The Preparation and Some Reactions of Tricyclo[4.4.4.0]tetradecane-2,7-dione ([4.4.4]Propellane-2,7-dione): *X*-Ray Crystal Structure of 2,7-bis(trimethylsilyloxy)tetracyclo-[4.4.4.0.0^{2,7}]tetradecane

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Tricyclo[4.4.4.0]tetradecane-2,7-dione (1) has been made by reductive alkylation of bicyclo[4.4.0]-dec-1-ene-2,7-dione, using Na–NH_3 and $Br(CH_2)_4Br$. Reduction of (1) with sodium–potassium alloy in benzene in the presence of chlorotrimethylsilane yields 2,7-bis(trimethylsilyloxy)tetracyclo[4.4.4.0.0^{2,7}]-tetradecane (13), whose crystal structure is reported. Reduction of (1) with $LiAlH_4$ and with Na–NH_3–Bu^tOH–THF gave mixtures of the three possible diastereoisomeric diols (15)—(17), which could not be separated, but whose isomeric composition could be estimated by ^{13}C n.m.r. spectroscopy. Conformational equilibria in dione (1) and in diol (15) are discussed with the aid of force field calculations.

As part of a project to gain access to the bicyclo[4.4.4]tetradecane skeleton † through Grob-type fragmentations, we have explored synthetic routes to 2,7-difunctionalised [4.4.4]-propellanes,‡ and report our limited success in this paper.

Discussion

Our initial target was tricyclo[4.4.4.0]tetradecane-2,7-dione (1), with the bicyclic diones (2) and (3)[8] as obvious, reasonably accessible precursors. Dione (3) could not be induced to react with butadiene (even with Lewis acid catalysis) or with dienes (4) and (5).[9] The low dienophilic reactivity of (3) is not surprising.

Reductive alkylation of (3) with Na–NH_3–$Br(CH_2)_4Br$ produced (1) in 16% yield. Despite numerous attempts, we were unable to raise this disappointing yield by variation of the conditions or reagents. All attempts to generate the dienolate (6) from (2), to generate the corresponding bis-(trimethylsilyl) ether, and to utilise the bis-enol acetate (which we did make), were uniformly fruitless; we have no explanation for these failures. Although Stork and Logusch[10] have reported efficient reductive monoalkylation of enediones, the conversion of (3) into (1) appears to be the first example of their reductive dialkylation.

Huang–Minlon reduction of the propellanedione (1) gave [4.4.4]propellane with appropriate physical and spectroscopic characteristics. The dione can exist in two all-chair conformations (1a and b); (1a) has ΔH_f −99.4 kcal mol^{-1} and a dipole moment of 3.35 D and (1b) has ΔH_f −99.6 kcal mol^{-1} and a dipole moment of 3.40 D, according to MM2 calculations.[11] The differences between these conformers are remarkably subtle. At normal probe temperature the ^{13}C n.m.r. spectrum of the propellanedione shows only seven lines (rapid ring inversion) but at −70 °C two sets of seven ^{13}C lines are seen in a 2.2 : 1 ratio (see Experimental section), which translates into $\Delta\Delta G$ 0.32 kcal mol^{-1} between the isomers. Unfortunately there seems to be no way of definitively assigning the major isomer. Two ^{13}C lines undergo substantial shifts between major and minor isomers; the line at δ 29.2 (major) shifts to 32.5 (minor) and the line at 31.9 (major) shifts to 25.4 p.p.m. (minor). These lines are certainly due to (C-5 + C-10) and (C-11 + C-14), but the assignment of each pair of signals is uncertain. The upfield lines are certainly due to carbons which are eclipsed with oxygen in a C–C–C=O fragment [in *trans*-decalin-1,5-dione, *trans*-(2), C-4 and -8 are 10.3 p.p.m. upfield of the corresponding carbons in *trans*-decalin]. In the absence of definite experimental evidence, we assume (1b) is the major isomer, as the calculations indicate.

