

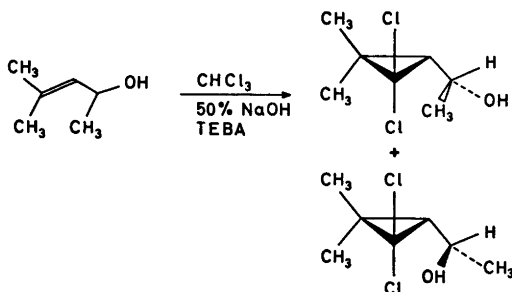
The Crystal Structure of 1-(2,2-Dichloro-3,3-dimethylcyclopropyl)ethanol

CHRISTIAN RØMMING and LEIV KR. SYDNES

Department of Chemistry, University of Oslo, Oslo 3, Norway

The crystal structure of one of the diastereomers of the title compound has been determined by X-ray methods using 1120 observed reflections. The crystals are trigonal, space group $R\bar{3}$ with hexagonal axes $a = 26.773(3)$ Å, $c = 7.093(1)$ Å, 18 molecules in the unit cell. The structure was solved by use of the program assembly MULTAN and refined by full-matrix least-squares methods to a conventional R -factor of 0.042. Estimated standard deviations are 0.003–0.006 Å in distances and 0.2–0.3° in angles not involving hydrogen atoms. The (corrected) bond lengths in the cyclopropane ring are found to be 1.515, 1.498, and 1.527 Å. The conformation of the molecule is discussed.

When 4-methyl-3-penten-2-ol (*1*) is reacted with dichlorocarbene under two-phase conditions 1-(2,2-dichloro-3,3-dimethylcyclopropyl)ethanol (*2*) is formed in high yield as a 90:10 mixture of diastereomers ¹ (Scheme 1). From a mechanistic point of view it was of interest to know the structure of the predominant diastereomer. It was also of interest to continue the study of the influence of the substituents on the bond lengths in the cyclopropane ring because substitution has turned out to cause changes in the geometry of the ring.^{2,3}



Scheme 1.

EXPERIMENTAL AND STRUCTURE DETERMINATION

The title compound was prepared as described in Ref. 1. After two recrystallizations of the mixture of diastereomers from pentane, the most abundant was isolated pure, m.p. 71–72°C. A crystal of approximate dimensions 0.25 × 0.25 × 0.65 mm³ was used for the X-ray experiments which had to be carried out with the specimen sealed in a capillary because of rapid sublimation.

Oscillation and Weissenberg photographs showed the crystals to be trigonal. Determination of unit cell dimensions and collection of intensity data were carried out on a SYNTEX PI four-circle diffractometer at 18°C, using graphite crystal monochromated MoK α radiation. In the least-squares refinement of the cell dimensions the coordinates of fifteen symmetry independent reflections were used. The $\theta/2\theta$ scanning mode was employed with a scan speed (2θ) of 4° min⁻¹; the scan range was from 1° below $2\theta(\alpha_1)$ to 1° above $2\theta(\alpha_2)$. Background was counted for 0.35 times the scan time at each of the scan range limits. After every 97 reflections three standard reflections were measured; they showed no systematic fluctuation. 2026 reflections with $2\theta < 50^\circ$ were measured; of these 1120 were found to have intensities larger than 2.5 times the estimated standard deviation and were regarded as observed. The remaining reflections were excluded from the refinement procedure. The standard deviations were taken as $\sigma(I) = (C_T + (0.03 C_N)^2)^{1/2}$ where C_T is the total number of counts and C_N is the net count. The data set was corrected for Lorenz and polarization effects; no absorption correction was carried out.

The atomic form factors used were those of Doyle and Turner⁴ for chlorine, oxygen, and carbon atoms and of Stewart, Davidson, and Simpson⁵ for hydrogen. The full-matrix least-squares program employed minimizes the quantity $\sum w \Delta F^2$ where w is the inverse of the variance of the observed structure factors.

