Adamantane Chemistry. Part II.† *X*-Ray Structure Analysis of 5-Chloromethyl-4-oxahomoadamantan-5-ol

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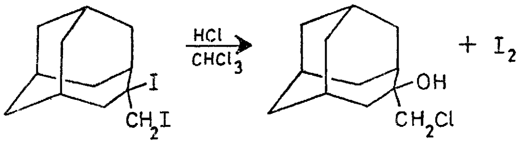
The crystal structure of the title compound was determined by *X*-ray diffraction from diffractometer data by direct methods. Crystals are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions: $a = 6{\cdot}464 \pm 0{\cdot}003$, $b = 12{\cdot}927 \pm 0{\cdot}005$, $c = 12{\cdot}537 \pm 0{\cdot}004$ Å, $\beta = 91{\cdot}56° \pm 0{\cdot}03°$; the structure was refined by block-diagonal least-squares to R 0·039 for 1435 independent reflections.

IN a previous paper[1] it was reported that reaction of 2-methyladamantan-2-ol with lead tetra-acetate and iodine yielded an abnormal product of a hypoiodite reaction, formally identified as 5-iodo-5-iodomethyl-4-oxahomoadamantane. The structural assignment rests appreciably on the chemical degradative evidence since unusual and incompletely explained features exist in the i.r. and n.m.r. spectra of this di-iodo-ether. Attempted *X*-ray structure analysis was abandoned when it was found that crystals were triclinic with $Z = 8$. The structural assignments also for many of the degradation products derived from the di-iodo-ether must be treated with some reservation, in the absence of unambiguous proof, because the spectroscopic evidence bears upon only parts of these molecules. The closest degradation product of the di-iodo-ether, and a key compound in the subsequent chemical degradative scheme, was therefore chosen for *X*-ray analysis; this was 5-chloromethyl-4-oxahomoadamantan-5-ol, produced from the di-iodo-ether by treatment with concentrated hydrochloric acid in chloroform solution [reaction (1)]. The mechanism of this interesting transformation, in which an oxidation has occurred without, apparently, there being present a suitable oxidising agent, will be discussed elsewhere.



(1)

EXPERIMENTAL

Transparent colourless prisms of racemic 5-chloromethyl-4-oxahomoadamantan-5-ol were obtained from light petroleum (b.p. 60—80°). Oscillation and Weissenberg photographs were taken about the *a* and *c* axes. *X*-Ray intensity data were collected for a crystal *ca.* 0·5 × 0·3 × 0·3 mm mounted about the *a* axis on a Hilger and Watts Y 290 automatic four-circle diffractometer by use of Mo-K_α radiation. A 2θ—ω scan up to the value θ 25° was employed. Background was measured at the ends of each scan and reflections with a net count $< 3\sigma$ were considered unobserved. A total of 1435 independent reflections were thus obtained and intensities were corrected for Lorentz polarisation factors.

Crystal Data.—$C_{11}H_{17}ClO_2$, $M = 216{\cdot}7$. Monoclinic, $a = 6{\cdot}464 \pm 0{\cdot}003$, $b = 12{\cdot}927 \pm 0{\cdot}005$, $c = 12{\cdot}537 \pm 0{\cdot}004$ Å, $\beta = 91{\cdot}56 \pm 0{\cdot}03°$,‡ $U = 1047$ Å^3, $D_m = 1{\cdot}36$, $Z = 4$, $D_c = 1{\cdot}374$ g cm^{-3}, $F(000) = 464$. Space group $P2_1/c$. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; $\mu(\text{Mo-}K_\alpha) = 3{\cdot}40$ cm^{-1}.

Structure Analysis.—Preliminary attempts to locate the chlorine atom co-ordinates from a Patterson synthesis by use of observed intensity data proved unsuccessful. Resort was made to analysis by direct methods. The multi-solution program MULTAN[2] yielded two results with high figures of merit, respectively 1·237 and 1·236. The first solution was used in the *E* map calculation, and fourteen of the fifteen strongest peaks enabled location of the non-hydrogen atoms in the asymmetric unit. The co-ordinates

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† Part I, R. M. Black and G. B. Gill, *J. Chem. Soc.* (*C*), 1970, 671.

‡ Error limits 3σ.

[1] R. M. Black and G. B. Gill, *Chem. Comm.*, 1971, 172.

[2] G. Germain, P. Main, and M. M. Wolfson, *Acta Cryst.*, 1971, **A27**, 368.

of the strongest peak in the E map proved to be those of the chlorine atom, and represented one of the solutions possible in the Patterson synthesis.