The coalescence temperature for the δ 31.9 and 25.4 p.p.m. pair of signals is 241 K and that for the δ 22.9 and 20.8 p.p.m. pair of signals in (1) is 228 K at 22.5 MHz, giving $\Delta G^\ddagger$ 11.2 kcal mol^{-1}. This is much lower than for difluoro[4.4.4]propellane (15.7 kcal mol^{-1}),[12] for the 1-azoniatricyclo[4.4.4.0]-tetradecane ion (17.2 kcal mol^{-1}),[3] and for the 1,6-diazoniatricyclo[4.4.4.0]tetradecane dication (17.4 kcal mol^{-1}),[5] but the difference is reasonable in view of the reduced barrier in cyclohexanone compared with cyclohexane[13] and the expected stepwise inversion in these propellanes.[12,14] We find that *cis*-decalin-1,5-dione, *cis*-(2), still shows a fast exchange (five line) ^{13}C n.m.r. spectrum at −100 °C so that we have been unable to make direct comparison with the situation in (1).

As a first attempt to achieve Grob-type fragmentation of a [4.4.4]propellane to a bicyclo[4.4.4]tetradecane derivative, we sought to effect two-electron reduction of the dione (1), in the hope of obtaining bis-enolate (7) and/or (8). Bridgehead unsaturation is actually highly favourable in a strain-energy sense for bicyclo[4.4.4]tetradecane,[2,4,15] and dienes (9) ΔH_f 6.40, (10) ΔH_f 4.15, and (11) ΔH_f 8.22 kcal mol^{-1}, are hardly more strained than the isomeric *cis*-9,10-divinyldecalin, (12) ΔH_f 2.68, according to force-field (MM2) calculations.§ However, the dione (1) is the product of a reaction in Na–NH_3 and we checked that it survived these reduction conditions. Exceedingly powerful reducing conditions were therefore called for and, after some experimentation, it was found that (1) was reduced by sodium–potassium alloy in benzene in the presence of chlorotrimethylsilane to trap any RO^- species formed. Under these conditions one product was formed (t.l.c.) and isolated in 50% yield. This product showed eight ^{13}C n.m.r. lines but none in the regions expected for the unsaturated carbons of silyl enol ethers. We suspected that the product was (13), but since alternative structures such as that formed by formal 2 + 2 cycloaddition in dienolate (7) could not easily be eliminated by spectroscopic means, an *X*-ray diffraction study of the product was undertaken. This confirmed that the product was (13), 2,7-bis(trimethylsilyloxy)tetracyclo[4.4.4.0.0^{2,7}]tetradecane, formed formally

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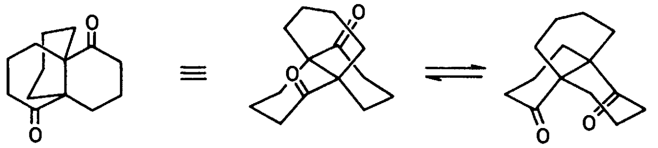
† Although the properties of this hydrocarbon have been discussed quite extensively,[1,2] the only known derivatives are the bridgehead aza- and diaza-derivatives prepared in our laboratories.[3–6]

‡ This functionalisation pattern is previously unreported.[7]

§ We thank C. St. J. Boothby for the calculations on these molecules.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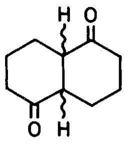
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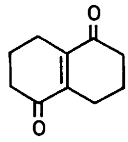
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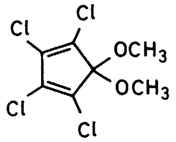
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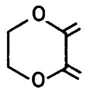
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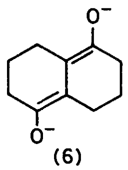
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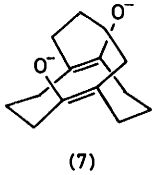
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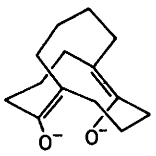
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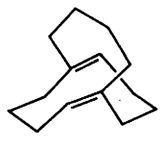
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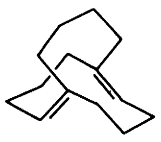
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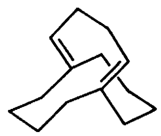
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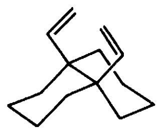
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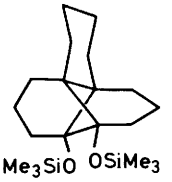

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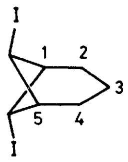

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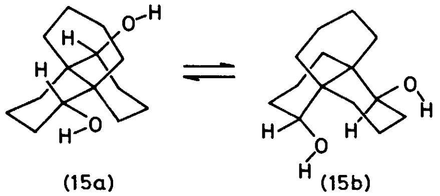
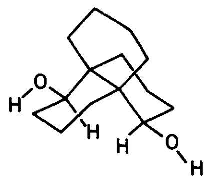

