marchand and T.-C. Chou, *Tetrahedron*, 1975, **31**, 2655.
11 A. T. Blomquist and E. C. Winslow, *J. Org. Chem.*, 1945, **10**, 149.
12 A. Roedig and L. Hörnig, *Chem. Ber.*, 1955, **88**, 2003.
13 E. T. McBee and R. K. Meyers, *J. Am. Chem. Soc.*, 1955, **77**, 88.
14 M. Nakazaki, *Top. Stereochem.*, 1984, **15**, 199.
15 M. Nakazaki, K. Naemura and H. Yoshihara, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 3278.
16 K. V. Scherer, R. S. Lunt and G. A. Ungefug, *Tetrahedron Lett.*, 1965, 1199.
17 R. Askani and W. Schwertfeger, *Chem. Ber.*, 1977, **110**, 3046.
18 G. Mehta and S. C. Suri, *Tetrahedron Lett.*, 1980, **21**, 2093.
19 J. A. Jenkins, R. E. Doehner and L. A. Paquette, *J. Am. Chem. Soc.*, 1980, **102**, 2131.
20 M. Nakazaki, K. Naemura, Y. Sugano and Y. Kataoka, *J. Org. Chem.*, 1980, **45**, 3232.
21 R. Stober, H. Musso and E. Osawa, *Tetrahedron*, 1986, **42**, 1757.
22 P. E. Eaton, R. Millikan and P. Engel, *J. Org. Chem.*, 1990, **55**, 2823.
23 S. Wawzonek, *Synthesis*, 1971, 285, and refs. quoted therein.
24 R. A. Snow, C. R. Degenhardt and L. A. Paquette, *Tetrahedron Lett.*, 1976, 4447, and refs. quoted therein.
25 C. B. Warren, J. J. Bloomfield, J. S. Chickos and R. A. Rouse, *J. Org. Chem.*, 1973, **38**, 4011.
26 B. C. L. Weedon, *Chem. Soc. Rev.*, 1952, **6**, 390; *Adv. Org. Chem.*, 1960, **1**, 1.
27 J. H. Leftin, D. Redpath, A. Pines and E. Gil-Av, *Isr. J. Chem.*, 1973, **11**, 75.
28 V. VanRheenen, R. C. Kelly and D. Y. Cha, *Tetrahedron Lett.*, 1976, 1973.
29 A. Hassner, L. R. Krepski and V. Alexanian, *Tetrahedron*, 1978, **34**, 2069.

Paper 3/06274K
Received 20*th October* 1993
Accepted 12*th November* 1993