Hydrogenation of Cyclobutanes in Strained Cage Compounds. Synthesis of Ditwistane and Bisnorditwistane (Ditwistbrendane)[1]

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The central bond of the bicyclo[2.2.0]hexane system of the dimeric cage compound synthesized photochemically from *N*-chloroacetyltyramine was hydrogenated with 10% Pd–C to give the dihydro-compound. Similarly 7,10-dihydroxy-1,4,7,10-tetramethylpentacyclo[6.4.0.0^{2,5}.0^{3,12}.0^{4,9}]dodecane-6,11-dione gave 6,12-dihydroxy-2,6,9,-12-tetramethyltetracyclo[6.2.2.0^{2,7}.0^{4,9}]dodecane-5,11-dione, and its spectral data revealed the correct structure, which was confirmed by the *X*-ray analysis. This hydrogenation was extended to the synthesis of [8]-ditwistane and bisnorditwistane (ditwistbrendane). Thus, pentacyclo[6.4.0.0.^{2,5}0^{3,12}.0^{4,9}]dodecane-6,11-dione synthesized from salicyl alcohol was hydrogenated to give ditwistanedione. Dithioketalization and desulphurization gave ditwistane. All the rings of this compound are six-membered and in the distorted twist-boat conformation. Similarly, hydrogenation of pentacyclo[5.3.0.0^{2,5}.0^{3,10}.0^{4,8}]decane and its 6-one gave bisnorditwistane.

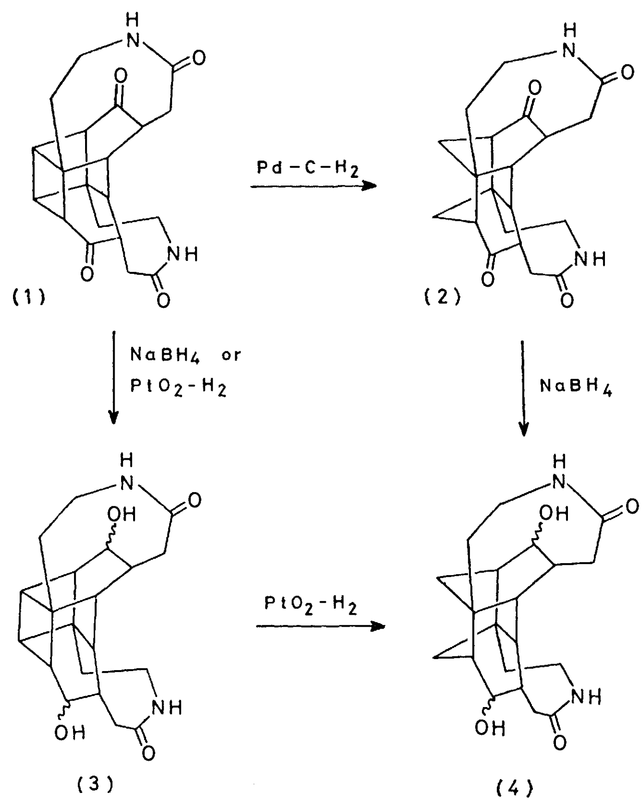
IN contrast with cyclopropanes, the hydrogenolysis of cyclobutanes usually requires quite drastic conditions,[2] and hence its synthetic utility has remained largely undeveloped. However, since the opening of the cyclobutane ring in basketane was found to occur readily [3] and selectively [4] under mild catalytic hydrogenation conditions, several reports on reductive ring cleavages of strained cyclobutanes, especially in cage compounds, and on their applications have been published.[5] During the course of our chemical studies of the dimeric cage compound (1) synthesized photochemically from *N*-chloroacetyltyramine [6] we found that the central bond in the bicyclo[2.2.0]hexane system of (1) was easily cleaved by catalytic hydrogenation.[1] We report here our detailed studies on this reaction, its extension to model cage compounds including the synthesis of ditwistane and bisnorditswistane, and the substitution effect on this hydrogenolysis.

RESULTS AND DISCUSSION

Hydrogenolysis of Strained Four-membered Rings in Cage Compounds.—When the dimeric photoproduct (1) synthesized from *N*-chloroacetyltyramine [6] was hydrogenated in the presence of 10% Pd–C at 3 atm, the dihydro-compound (2) was easily isolated. Since the original carbonyl groups remained unchanged in the i.r. spectrum of (2), a C–C bond must have been cleaved. On the other hand, hydrogenation in the presence of Adams catalyst instead of Pd–C gave the tetrahydro-compound (3), and its i.r. spectrum clearly shows that both the ketone groups were reduced to hydroxy-groups. Compound (3) was identical to the reduction product of (1) with sodium borohydride. On further hydrogenation in aqueous methanol containing acetic acid, (3) consumed 1 mol of hydrogen and was converted into the hexahydro-compound (4), which was also obtained by the sodium borohydride reduction of (2).