(15a) (15b)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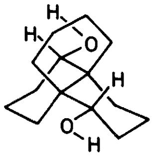
(17)

by pinacolic reduction of dione (1) in its conformation (1b). We are only aware of one previous example of pinacolic reduction of a 1,4-dione to give a cyclobutanediol. Reduction of hexane-2,5-dione with $TiCl_4$–Mg(Hg) in THF gave an 81% yield of 1,2-dimethylcyclobutane-1,2-diol.[16] The product was entirely the *cis*-isomer, whereas (13) is a *trans*-cyclobutane-1,2-diol.

The molecular structure of (13) is illustrated in the Figure and bond lengths and inter-bond angles are listed in Tables 1 and 2 for the non-hydrogen atoms. In the solid state the tetradecane skeleton of (13) conforms closely to (non-crystallographic) C_2 molecular symmetry [C_2 axis passing through the mid points of bonds C(1)–C(6), C(2)–C(7), and C(12)–C(13)]. The central cyclobutane ring is substantially puckered with internal C–C angles all equal within experimental error [average 86.4(2)°],* thereby producing intra-ring torsion angles of ±28.2(2)° and transannular C · · · C contacts of 2.122(5) Å. Such puckering although observed for the vast majority of cyclobutane derivatives is here accentuated by the strained C_3 chains linking C(1) to C(7) and C(2) to C(6); the six-membered rings formed by these linkages show half-chair conformations with C–C–C–C torsion angles at C(5)–C(4), C(4)–C(3), C(10)–C(9), and C(9)–C(8) averaging ±6.3(7)°.

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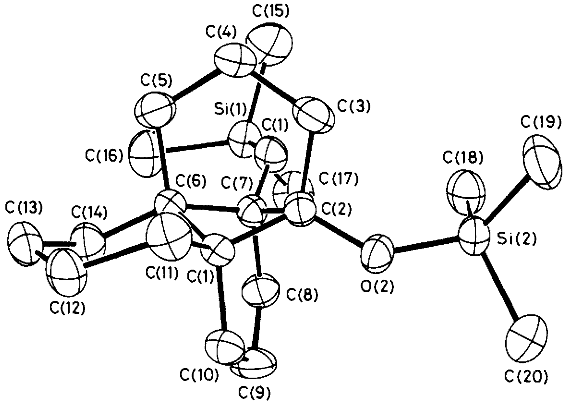
* Estimated standard deviations in parameters are given in parentheses here and throughout this paper.



Molecular structure of (13) showing the crystallographic labelling scheme. Methylene and methyl hydrogens have been omitted for clarity. Thermal ellipsoids are drawn to enclose 50% probability density

The last C_6 ring including the C(1)–C(6) bond adopts a less strained chair conformation with torsion angles in the range 38.5(3)—67.9(3)°. Bond lengths show less significant distortions with the endocyclic cyclobutane bond lengths being marginally longer than other C–C distances on average. The most marked bond angle distortions are those at C(1) and C(6) [C(2)–C(1)–C(11) 129.4(3)°, C(7)–C(6)–C(14) 130.7(3)°] where the equatorial sites on the cyclobutane ring are joined by the C_4 chain.

In relation to previously known simpler structures, the most unusual feature of the novel tetracyclo[4.4.4.0.$0^{2,7}$]tetradecane skeleton of (13) is the almost perfect flattening of the C(2)–C(3)–C(4)–C(5), and C(7)–C(8)–C(9)–C(10) bridges. Tricyclo[4.4.0.$0^{2,7}$]decane skeletons are present in a number of terpenes of the copaene and ylangene type, but apparently no structural data exist. In the simpler bicyclo[3.1.1]heptane series, well known in the pinanes, the parent hydrocarbon has a three-carbon bridge puckered by 37° according to electron diffraction results.[17] The *X*-ray structure of (14)[18] shows C(3) only 3° out of the C(1)–C(2)–C(4)–C(5) plane. It was suggested[18] that this flattening was due to the steric requirements of the iodine atoms which occupy the pseudo-axial sites on C(6) and C(7) of the bicyclo[3.1.1]heptane. Although the equivalent sites are occupied in (13) the steric bulk of the substituents at these positions (CH_2 and O) is considerably less than that of iodine atoms.