Initially four cycles of block-diagonal least-squares refinement of atomic positions and isotropic temperature factors were carried out with all data and unit weights. After the fourth cycle the value of the agreement factor R was 0·151 and in subsequent refinement the atomic temperature factors were allowed to vary anisotropically. Four further cycles, as before, reduced the value of R to 0·087. A Fourier difference synthesis revealed seventeen particularly intense peaks; the first sixteen corresponded to the co-ordinates calculated for all hydrogen atoms attached to carbon, the remaining one being assigned to the OH hydrogen atom. Four cycles of block-diagonal least-squares refinement of atomic positions (hydrogen atoms isotropic, others anisotropic) reached convergence at R 0·042. A weighting scheme was adopted of the form $w = (A/|F_o|)^2$ with $A = 35{\cdot}0$; unit weights were assigned to those reflections having $|F_o| \leqslant A$. Two final full-matrix refinements indicated convergence at R 0·039. The accuracy of the structure was confirmed by computing a final difference map which showed no peaks or depressions $> 0{\cdot}2$ eÅ^{-3} except in the direct neighbourhood of the chlorine atom where a depression of *ca.* 0·4 eÅ^{-3} remained.

Final positional and thermal parameters are listed in Table 1. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21147 (11 pp., 1 microfiche).*

TABLE 1

Atomic co-ordinates and thermal parameters (all × 10^4),* with standard deviations in parentheses

(*a*) Non-hydrogen atoms

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{33}
C(1)	9423(3)	4551(2)	1453(2)	367(12)	626(15)	331(11)	36(11)	80(9)	19(11)
C(2)	9957(4)	3818(2)	2380(2)	443(13)	560(14)	412(13)	134(11)	45(10)	25(11)
C(3)	8257(4)	3697(2)	3191(2)	525(14)	331(11)	344(11)	49(10)	38(10)	−1(9)
O(4)	8200(2)	4503(1)	3993(1)	540(9)	328(8)	297(7)	12(7)	−8(6)	41(6)
C(5)	8347(3)	5584(2)	3750(2)	364(11)	331(11)	336(11)	−29(9)	−11(9)	37(9)
C(6)	7702(3)	5897(2)	2606(2)	399(12)	359(11)	352(11)	8(10)	−45(9)	45(9)
C(7)	5610(3)	5461(2)	2212(2)	346(12)	570(14)	406(12)	57(11)	−42(9)	23(11)
C(8)	5682(4)	4355(2)	1790(2)	342(12)	579(15)	399(12)	−50(11)	−25(10)	−33(11)
C(9)	7332(4)	4254(2)	948(2)	523(14)	610(16)	327(11)	−16(12)	−6(10)	−24(11)
C(10)	9383(4)	5677(2)	1794(2)	400(12)	581(15)	309(11)	−97(11)	−19(9)	137(10)
C(11)	6136(4)	3558(2)	2660(2)	524(14)	483(14)	413(12)	−131(11)	51(11)	−5(11)
C(12)	6919(4)	6016(2)	4595(2)	505(14)	378(12)	386(12)	5(10)	27(10)	−8(10)
Cl(13)	7084(1)	7377(1)	4748(1)	1083(6)	383(3)	639(4)	61(4)	160(4)	−43(3)
O(14)	10386(2)	5923(1)	3922(1)	398(9)	560(10)	336(9)	−67(8)	−46(7)	54(8)

(*b*) Hydrogen atoms

	x/a	y/b	z/c	U		x/a	y/b	z/c	U
H(1)	10575(36)	4488(18)	941(18)	214(63)	H(10A)	10756(39)	5905(20)	2069(20)	314(71)
H(2A)	11186(36)	4022(18)	2774(18)	163(60)	H(10B)	9078(35)	6100(18)	1213(18)	189(62)
H(2B)	10233(36)	3148(19)	2091(18)	252(65)	H(11A)	6080(39)	2838(19)	2345(19)	282(68)
H(3)	8616(31)	3095(15)	3641(16)	50(50)	H(11B)	5072(38)	3558(19)	3193(19)	273(69)
H(6)	7567(32)	6636(18)	2674(17)	149(58)	H(12A)	7317(38)	5751(19)	5284(20)	283(69)
H(7A)	5136(36)	5890(19)	1659(19)	244(64)	H(12B)	5506(35)	5837(18)	4405(18)	166(59)
H(7B)	4502(39)	5528(19)	2754(20)	318(71)	H(14)	10696(39)	5838(19)	4516(21)	177(71)
H(8)	4316(42)	4197(19)	1464(20)	279(69)					
H(9A)	7398(38)	3545(20)	692(19)	315(70)					
H(9B)	7026(37)	4724(19)	366(19)	248(67)					

* In the form: $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$.

DISCUSSION

Bond lengths and angles of the framework atoms are listed in Table 2. The atom numbering system is based on the von Baeyer name of the title compound, namely 5-chloromethyl-4-oxatricyclo[4.3.1.1^{3,8}]undecan-5-ol, and is given in Figure 1. Hydrogen atoms (Table 1) are numbered according to the framework atoms to which they are attached.