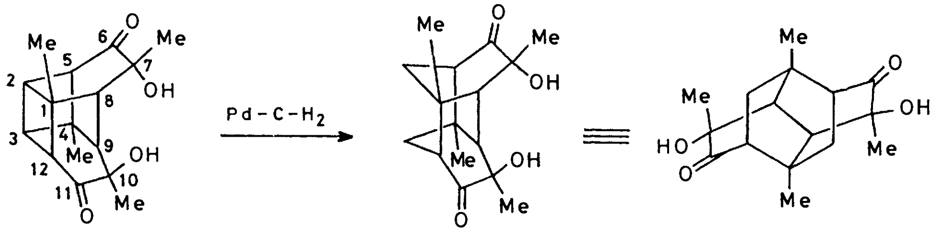
The tetra-acetate (5) of (4) has only two sharp peaks, at δ 2.00 and 2.45, assignable to the methyl groups in its n.m.r. spectrum, indicating that it is symmetrical. Although conclusive proof was lacking, it was most probable that the hydrogenolysis must have occurred at the most strained central bond in the bicyclo[2.2.0]hexane system. This was proved, though indirectly, through a study of the following model cage compound (6).

Compound (6), synthesized from 2,4-dimethylphenol,[7] was hydrogenated over Pd–C under similar conditions to give the dihydro-compound (7). Compound (7), as well



as (6), has no exchangeable C–H bond when heated in deuteriomethanol containing sodium methoxide.[8] In the n.m.r. spectrum, (7) has signals due to two methyls, four C–H, and one OH. This indicates clearly that (7) has a two-fold symmetry, which is confirmed by the ^{13}C n.m.r. spectrum having eight different kinds of carbon signals (Figure 1). Finally the structure of (7), having a ditwistane ring system, was determined by X-ray analysis.

Bond lengths and valency angles are given in Tables 1 and 2 in the Experimental section.* Most of the bond lengths lie within normal ranges, but the lengths of C(1)–C(3) and C(1)–C(5) are significantly longer than the average value of the other C(sp^3)–C(sp^3) bonds. All the rings are six-membered and in the distorted twist-boat conformation. The molecules are linked mainly through hydrogen bonds, O(1)–H(01) · · · O(2)=C(7).



(6) (7)

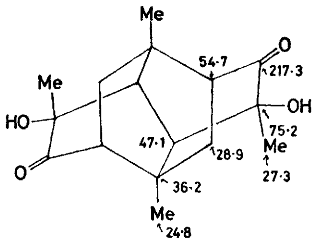


FIGURE 1 ^{13}C N.m.r. chemical shifts (δ) for compound (7)

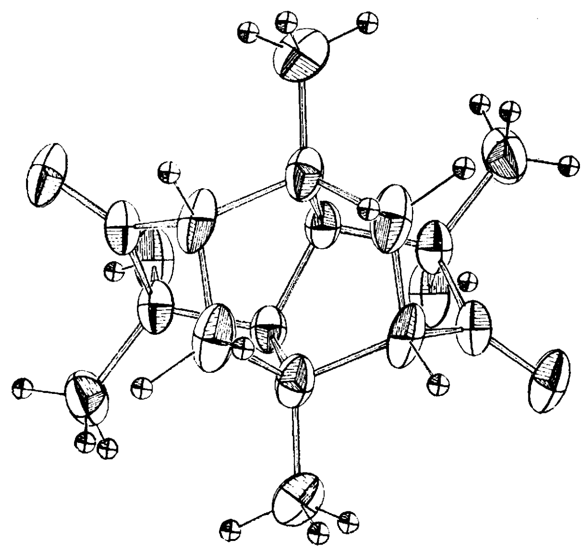


FIGURE 2 Perspective ORTEP drawing of compound (7)

Synthesis of Ditwistane and Bisnorditwistane (*Ditwistbrendane*).†—Since it was clarified that the pentacyclo-[6.4.0.0^{2,5}.0^{3,12}.0^{4,9}]dodecane derivatives could be hydrogenolysed to ditwistane derivatives, ditwistane (9) itself, a homologue of twistane (8) [12] and the parent compound of new symmetrical cage compounds [(2), (7)], was next synthesized from (10).

Compound (10), easily synthesized from salicyl alcohol,[7d] was converted into pentacyclo[6.4.0.0^{2,5}.0^{3,11}.0^{4,9}]dodecane-6,11-dione (14) [8] *via* four successive reactions (Scheme 1). Hydrogenation of (14) gave a mixture containing mainly diacetates of the hexahydro-compound (15), which was hydrolysed with sodium hydroxide, followed by oxidation with chromic anhydride in 90% acetic acid, to give ditwistanedione (17).

Tetracyclo[6.2.2.0^{2,7}.0^{4,9}]dodecane (9), [8]-ditwistane,‡ was synthesized from (14) *via* the ethylenedithioacetal (18) in the usual way and, after purification by sublimation, isolated as rather volatile fine prisms. The ^{1}H n.m.r. spectrum of (9) is quite similar to that of twistane,[12] but gives no conclusive structural information.

(8) (9)

The ^{13}C n.m.r. spectrum has six sharp signals showing the correct structure to be (9).