Reduction of dione (1) with excess of $LiAlH_4$ produces, in 95% yield, a mixture of the three possible diols (15)—(17). That the major product is the axial, equatorial isomer (15) is clear from the following evidence. The ambient-temperature ^{13}C n.m.r. spectrum shows a set of sharp lines for the conformationally homogeneous isomers (16) and (17) (11 of the possible 14 lines seen) and a set of broad lines which are resolved on cooling to −30 °C into two sets of sharp lines for (15a) and (15b) (27 of the possible 28 lines are resolved). Conformers (15a and b) are present in a 2 : 1 or 1 : 2 ratio; it is again not possible to assign the major isomer. From the intensities of the quaternary carbon and C–OH peaks, isomer (15) constitutes *ca.* 72% of the mixture, the minor isomers being present in *ca.* 18% and 10% amounts; again one cannot say which is (16) or (17). Formation of (15) as the major product is expected if hydride addition is from an equatorial direction, assuming conformational equilibrium in the intermediate hydroxy-ketones. Reduction of the dione (1) with Na–NH_3–THF–Bu^{t}OH gives a diol mixture which contains 50% of (15), 40% of the isomer present to the extent of 18% in the $LiAlH_4$ product and 10% of the remaining isomer.

Table 1. Bond lengths (Å)

Si(1)–O(1)	1.632(2)	Si(1)–C(15)	1.857(5)
Si(1)–C(16)	1.861(5)	Si(1)–C(17)	1.861(5)
Si(2)–O(2)	1.645(2)	Si(2)–C(18)	1.853(4)
Si(2)–C(19)	1.857(5)	Si(2)–C(20)	1.846(4)
O(1)–C(7)	1.400(4)	O(2)–C(2)	1.401(4)
C(1)–C(2)	1.548(4)	C(1)–C(6)	1.546(4)
C(1)–C(10)	1.546(5)	C(1)–C(11)	1.510(4)
C(2)–C(3)	1.545(5)	C(2)–C(7)	1.555(5)
C(3)–C(4)	1.491(5)	C(4)–C(5)	1.541(5)
C(5)–C(6)	1.559(5)	C(6)–C(7)	1.551(4)
C(6)–C(14)	1.503(5)	C(7)–C(8)	1.543(5)
C(8)–C(9)	1.500(5)	C(9)–C(10)	1.544(5)
C(11)–C(12)	1.557(5)	C(12)–C(13)	1.536(5)
C(13)–C(14)	1.552(5)		

Table 2. Bond angles (°)

O(1)–Si(1)–C(15)	103.5(2)	O(1)–Si(1)–C(16)	111.2(2)
O(1)–Si(1)–C(17)	112.0(2)	O(2)–Si(2)–C(18)	111.8(2)
O(2)–Si(2)–C(19)	111.5(2)	O(2)–Si(2)–C(20)	104.9(2)
Si(1)–O(1)–C(7)	135.0(2)	Si(2)–O(2)–C(2)	133.9(2)
C(2)–C(1)–C(6)	86.6(2)	C(2)–C(1)–C(10)	106.6(3)
C(6)–C(1)–C(10)	111.8(3)	C(2)–C(1)–C(11)	129.4(3)
C(6)–C(1)–C(11)	111.3(3)	C(10)–C(1)–C(11)	109.1(3)
O(2)–C(2)–C(1)	116.4(3)	O(2)–C(2)–C(3)	110.0(3)
C(1)–C(2)–C(3)	112.1(3)	O(2)–C(2)–C(7)	119.9(3)
C(1)–C(2)–C(7)	86.3(2)	C(3)–C(2)–C(7)	110.3(3)
C(2)–C(3)–C(4)	113.9(3)	C(3)–C(4)–C(5)	114.8(3)
C(4)–C(5)–C(6)	114.9(3)	C(1)–C(6)–C(5)	111.4(3)
C(1)–C(6)–C(7)	86.5(2)	C(5)–C(6)–C(7)	106.5(2)
C(1)–C(6)–C(14)	111.2(3)	C(5)–C(6)–C(14)	108.3(3)
C(7)–C(6)–C(14)	130.7(3)	O(1)–C(7)–C(2)	116.9(3)
O(1)–C(7)–C(6)	120.2(3)	C(2)–C(7)–C(6)	86.1(2)
O(1)–C(7)–C(8)	109.5(3)	C(2)–C(7)–C(8)	110.5(3)
C(6)–C(7)–C(8)	111.8(3)	C(7)–C(8)–C(9)	113.8(3)
C(8)–C(9)–C(10)	114.4(3)	C(1)–C(10)–C(9)	115.1(3)
C(1)–C(11)–C(12)	108.0(3)	C(11)–C(12)–C(13)	116.6(3)
C(12)–C(13)–C(14)	116.6(3)	C(6)–C(14)–C(13)	108.9(3)