Table 1. Fractional atomic coordinates and thermal parameters ($\times 10^4$) with estimated standard deviation for the heavy atoms. The temperature factor is given by $\exp -(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)$. For numbering of atoms, see Fig. 1.

Atom <i>x</i>	<i>y</i>	<i>z</i>	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	
C11	2276(1)	2507(1)	1864(2)	27(1)	30(1)	444(4)	22(1)	1(2)	-128(2)
C12	2569(1)	1610(1)	1808(2)	30(1)	34(1)	297(3)	32(1)	-43(2)	26(2)
O	1154(1)	766(2)	6(6)	17(1)	16(1)	386(9)	16(1)	17(4)	14(4)
C1	2321(1)	1991(1)	472(5)	18(1)	18(1)	224(9)	18(1)	-6(4)	-26(4)
C2	2495(1)	2120(1)	-1562(5)	18(1)	16(1)	236(10)	16(1)	6(5)	6(4)
C3	1880(2)	1686(1)	-1010(5)	17(1)	17(1)	245(9)	21(1)	-5(5)	1(5)
C4	2606(2)	2689(2)	-2381(8)	31(1)	20(1)	414(15)	17(2)	2(8)	53(7)
C5	2881(2)	1916(2)	-2392(7)	24(1)	29(1)	312(12)	26(2)	54(7)	-6(7)
C6	1594(2)	1052(2)	-1361(5)	20(1)	17(1)	252(11)	21(2)	1(5)	-8(5)
C7	1356(3)	904(3)	-3316(8)	47(2)	34(1)	315(14)	28(3)	-61(8)	-79(8)

Positions of the heavy atoms were determined using the program assembly MULTAN⁶ and refined by full-matrix least-squares methods.⁷ For the hydrogen atoms not involved in hydrogen bonding the positions were postulated from stereochemical consideration. Preliminary results showed that the distances from the oxygen atom to the oxygen atoms in two neighbouring molecules correspond to that of a hydrogen bond. Hydrogen atoms were therefore postulated to be situated in the direction of both of these and the population factor was refined for both. The resulting population factors were insignificantly different from 0.5 and we conclude that the structure is disordered with respect to these hydrogen atoms.

Final refinements including all positional parameters, anisotropic thermal parameters

for the heavy atoms, one common isotropic thermal parameter for the methyl hydrogen atoms and one for the others yielded a conventional *R*-factor of 0.042, $R_w = 0.040$, and goodness of fit $S = (\sum w\Delta F^2/n - m)^{1/2} = 1.43$. The corresponding atomic parameters are listed in Tables 1 and 2; interatomic distances and selected bond angles and dihedral angles are listed in Table 3; the numbering of the atoms is shown in Fig. 1. Upon request the structure factor list may be obtained from the authors.

The thermal parameters were analysed in terms of rigid-body motion of the molecule. When the oxygen and C7 atoms were excluded from the analysis, the r.m.s. ΔU decreased from 4.9×10^{-3} to 2.1×10^{-3} Å². It is therefore obvious that these atoms do not belong to the rigid body; consequently a system consisting of the cyclopropyl group and the atoms directly bonded to it served as the basis for correction of the corresponding bond lengths for libration. The C6-C7 and C6-O bonds were corrected for riding motion. The corrected bond lengths as well as selected bond angles are given in Fig. 1.

Table 2. Fractional atomic coordinates ($\times 10^3$) and isotropic thermal parameters with estimated standard deviations for hydrogen atoms.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H3	163(1)	181(1)	-118(4)	2.9(4)
H41	233(2)	281(2)	-168(6)	9.2(4)
H42	254(2)	265(2)	-371(6)	9.2
H43	297(2)	297(2)	-209(6)	9.2
H51	281(2)	155(2)	-177(6)	9.2
H52	327(2)	217(2)	-208(6)	9.2
H53	284(2)	189(2)	-377(6)	9.2
H6	188(1)	93(1)	-119(4)	2.9
H71	118(2)	51(2)	-344(7)	9.2
H72	168(2)	103(2)	-420(6)	9.2
H73	107(2)	103(2)	-349(7)	9.2
HO1	100(3)	41(5)	15(7)	2.9
HO2	93(5)	88(5)	13(14)	2.9