The hydrogenolysis was next extended to the synthesis of bisnorditwistane (19), tetracyclo[5.2.1.0^{2,6}.0^{4,8}]decane,§ which was prepared by three routes (Scheme 2). Hydrogenation of (20) [15] proceeded rather fast to give a mixture of tetrahydroacetates (21), which was converted into bisnorditwistanone (23).[16] The ethyleneketal (24) of (20) was hydrogenated to the dihydro compound (25), followed by hydrolysis to give (23), which was smoothly converted into bisnorditwistane (19) *via* the thioketal (26). Compound (19) was also obtained directly from (27) [17] and was isolated again as volatile crystals.[5e,f]

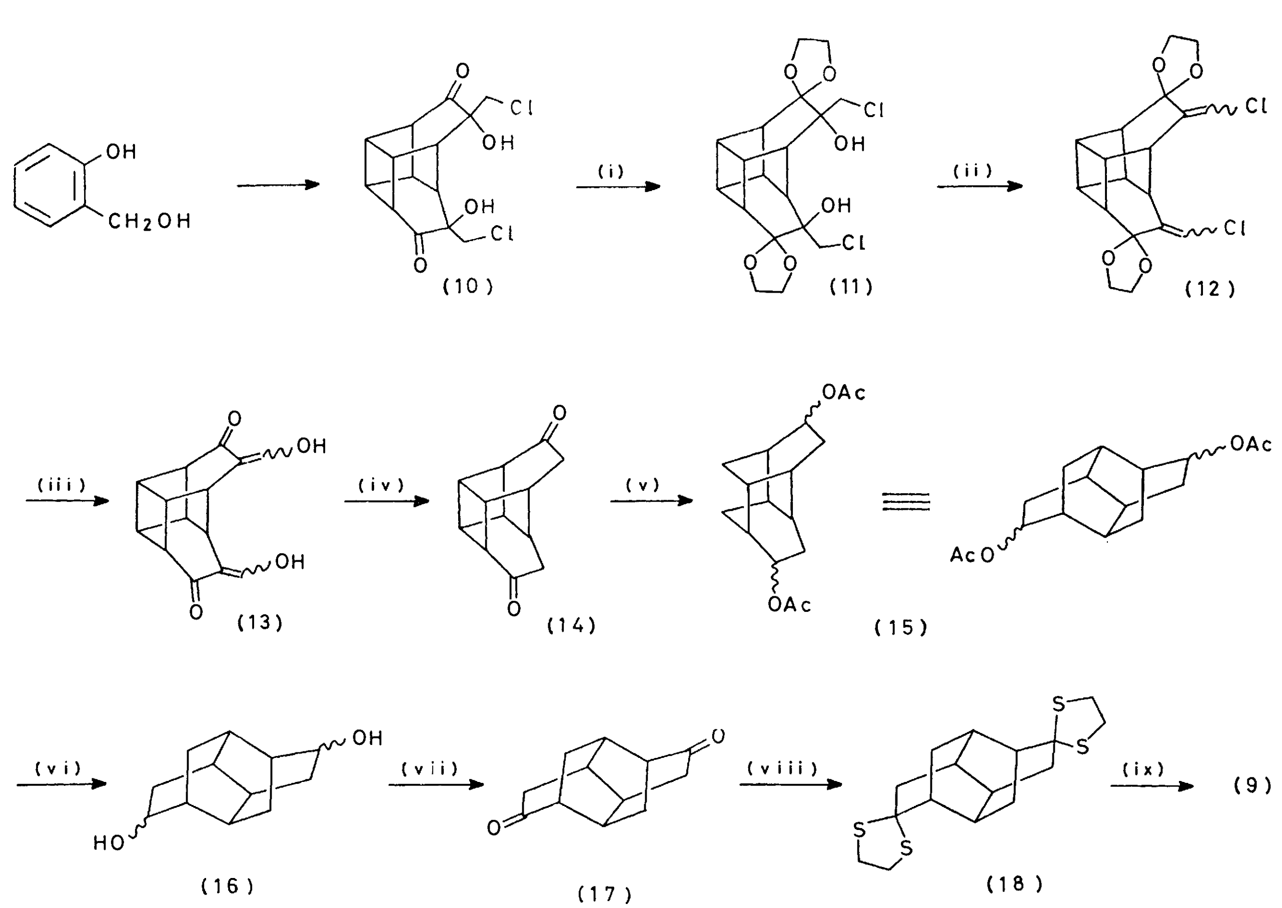
Substitution Effect on the Hydrogenolysis.—Although the central bonds in the bicyclo[2.2.0]hexane system of the starting strained cage compounds are not always the longest,[6a,18] the hydrogenolysis of these bonds was expected to be much more energetically favourable than

* The structure was solved by the symbolic addition procedure [9] refining by the block-diagonal matrix least squares method.[10] For the numbering, see the Experimental section. Figure 2 was plotted with ORTEP.[11]

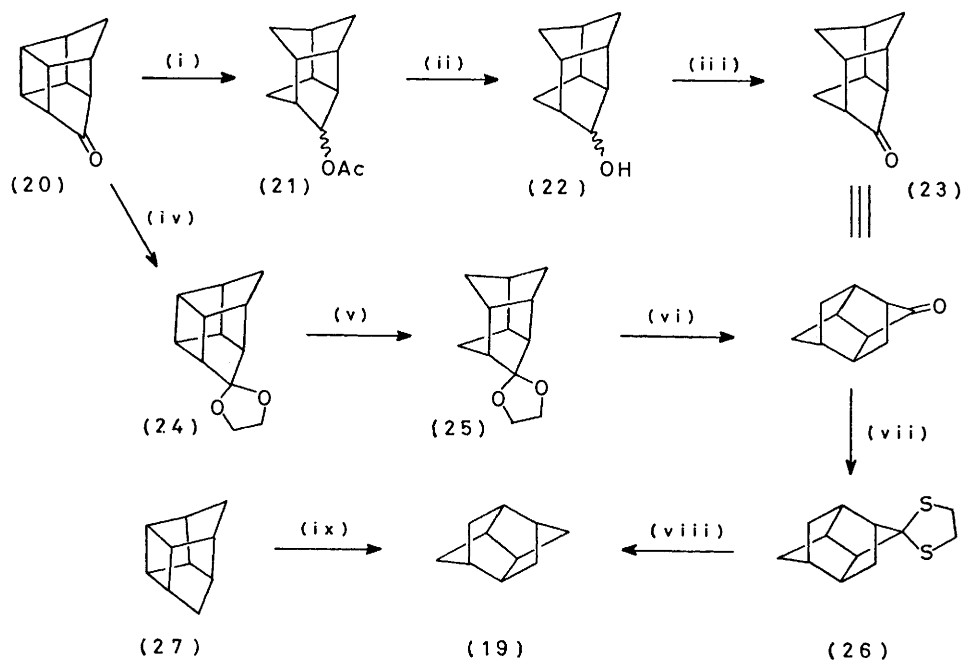
† Bisnorditwistane has been named ditwistbrendane by Nakazaki.[5f]