Force-field (MM2) calculations on the diols produce regular conformations similar to those depicted with ΔH_f −124.2 and μ 1.94 for (15a), ΔH_f −124.6 and μ 2.19 for (15b) [*i.e.* (15b) is preferred], ΔH_f −127.2 and μ 2.86 for (16), and ΔH_f −127.4 kcal mol^{-1} and μ 0.27 D for (17). Despite the substantial dipole-moment differences (largely related to conformations about C–O bonds), we have so far been unsuccessful in attempts to separate these diols by chromatographic methods.

Experimental

Preparation of Tricyclo[4.4.4.0]*tetradecane*-2,7-*dione* (1).— To a stirred solution of sodium (2.5 g, 0.11 mol) in ammonia (10 ml, freshly distilled from sodium) under nitrogen at −78 °C, a solution of bicyclo[4.4.0]dec-1-ene-2,7-dione (3)[8] (8.2 g, 0.05 mol) in THF (10 ml) was added dropwise over 5 min. After 15 min 1,4-dibromobutane (16.2 g, 0.15 mol) was added dropwise. After 1 h at −78 °C the mixture was allowed to warm to room temperature. When all the ammonia had evaporated ethanol (5 ml) was added followed by water (15 ml). The mixture was extracted into ether, the extracts combined, dried ($MgSO_4$), and evaporated to yield a red gum (*ca.* 22 g). This was chromatographed on an alumina column eluting with light petroleum–ether (4 : 1 v/v). First fractions contained unreacted 1,4-dibromobutane (by i.r.) followed by propellane (3) (1.76 g, 16%), crystals (from methanol), m.p. 135—137 °C (Found: C, 76.1; H, 8.9. $C_{14}H_{20}O_2$ requires C, 76.33; H, 9.15%),

$\nu_{max.}$ 1 705 cm^{-1}, *m*/*z* 220(32%), 165(26), 152(16), 151(100), 149(18), 137(15), 110(11), 108(12), 93(14), and 79(14), δ_H(CDCl$_3$) 1.30 (m, 2 H), 1.60 (m, 6 H), 1.93 (m, 6 H), 2.33 (m, 2 H), and 2.48 (m, 4 H) (the spectrum is considerably modified at −50 °C, but not in a readily interpretable manner), δ_C(CD$_2$Cl$_2$; ambient temperature) 21.6, 22.3, 29.6, 30.9, 37.2 [C(3) and C(8)], 55.0 [C(1) and C(6)], and 213.0 p.p.m. (C=O). At −70 °C in CD$_2$Cl$_2$, the major isomer shows lines at δ_C 21.8, 22.9, 29.2, 31.9, 37.0, 54.7, and 213.9 and the minor isomer lines at 20.8, 21.4, 25.4, 32.5, 37.5, 55.1, and 215.2 p.p.m.

Huang-Minlon Reduction of Dione (1) *to* [4.4.4]*Propellane*.—A mixture of tricyclo[4.4.4.0]tetradecane-2,7-dione (100 mg), potassium hydroxide (0.8 g), hydrazine hydrate (1.0 ml), and diethylene glycol (5 ml) was refluxed for 3 h under nitrogen. Water (3 ml) was added and the mixture distilled until the temperature of the liquid rose to 225 °C. The distillate was extracted with light petroleum, the extracts dried and evaporated, and the crude product recrystallised from methanol to give tricyclo[4.4.4.0]tetradecane, [4.4.4]propellane, as a solid (43 mg, 50%), m.p. 111—114 °C, with spectroscopic properties in accord with those reported,[19] δ_C{CDCl$_3$ with added Cr[(CH$_3$CO)$_2$CH]$_3$} 21.8, 32.6, and 34.9 p.p.m. (quaternary carbons).