The crystallographic results satisfy the immediate aims of this study, that is the validation of the structure of the chloro-alcohol. Two views of the molecule, which show the various important features in the molecular configuration, are given in Figure 1. The arrangement of the molecules in the unit cell is shown in Figure 2.

The torsion angles (Table 3) indicate that both the six- and seven-membered rings have adopted distorted chair-like geometries. For example, the torsion angles for the six-membered rings depart appreciably from the ideal ±60° angles for chair cyclohexane, and indeed from the ±54·4° angles computed for the minimum-energy chair conformation of cyclohexane, which takes account of bond-angle bending and non-bonded interactions.[3] The torsion angles for the seven-membered rings, although very much closer to those calculated for the twist-chair conformation of cycloheptane than for the chair conformation,[3] do not correlate well with the torsion angles found for the septanose sugars which

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* See Notice to Authors No. 7, in *J.C.S. Perkin II*, 1973, Index issue.

[3] J. B. Hendrickson, *J. Amer. Chem. Soc.*, 1967, **89**, 7036.

adopt the twist-chair conformation.[4] Like septanose sugars, the title compound is a seven-membered lactol, and these sugars are therefore more realistic models for comparison purposes. In the twist-chair cycloheptane–chloro-alcohol comparison, the ether oxygen atom O(4) was, among the four possibilities, correlated best with C(1) of cycloheptane, and this led to an apparently good comparison of torsion angles. In the septanose–chloro-alcohol correlation there is no choice but to relate the ether oxygen atoms of the two molecules and C(1) of the sugar with C(5) of the chloro-alcohol. The choice of a best fit no longer arose, and a complete lack of correlation of torsion angles was observed.

TABLE 2

(*a*) Interatomic distances (Å), and standard deviations

C(1)–C(2)	1·532(3)	C(1)–C(9)	1·526(3)
C(2)–C(3)	1·525(3)	C(1)–C(10)	1·518(3)
C(3)–O(4)	1·450(3)	C(3)–C(11)	1·518(3)
O(4)–C(5)	1·434(2)	C(5)–C(12)	1·529(3)
C(5)–C(6)	1·537(3)	C(5)–O(14)	1·400(3)
C(6)–C(7)	1·535(3)	C(6)–C(10)	1·535(3)
C(7)–C(8)	1·526(3)	C(8)–C(11)	1·523(3)
C(8)–C(9)	1·527(3)	C(12)–Cl(13)	1·774(2)

(*b*) Interatomic angles (deg.); standard deviations all 0·2°

C(2)–C(1)–C(9)	109·7	C(12)–C(5)–O(14)	111·3
C(2)–C(1)–C(10)	112·6	C(5)–C(6)–C(7)	114·7
C(9)–C(1)–C(10)	109·7	C(5)–C(6)–C(10)	113·0
C(1)–C(2)–C(3)	114·7	C(7)–C(6)–C(10)	110·6
C(2)–C(3)–O(4)	114·9	C(6)–C(7)–C(8)	114·9
C(2)–C(3)–C(11)	112·2	C(7)–C(8)–C(9)	110·4
O(4)–C(3)–C(11)	110·4	C(7)–C(8)–C(11)	113·1
C(3)–O(4)–C(5)	123·4	C(9)–C(8)–C(11)	108·2
O(4)–C(5)–C(6)	116·0	C(1)–C(9)–C(8)	108·6
O(4)–C(5)–C(12)	99·4	C(1)–C(10)–C(6)	112·5
O(4)–C(5)–O(14)	109·9	C(3)–C(11)–C(8)	112·9
C(6)–C(5)–C(12)	113·4	C(5)–C(12)–Cl(13)	113·7
C(6)–C(5)–O(14)	107·0		

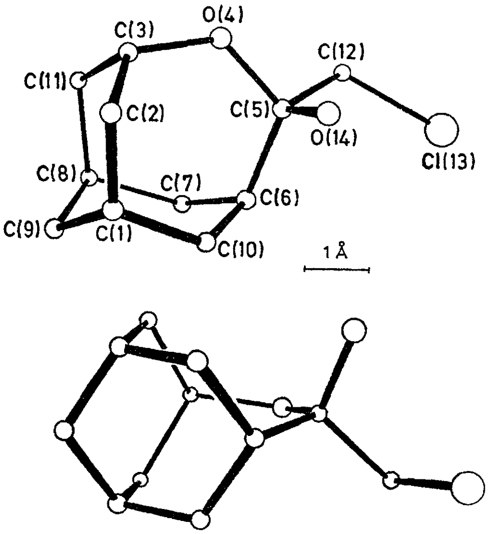

FIGURE 1 The atom numbering system and two views of the molecule

Since the alleviation of strain by the adoption of a twist-chair conformation of the seven-membered rings is prohibited by the cage-like nature of the molecule, the unusually large value of 123·4° for the ether oxygen bond angle, C(3)–O(4)–C(5), is perhaps not surprising. This bond angle is some 10° greater than the related angle in septanosides, and the other bond angle of the two-atom bridge, O(4)–C(5)–C(6), has likewise been somewhat enlarged.