‡ According to the proposed nomenclature by Schleyer,[13] (9) is named [8]-ditwistane.

§ Compounds having this ring system have been synthesized as 3-ols and 3-ones from the tosylate of tricyclo[5.2.1.0^{2,6}]dec-8-en-4-ol.[14]

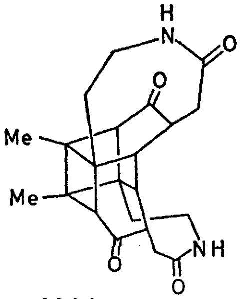


SCHEME 1 (*i*) $(CH_2OH)_2$–TsOH; (*ii*) $SOCl_2$–pyridine; (*iii*) HCl–dioxan–water; (*iv*) 5% KOH–benzene; (*v*) Pd–C–H_2–AcOH; (*vi*) NaOH–MeOH–water; (*vii*) CrO_3–AcOH; (*viii*) $(CH_2SH)_2$–BF_3–AcOH; (*ix*) Raney nickel



SCHEME 2 (*i*) Pd–C–H_2–AcOH; (*ii*) NaOH–MeOH–water; (*iii*) CrO_3–AcOH; (*iv*) $(CH_2OH)_2$; (*v*) Pd–C–H_2–MeOH; (*vi*) HCl–THF; (*vii*) $(CH_2SH)_2$; (*viii*) Raney Ni; (*ix*) Pd–C–H_2–AcOH that of the others, and this was confirmed by force-field calculations.[5a]

As already suggested,[4,5c] though there is no good evidence, the interaction of the compound with the catalyst surface must be another important factor in the hydrogenolysis. In contrast with basketane,[3,4,5b] homocubane,[5c] and cubane,[5d] the starting cage compounds presented here, as well as bicyclo[2.2.0]hexane itself,[19] have only one reducible bond, the central bond, and introduction of some substituents in the cage system may provide a good probe to examine the steric effects on the hydrogenolyses.



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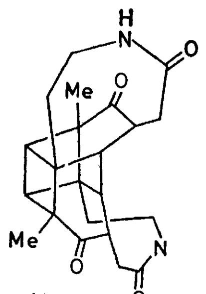

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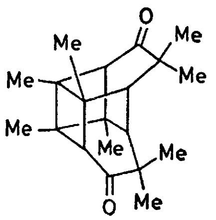

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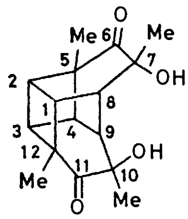

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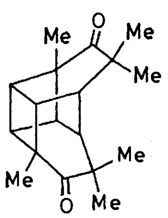

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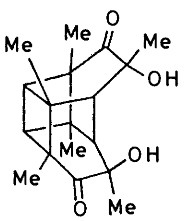


(33)

Compound (28), which has methyl groups attached to the central bond, was completely unreactive to hydrogenolysis, because the central bond could not come directly in contact with the catalyst furface. The corresponding model cage compound (30) gave the same results.[20]

Interestingly, the dimethyl compounds (31) and (32), substituted at C-5 and C-12 instead of at C-1 and C-4 in (6), also resisted hydrogenolysis. This reactivity difference between the regioisomers, (6) and (31), can be explained in terms of the steric factor. The C-1 (C-4) bond is equivalent, of course, to the C-5 (C-12) bond in bicyclo[2.2.0]hexane itself; however, the bicyclo[2.2.0]-hexane system in the cage compounds is strongly twisted such that the C-1 (C-4) bond becomes more parallel to the central bond, whereas the C-5 (C-12) bond becomes more perpendicular. Therefore, the C-5 (C-12) methyl group hinders the close contact of the central bond and the catalyst, which must be a stringent requirement for such hydrogenolyses. Finally the tetrasubstituted compounds, (29) and (30), likewise resisted hydrogenolysis.

EXPERIMENTAL

Hydrogenolysis of the Dimeric Cage Compound (1) *to the Dihydro-compound* (2).—A solution of (1) (100 mg, 0.28 mmol) in 40% aqueous MeOH (25 ml) was hydrogenated in a Parr apparatus with 10% Pd–C (100 mg) and hydrogen at an initial pressure of 3 atm for 12 h. After removal of the catalyst by filtration, the filtrate was concentrated *in vacuo* and the residue recrystallized (aqueous MeOH) to give (2) (53 mg, 53%), m.p. >270 °C (colourless needles) (Found: C, 66.95; H, 6.8; N, 7.7. $C_{20}H_{24}N_4$ requires C, 67.39; H, 6.79; N, 7.86%); $\lambda_{max.}$ (H_2O) 294 nm (ϵ 104); $\nu_{max.}$ (Nujol) 1 730 and 1 680 cm^{-1}; *m/e* 356 (M^+), 328, 299, and 271.