Reduction of Tricyclo[4.4.4.0]*tetradecane*-2,7-*dione with Sodium–Potassium Alloy*.—Dione (1) (200 mg) was placed in a two-necked round-bottomed flask and benzene (15 ml; distilled from LiAlH$_4$) and chlorotrimethylsilane (5 ml) distilled in under nitrogen. Then excess of sodium–potassium alloy was carefully pipetted into the rapidly stirred solution. After stirring for 3 h at room temperature, the reaction mixture was refluxed for 2 h. After cooling, the solution was filtered (under nitrogen) through a sintered glass frit and the solvent stripped from the filtrate. The crude product was chromatographed on alumina in hexane. The first fraction produced a solid which was sublimed (100 °C at 0.5 mmHg) to give 2,7-bis(trimethylsilyloxy)tetracyclo[4.4.4.0.0^{2,7}]tetradecane (13) (170 mg, 52%), m.p. 91—92 °C (Found: C, 65.4; H, 10.7. C$_{20}$H$_{38}$O$_2$Si$_2$ requires C, 65.55; H, 10.45%), $\nu_{max.}$ (CDCl$_3$) 1 270, 1 150, 1 080, and 860 cm^{-1}, *m*/*z* 367(14%), 366(43, molecular ion), 277(17), 276(40), 224(30), 223(56), 221(24), 147(14), 75(16), and 73(100), δ_H(CDCl$_3$) 0.1 (s, 18 H) and 1.2—2.1 (m, 20 H), δ_C(CDCl$_3$) 2.1, 15.2, 19.5, 24.2, 26.0, 28.8, 44.0, and 85.2 p.p.m.

Reduction of Tricyclo[4.4.4.0]*tetradecane*-2,7-*dione* (1) *with* LiAlH$_4$.—Lithium aluminium hydride (370 mg, 10 mmol) was added to a solution of dione (1) (220 mg, 1 mmol) in tetrahydrofuran (5 ml) and the solution stirred overnight at room temperature, carefully acidified with dilute hydrochloric acid and extracted with ether. From the extracts a gum was obtained, which solidified on standing. Recrystallisation from methanol gave a mixture of the stereoisomers of tricyclo-[4.4.4.0]tetradecane-2,7-diol (15)—(17) (210 mg, 95%), m.p. 135—185 °C (Found: C, 73.9; H, 11.0. Calc. for C$_{14}$H$_{24}$O$_2$: C, 74.7; H, 10.95%), $\nu_{max.}$ (Nujol) 3 600 (free OH) and 3 350 (broad) (bonded OH), δ_H(CDCl$_3$) 1.0—2.2 (m, 22 H, CH$_2$ and OH) and 3.4—4.4 (m, 2 H, C*H*OH), δ_C(CDCl$_3$; −30 °C) for major conformer of (15) 15.6, 20.6, 21.7, 22.8, 24.5, 25.5, 28.5, 30.1, 31.0, 32.5, 39.8 (double intensity, probably both bridgehead carbons), 69.4 (C–OH eq), and 79.4 p.p.m. (C–OH ax), for minor conformer of (15) 15.5, 19.4, 20.1, 23.9, 24.9, 27.1, 29.1, 30.5, 30.6, 32.7, 39.1, 39.4, 68.8 (C–OH eq), and 79.1 p.p.m. (C–OH ax), for the major of the two diequatorial diols, (16) or (17) 19.3, 20.7, 24.0, 25.2, 29.7, 41.1, and 68.4 p.p.m., for the minor diequatorial diol 19.5, 29.7, 40.8, and 68.5 p.p.m., the remaining lines for this isomer were hidden under other absorptions. The isomer and conformer ratios, given in the Discussion section, were determined from the intensities of both the C–OH and the quaternary carbon resonances and the results averaged. At +30 °C, the peaks due to the conformers of (15) were averaged to a set of broad peaks of which 11 (out of 14) could be clearly distinguished.