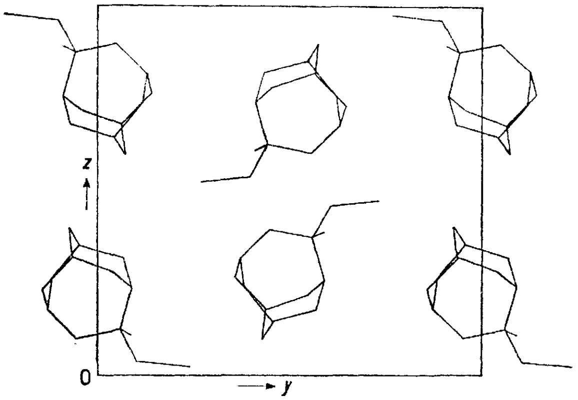

FIGURE 2 Projection along the *x* axis of the molecules in the unit cell

TABLE 3

Torsion angles (deg.), and standard deviations

(*a*) Seven-membered rings

C(1)–C(2)–C(3)–O(4)	−82·8(3)	O(4)–C(5)–C(6)–C(7)	49·1(2)
C(2)–C(3)–O(4)–C(5)	46·0(2)	C(5)–C(6)–C(7)–C(8)	−82·4(3)
C(3)–O(4)–C(5)–C(6)	23·8(2)	C(6)–C(7)–C(8)–C(11)	69·0(3)
O(4)–C(5)–C(6)–C(10)	−79·0(2)	C(7)–C(8)–C(11)–C(3)	−63·4(3)
C(5)–C(6)–C(10)–C(1)	80·1(2)	C(8)–C(11)–C(3)–O(4)	81·2(3)
C(6)–C(10)–C(1)–C(2)	−63·0(3)	C(11)–C(3)–O(4)–C(5)	−82·2(3)
C(10)–C(1)–C(2)–C(3)	71·3(2)		

(*b*) Six-membered rings

C(1)–C(9)–C(8)–C(11)	−65·2(2)	C(1)–C(10)–C(6)–C(7)	−50·0(3)
C(9)–C(8)–C(11)–C(3)	59·2(2)	C(10)–C(6)–C(7)–C(8)	46·9(2)
C(8)–C(11)–C(3)–C(2)	−48·5(2)	C(6)–C(7)–C(8)–C(9)	−52·4(2)
C(11)–C(3)–C(2)–C(1)	44·5(3)	C(7)–C(8)–C(9)–C(1)	59·1(2)
C(3)–C(2)–C(1)–C(9)	−51·1(3)	C(8)–C(9)–C(1)–C(10)	−63·2(3)
C(2)–C(1)–C(9)–C(8)	61·0(2)	C(9)–C(1)–C(10)–C(6)	59·5(2)

(*c*) Acyclic

Cl(13)–C(12)–C(5)–C(6)	−68·7(2)
Cl(13)–C(12)–C(5)–O(4)	167·6(2)
Cl(13)–C(12)–C(5)–O(14)	51·9(2)
O(14)–C(5)–O(4)–C(3)	−97·6(2)
O(14)–C(5)–C(6)–C(7)	172·0(2)
O(14)–C(5)–C(6)–C(10)	44·0(2)

The uneven distortion at the bridgehead angles also merits some comment: C(2)–C(3)–O(4) is appreciably larger than O(4)–C(3)–C(11) even though C(2) and C(11) are virtually equivalent atoms [they are equivalent in the absence of asymmetry at C(5)]. Inspection of the

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[4] J. F. McConnell and J. D. Stevens, *J.C.S. Perkin II*, 1974, 345.

data reveals several more cases of significant differences in the values of related bond angles.

The atoms C(9), C(3), O(4), C(5), and C(6) are relatively coplanar; their distances from the mean plane are respectively —0·003, 0·058, —0·111, 0·098, and 0·042 Å. Additionally, O(4) and C(5) are calculated to be —0·15 and 0·11 Å from the plane defined by C(9), C(3), and C(6).

Examination of the contact distances revealed the intramolecular separation of H(14) · · · O(4) to be 2·031(26) Å, but the hydrogen atom is not suitably oriented for bonding with the oxygen lone-pair orbitals. That an intermolecular hydrogen bond exists in the crystalline state is shown by the expectedly small [*i.e.* 2·440(25) Å] separation of H(14) and O(4) on adjacent molecules.

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