Reduction of (1) *to the Diol* (3).—(*a*) A solution of (1) (100 mg) in 50% aqueous MeOH (25 ml) was hydrogenated over PtO_2 (100 mg) (3 atm, 12 h) to give (3) (70.5 mg, 70%), m p. >270° (colourless prisms from H_2O) (Found: C, 65.2; H, 7.4; N, 7.95. $C_{20}H_{26}N_2O_4$·$0.5H_2O$ requires C, 65.39; H, 7.41; N, 7.62%); $\nu_{max.}$ (Nujol) 3 400 (br) and 1 650 cm^{-1}.

(*b*) To a stirred 33% aqueous MeOH solution of (1) (300 mg, 0.85 mmol) was added $NaBH_4$ (100 mg, 2.64 mmol) at 0—5 °C. After 3 h, the solution was neutralized with 10% HCl and evaporated to dryness. To the residue was added MeOH (10 ml) and insoluble inorganic salts were removed by filtration. After evaporation ot the filtrate the residue was stirred in EtOH (10 ml) for 30 min to give precipitated (3) (182 mg, 60%).

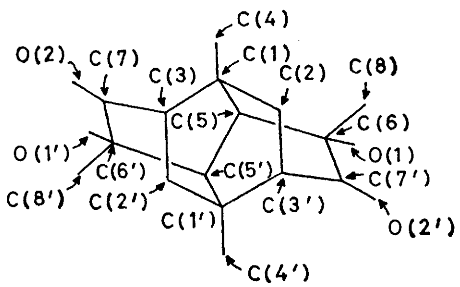
Hydrogenation of (3) *to* (4).—A solution of (3) (60 mg) in 50% aqueous MeOH (15 ml) containing AcOH (0.5 ml) was hydrogenated over PtO_2 (60 mg) (3 atm, 18 h) to give (4) (51 mg, 83%), m.p. >270 °C (colourless prisms from H_2O); $\nu_{max.}$ (Nujol) 3 380, 1 680, and 1 650 cm^{-1}.

Tetra-acetate (5).—(*a*) Compound (4) (40 mg, 0.11 mmol) in Ac_2O (15 ml) was heated under reflux for 2 h. After concentration of the solution, recrystallization from $CHCl_3$–isopropyl ether gave (5) (43 mg, 74.2%, colourless prisms), m.p. 287—292 °C (decomp.) (Found: C, 63.95; H, 6.9; N, 5.15. $C_{28}H_{36}N_2O_8$ requires C, 63.62; H, 6.87; N, 5.39%); $\nu_{max.}$ (Nujol) 1 735, 1 704, and 1 688 cm^{-1}; *m/e* 528 (M^+), 468, 426, and 408; δ($CDCl_3$) 2.00 (6 H, s), 2.45 (6 H, s), and 4.72 (2 H, d, *J* 4 Hz).

(*b*) Compound (2) (50 mg, 0.14 mmol) in 50% aqueous MeOH (10 ml) was reduced with $NaBH_4$ (40 mg, 1.06 mmol) at 0—5 °C. After 2 h, the solution was neutralized with AcOH and then evaporated to dryness. The residue (4) was crystallized in ether (20 ml) and acetylated with refluxing Ac_2O (10 ml) for 1 h to give (5) (30 mg, 42.2%), m.p. 291—294 °C (decomp).

6,12-*Dihydroxy*-2,6,9,21-*tetramethyltetracyclo*[6.2.2.$0^{2,7}$.$0^{4,9}$]*dodecane*-5,11-*dione* (7).—Compound (6) (100 mg) in MeOH (30 ml) was hydrogenated over 10% Pd–C (100 mg) (3.2 atm, 48 h). Work-up gave (7) (71.2 mg, 72%), m.p. 231—233° (colourless prisms from EtOAc) (Found: C, 69.1; H, 8.0. $C_{16}H_{22}O_4$ requires C, 69.04; H, 7.97%); $\nu_{max.}$ (Nujol) 3 460 and 1 715 cm^{-1}; *m/e* 278 (M^+); δ_H($CDCl_3$) 1.12 (6 H, s), 1.52 (6 H, s), 1.80 (2 H, s), 1.92 (2 H, d, *J* 5 Hz), 2.05 (2 H, s), 2.16 (2 H, d, *J* 5 Hz), and 3.02 (2 H, br s); δ_C($CDCl_3$) 24.8 (q), 27.3 (q), 28.9 (t), 36.2 (s), 47.1 (d), 54.7 (d), 75.2 (s), and 217.3 (s).