Table 3. Atomic co-ordinates (× 10^4) and isotropic thermal parameters (Å^2 × 10^3)

	x	*y*	*z*	*U*
Si(1)	1 928(1)	−1 133(2)	2 919(1)	52(1) *
Si(2)	4 710(1)	−1 342(1)	1 167(1)	48(1) *
O(1)	2 327(1)	−1 037(3)	2 140(1)	47(1) *
O(2)	3 850(1)	−104(3)	915(1)	46(1) *
C(1)	2 334(2)	1 236(4)	619(2)	35(1) *
C(2)	2 905(2)	−232(4)	965(2)	41(1) *
C(3)	2 579(2)	−2 046(4)	726(2)	54(1) *
C(4)	1 586(3)	−2 345(5)	806(2)	65(2) *
C(5)	1 044(2)	−729(4)	1 015(2)	54(1) *
C(6)	1 633(2)	905(4)	1 184(2)	36(1) *
C(7)	2 447(2)	283(4)	1 652(2)	39(1) *
C(8)	2 956(3)	1 815(4)	2 002(2)	53(1) *
C(9)	3 235(3)	3 196(5)	1 504(2)	65(2) *
C(10)	2 867(3)	2 937(4)	751(2)	54(1) *
C(11)	1 881(3)	1 305(5)	−95(2)	57(1) *
C(12)	1 145(3)	2 754(5)	−92(2)	55(1)*
C(13)	1 538(2)	2 819(5)	541(2)	55(1) *
C(14)	1 006(2)	2 428(5)	1 258(2)	54(1) *
C(15)	1 649(4)	−3 462(6)	3 027(3)	83(2) *
C(16)	898(3)	249(7)	2 992(2)	76(2) *
C(17)	2 791(3)	−476(7)	3 596(2)	82(2) *
C(18)	4 564(3)	−2 206(6)	2 055(2)	67(2) *
C(19)	4 871(3)	−3 170(6)	556(3)	77(2) *
C(20)	5 715(3)	89(6)	1 158(3)	77(2) *

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalised U_{ij} tensor.

Reduction of Tricyclo[4.4.4.0]*tetradecane*-2,7-*dione* (1) *with* Na–NH$_3$–Bu^{t}OH–THF.—Dione (1) (110 mg) in THF (3 ml) was added to a solution of sodium (50 mg, 2.3 equiv.) in liquid ammonia (15 ml) at −78 °C under nitrogen. After stirring for 15 min a few drops of Bu^{t}OH was added and stirring continued at −78 °C for 1 h before warming to room temperature. Conventional work-up produced a mixture of diols (15)—(17) (91 mg) which from ^{13}C n.m.r. peak intensities consisted of 50% (15), 40% of the isomer (16) or (17) which was 18% of the product from the LiAlH$_4$ reduction, and 10% of the remaining isomer.

Crystal Structure Determination.—Diffracted intensities were measured at 293 K from a crystal of approximate dimensions 0.3 × 0.25 × 0.2 mm using a Nicolet P3*m* diffractometer in the θ/2θ mode. Of 3 117 reflections measured in one quadrant of reciprocal space in the range $4° < 2\theta < 50°$, 2 153 unique data with $I > 2\sigma(I)$ were corrected for Lorentz and polarisation effects and used in solution and refinement of the structure. The intensities of two reflections remeasured after every 50 reflections showed a gradual fall to *ca*. 92% of their initial values during the course of data collection.

Crystal Data.—C$_{20}$H$_{38}$O$_2$Si$_2$, $M = 366.7$, monoclinic, $a = 14.707(7)$, $b = 7.718(2)$, $c = 19.258(9)$ Å, $\beta = 91.85(4)°$, $U = 2\,185$ Å^3, $Z = 4$, $D_c = 1.11$ g cm^{-3}, $F(000) = 808$, space group $P2_1/n$ (No. 14), Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 1.66 cm^{-1}.

Structure Solution and Refinement.—The silicon, oxygen, and cyclobutane ring carbon atoms were located by direct methods, and the remaining non-hydrogen atoms by electron-density-difference synthesis. The structure was refined by blocked-cascade least-squares, with hydrogen atoms in idealised tetrahedral geometries with C–H bond lengths fixed at 0.96 Å. Anisotropic thermal parameters for non-hydrogen atoms, and isotropic thermal parameters for methyl hydrogens, were refined. Remaining hydrogen atoms were assigned isotropic thermal parameters fixed at *ca.* 1.2 times the equivalent isotropic thermal parameter of the carbon to which they were attached. The final residual indices were R 0.048 and R_w 0.046 and final atomic parameters are given in Table 3 for the non-hydrogen atoms. Listings of full thermal parameters, hydrogen atom parameters, and observed and calculated structure factors are available in Supplementary Publication No. SUP 23699 (15 pp.).* All computations were performed using programs of the SHELXTL system on a Data General Eclipse minicomputer.

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* For details see Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 2*, 1983, Issue 1.

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