X-Ray Analysis of (7).—Refined cell parameters of (7) with monoclinic space group *P*2/*c* were determined by the least-squares method using 13 2θ values measured on a four-circle diffractometer, AFC/3 (Rigaku); $a = 14.962(2)$, $b = 7.011(2)$, $c = 8.521(5)$ Å, $\beta = 122.92$ (2)°. Three-dimensional intensity data were obtained for a hexagonal-plate crystal of 0.4 × 0.4 × 0.1 mm, aligned with its *b* axis along the ϕ axis of the diffractometer. All reflections within the range $2\theta \leqslant 135°$ were measured in the ω—2θ mode with graphite-monochromatized Cu-K_α radiation and 991 independent reflections having $|F_o| \geqslant 3\sigma(|F_o|)$ were used for the structure analysis. The final *R* was 0.046. The results are shown in Figure 2 [11] and Tables 1 and 2. The numbering scheme (atoms in the Tables) is as follows.



7,10-*Dihydroxy*-7,10-*bis*(*chloromethyl*)*pentacyclo*-[6.4.0.$0^{2,5}$.$0^{3,12}$.$0^{4,9}$]*dodecane*-6,11-*dione Bis*(*ethylene acetal*) (11).—A solution of (10) (2.0 g), *p*-$MeC_6H_4SO_3H$ (250 mg), and ethylene glycol (5 ml) in dioxan (15 ml) and benzene (200 ml) was heated under reflux for 10 h using a water separator. The solution was washed with saturated $NaHCO_3$ and H_2O, dried (Na_2SO_4), and evaporated to leave (11). Recrystallization from EtOAc gave colourless prisms (2.4 g, 94%), m.p. 237.5—238 °C (decomp.) (Found: C, 53.05; H, 5.6; Cl, 17.35. $C_{18}H_{22}O_6Cl_2$ requires C, 53.34; H, 5.47; Cl, 17.50%); $\nu_{max.}$ (Nujol) 3 480 cm^{-1}; *m/e* 406, 404 (M^+), 369, 333, and 168; δ($CDCl_3$) 2.4—2.8 (8 H), 3.1—3.4 (2 H), 3.5 (2 H, d, *J* 11 Hz), 3.66 (2 H, d, *J* 11 Hz), and 3.94 (8 H, s).

7,10-*Bis*(*chloromethylene*)*pentacyclo*[6.4.0.$0^{2,5}$.$0^{3,12}$.$0^{4,9}$]*dodecane*-6,11-*dione Bis*(*ethylene acetal*) (12).—To an ice-cooled solution of (11) (2.2 g) in pyridine (45 ml) was added dropwise $SOCl_2$ (4 g). The solution was stirred at room temperature for 4 d, then poured onto ice–water, neutralized (pH 4) with 10% HCl, and extracted with CH_2Cl_2. The extract was washed with H_2O, dried, and evaporated to give almost pure (12) (1.44 g, 67%), m.p. 176—177 °C (colourless needles from EtOAc) (Found: C, 58.4; H, 5.1; Cl, 19.2. $C_{18}H_{18}O_4Cl_2$ requires C, 58.55; H, 4.91; Cl, 19.30%); $\nu_{max.}$ (Nujol) 1 639 cm^{-1}; *m/e* 370, 368 (M^+), 333, 255, 183, and 149; δ($CDCl_3$) 2.5—2.9 (6 H), 3.46 (2 H, d, *J* 4 Hz), 3.8—4.2 (8 H), and 6.38 (2 H, s).

7,10-*Diformylpentacyclo*[6.4.$0^{2,5}$.$0^{3,12}$.$0^{4,9}$]*dodecane*-6,11-*dione* (13).—A solution of (12) (750 mg) in 25% HCl (12 ml) and dioxan (30 ml) was stirred for 2 d at room temperature and then extracted with CH_2Cl_2. The extract was washed with H_2O, dried, and evaporated to leave almost pure (13) (447 mg, 90%), m.p. 169—171 °C (decomp.) (colourless prisms from MeCN) (Found: C, 68.75; H, 5.0. $C_{14}H_{12}O_4$ requires C, 68.84; H, 4.95%); $\nu_{max.}$ (Nujol) 1 650 and 1 590 cm^{-1}; *m/e* 244 (M^+) and 122; δ($CDCl_3$) 2.5—2.8 (4 H), 2.9—3.2 (2 H), 3.4 (2 H, t, *J* 5 Hz), 7.43 (2 H, s), and 10.8—11.6 (2 H).

Pentacyclo[6.4.0.$0^{2,5}$.$0^{3,12}$.$0^{4,9}$]*dodecane*-6,11-*dione* (14).—Compound (13) (564 mg) in 5% KOH (50 ml) and benzene (50 ml) was refluxed for 4 d with stirring. The benzene layer was separated, washed with H_2O, dried, and evaporated to leave almost pure (14) (327 mg, 76%), m.p. 170—172 °C (colourless prisms from Bu^nOH) (Found: C, 76.75; H, 6.6. $C_{12}H_{12}O_2$ requires C, 76.57; H, 6.43%); $\nu_{max.}$ (Nujol) 1 718 cm^{-1}; *m/e* 188 (M^+), 146, 117, and 94; δ($CDCl_3$) 2.40 (6 H, br s) and 2.7—3.3 (6 H, m).

TABLE 1

Bond lengths (in Å) with estimated standard deviations in parentheses

C(1)–C(2)	1.532(6)	C(2)–H(21)	1.10(3)
C(1)–C(3)	1.586(4)	C(2)–H(22)	0.99(3)
C(1)–C(4)	1.519(6)	C(3)–H(31)	0.98(4)
C(1)–C(5)	1.573(5)	C(4)–H(41)	1.04(4)
C(2)–C(3')	1.542(6)	C(4)–H(42)	0.88(4)
C(3)–C(7)	1.500(5)	C(4)–H(43)	1.03(3)
C(5)–C(5')	1.552(5)	C(5)–H(51)	1.01(3)
C(5)–C(6)	1.545(6)	C(8)–H(81)	0.95(3)
C(6)–C(8)	1.525(4)	C(8)–H(82)	1.03(4)
C(6)–O(1)	1.429(4)	C(8)–H(83)	0.88(4)
C(7)–O(2)	1.212(6)	O(1)–H(01)	0.87(3)
C(7)–C(6')	1.544(5)		

Tetracyclo[6.2.2.$0^{2,7}$.$0^{4,9}$]*dodecane*-5,11-*dione* (17).—Compound (14) (150 mg) in AcOH (25 ml) was hydrogenated over 10% Pd–C (600 mg) (3.3 atm, 4 d). After removal of the catalyst, the solution was diluted with H_2O, neutralized with $NaHCO_3$, and extracted with EtOAc. The extract was washed with saturated NaCl, dried, and evaporated to leave (15) as a waxy solid (175 mg); $\nu_{max.}$ (neat) 3 400, 1 725, and 1 240 cm^{-1}.

TABLE 2

Bond angles (°) with estimated standard deviations in parentheses

C(2)–C(1)–C(3)	105.4(3)	C(1)–C(5)–C(6)	114.9(3)
C(2)–C(1)–C(4)	114.2(3)	C(1)–C(5)–C(5')	105.3(2)
C(2)–C(1)–C(5)	106.5(4)	C(6)–C(5)–C(5')	106.3(3)
C(3)–C(1)–C(4)	110.5(4)	C(5)–C(6)–C(8)	116.0(4)
C(3)–C(1)–C(5)	107.8(2)	C(5)–C(6)–O(1)	106.0(3)
C(4)–C(1)–C(5)	113.0(3)	C(5)–C(6)–C(7')	105.9(2)
C(1)–C(2)–C(3')	105.6(3)	O(1)–C(6)–C(7')	107.9(4)
C(1)–C(3)–C(7)	109.2(3)	C(3)–C(7)–C(2)	125.0(3)
C(1)–C(3)–C(2')	108.9(4)	O(2)–C(7)–C(6')	123.0(3)

The crude (15) was dissolved in MeOH (10 ml) and 10% NaOH (4 ml) and refluxed for 1 h. After evaporation of the solvent, the mixture was diluted with H_2O, neutralized with 5% HCl, and then extracted with EtOAc. The extract was dried and evaporated to leave (16) as a waxy solid (97.5 mg); $\nu_{max.}$ (neat) 3 400 and 1 720 cm^{-1}.

The crude (16) and CrO_3 (100 mg) in 90% AcOH (5 ml) was stirred for 25 h at room temperature. After treatment with a small amount of MeOH, the mixture was neutralized with $NaHCO_3$, and extracted with EtOAc. The extract was washed, dried, and evaporated to leave needles of (17) (69.3 mg, 47%), m.p. 225—227 °C (from EtOAc–hexane) (Found: C, 75.65; H, 7.4. $C_{12}H_{14}O_2$ requires C, 75.76; H, 7.42%); $\nu_{max.}$ (Nujol) 1 720 cm^{-1}; *m/e* 190 (M^+), 162, 91, 79, and 55; δ(CCl_4) 1.60—2.64 (14 H, m).

Tetracyclo[6.2.2.$0^{2,7}$.$0^{4,9}$]*dodecane*, [8]-*Ditwistane* (9).—

To a solution of (17) (257 mg) and ethane-1,2-dithiol (350 mg) in AcOH (2 ml) was added dropwise BF_3–ether (1 ml) in AcOH (2 ml) and the mixture was allowed to stand at room temperature for 1 h. The precipitated crystals were filtered off, washed with MeOH, and dried to give (18) (325 mg), m.p. 199—203 °C; *m/e* 342 (M^+) and 314.

To a solution of (18) in EtOH (40 ml) was added Raney nickel prepared from the alloy (6 g), and the mixture was refluxed for 6.5 h. After removal of the catalyst, the filtrate was diluted with H_2O and then extracted with pentane. The extract was washed with H_2O, dried, and evaporated to leave (9) as a waxy solid (143 mg, 65%). Recrystallization from MeOH gave prisms (90.8 mg, 41.5%), m.p. 104—107 °C, which were sublimed at 75—85 °C (bath temp) to give fine prisms, m.p. 117—118.5 °C (sealed tube); *m/e* 162 (M^+), 133, and 80; $\delta_H(CCl_4)$ 1.23—1.82 (18 H, m); $\delta_C(CDCl_3)$ 23.0 (t), 25.2 (t), 26.2 (t), 29.7 (d), 31.2 (d), and 32.3 (d).

Tetracyclo[5.2.1.0^{2,6}.0^{4,8}]*decan-5-one* (23).—(*a*) A solution of (20) (1.0 g) in AcOH (60 ml) was hydrogenated with 10% Pd–C (450 mg) (3.1 atm, 18 h). Work-up gave a waxy solid (965 mg) mainly containing (22); $\nu_{max.}$ (neat) 3 300 and 1 760 cm^{-1}. A solution of the crude (22) (960 mg) and CrO_3 (500 mg) in 90% AcOH (30 ml) was stirred at room temperature for 20 h. After neutralization with $NaHCO_3$, the mixture was extracted with ether. The extract was washed with saturated $NaHCO_3$ and saturated NaCl, dried, and evaporated to leave (23) as a crude oil which was stirred in saturated $NaHCO_3$ (20 ml) overnight. The precipitated colourless solid was collected by filtration, washed with ether, and then mixed with 10% NaOH. The mixture was extracted with ether, and the extract was washed with saturated NaCl, dried, and evaporated to leave (23) as a colourless solid (785 mg, 78% from 20). Sublimation (95 °C) and recrystallization from pentane gave colourless prisms, m.p. 170—171.5 °C (sealed tube); $\nu_{max.}$ (Nujol) 1 760 cm^{-1}; *m/e* 148 (M^+) and 66 (base peak); $\delta(CCl_4)$ 1.0—1.4 (2 H, m), 1.49 (2 H, s), 1.79 (3 H, br s), 1.90 (1 H, s), 2.1—2.4 (2 H, m), and 2.96 (2 H, br s). The semicarbazone had m.p. 219—220 °C (decomp.) (colourless prisms from EtOH) (Found: C, 64.55; H, 7.45; N, 20.4. $C_{11}H_{15}N_3O$ requires C, 64.36; H, 7.37; N, 20.47%).

(*b*) A solution of (25) (420 mg) in concentrated HCl (1 ml) and THF (5 ml) was stirred at room temperature for 6 h. After dilution with H_2O, the mixture was extracted with CH_2Cl_2. The extract was washed with H_2O, dried, and evaporated to leave (23) (305 mg, 94%). Recrystallization from pentane gave colourless prisms of (23) (278 mg, 86%).

Pentacyclo[5.3.0.0^{2,5}.0^{3,10}.0^{4,8}]*decan-6-one Ethylene Acetal* (24).—A solution of (20) (5.1 g), *p*-$MeC_6H_4SO_3H$ (1 g), and ethylene glycol (10 ml) in benzene (250 ml) was heated under reflux for 7 h using a water separator. The solution was washed with saturated $NaHCO_3$ and H_2O, dried, and evaporated to leave an oil, which was distilled to give (24) as a colourless oil (6.1 g, 91%), b.p. 118—120 °C at 8 Torr (Found: C, 75.3; H, 7.4. $C_{12}H_{14}O_2$ requires C, 75.76; H, 7.42%); $\nu_{max.}$ (neat) 1 100 cm^{-1}; *m/e* 190 (M^+), 125, 117, and 99.

Tetracyclo[5.2.1.0^{2,6}.0^{4,8}]*decan-5-one Ethylene Acetal* (25).—A solution of (24) (530 mg) in MeOH (10 ml) was hydrogenated over 10% Pd–C (500 mg) (3.5 atm, 24 h). After removal of the catalyst and the solvent, the residue was distilled to give (25) as a colourless oil (480 mg, 90%), b.p. 125—130 °C (bath temp) at 10 Torr (Found: C, 75.0; H, 8.35. $C_{12}H_{16}O_2$ requires C, 74.97; H, 8.39%); $\nu_{max.}$ (neat) 1 100 cm^{-1}; *m/e* 192 (M^+), 138, 113, 112, and 99; $\delta(CDCl_3)$ 0.94 (1 H, dd, *J* 6 and 12 Hz), 1.12—1.88 (7 H, m), 2.06 (2 H, q, *J* 6 Hz), 2.26 (1 H, br s), 2.49 (1 H, br s), and 3.85 (4 H, s).

Tetracyclo[5.2.1.0^{2,6}.0^{4,8}]*decane* (19).—(*a*) A solution of (27) (500 mg) in AcOH (40 ml) was hydrogenated over 10% Pd–C (250 mg) (3 atm, 10 h). After removal of the catalyst, the filtrate was diluted with H_2O. The precipitate was filtered and sublimed at 75—80 °C (bath temp) to give colourless fine plates of (19) (375 mg, 75%), m.p. 160—161 °C (sealed tube); *m/e* 134 (M^+), 119, 105, 92, 79, and 66; $\delta_H(CCl_4)$ 0.6—2.3 (14 H, m); $\delta_C(CDCl_3)$ 32.2 (t), 34.9 (d), 35.4 (t), 39.0 (d), and 47.4 (d).

(*b*) A solution of (23) (375 mg), ethane-1,2-dithiol (2 drops), and BF_3–ether (2 drops) in AcOH (30 ml) was allowed to stand at room temperature for 18 h. The solution was poured onto ice–water, brought to pH *ca.* 10 with 10% NaOH, and then extracted with ether. The extract was washed with 10% K_2CO_3 and saturated NaCl, dried, and evaporated to leave (26) as a colourless liquid (453 mg); *m/e* 224 (M^+) and 196; $\delta(CCl_4)$ 0.7—1.1 (2 H, m), 1.25 (2 H, br s), 1.62 (2 H, br s), 2.14 (3 H, br s), 2.25 (2 H, br s), 2.55 (1 H, br s), and 3.14 (4 H, s).

To a solution of (26) (415 mg) in MeOH (20 ml) and EtOH (10 ml) was added Raney nickel prepared from the alloy (3 g) and the mixture was stirred and refluxed for 10 h. After removal of the catalyst, the filtrate was diluted with H_2O and extracted with pentane. The extract was dried and evaporated to leave (19) (107.5 mg, 43%).

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