CRYSTAL DATA

1-(2,2-Dichloro-3,3-dimethylcyclopropyl)ethanol C₇H₁₄Cl₂O, trigonal, space group $R\bar{3}$ (No. 148). Axes (hexagonal): $a = 26.773(3)$ Å; $c = 7.093(1)$ Å. $V = 4404.3$ Å³ ($t = 18$ °C); $M = 183.08$; $Z = 18$; $D_{\text{calc}} = 1.24$ g cm⁻³; $\mu(\text{MoK}\alpha) = 6.4$ cm⁻¹.

DISCUSSION

The Newman projection along the C3-C6 bond (see Fig. 2) shows that the cyclopropane alcohol exists in a staggered conformation with the hydroxyl group and the dichloro-substituted

Table 3. Inter-atomic distances, selected bond angles, and dihedral angles. For numbering of atoms, see Fig. 1.

Bond distances (Å)			
C11—C1	1.750(3)	C6—O	1.420(5)
C12—C1	1.747(4)	C6—C7	1.495(6)
C1—C2	1.502(5)	C3—H3	0.91
C1—C3	1.484(5)	C4—H41	1.06
C2—C3	1.517(5)	C4—H42	0.95
C2—C4	1.516(6)	C4—H43	0.92
C2—C5	1.508(5)	C5—H51	1.01
C3—C6	1.493(5)	C5—H52	0.94
		C5—H53	0.98
		C6—H6	0.99
		C7—H71	0.93
		C7—H72	0.98
		C7—H73	0.98
		O—HO1	0.83
		O—HO2	0.80

Bond angles (°)			
C11—C1—C12	110.5(2)	C4—C2—C1	118.8(4)
C11—C1—C2	119.8(3)	C4—C2—C3	117.4(3)
C11—C1—C3	119.0(3)	C5—C2—C1	118.8(3)
C12—C1—C3	119.5(2)	C5—C2—C3	120.0(3)
C12—C1—C2	119.4(3)	C3—C6—O	108.3(4)
C2—C1—C3	61.1(2)	C7—C6—O	111.1(4)
C1—C2—C3	58.9(2)	C7—C6—C3	111.4(4)
C2—C3—C1	60.0(2)	C6—C3—C2	124.8(3)
C4—C2—C5	113.0(4)	C6—C3—C1	124.0(3)

Dihedral angles (°) (positive for a right-hand screw)	
C1—C3—C6—O	79.5(4)
C1—C3—C6—C7	-158.1(4)
C1—C3—C6—H6	-38.0(1.7)
C2—C3—C6—O	154.1(3)
C2—C3—C6—C7	-83.4(5)
C2—C3—C6—H6	36.7(1.7)

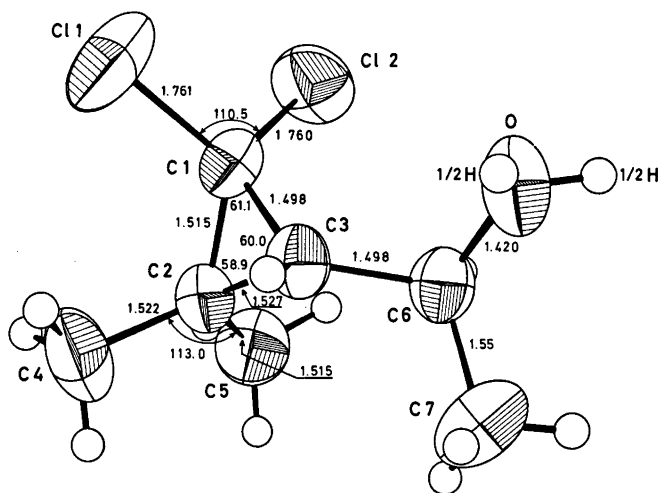


Fig. 1. Structure of the molecule with the numbering of the atoms, corrected bond lengths (Å), and selected angles (°). Non-hydrogen atoms are presented by thermal ellipsoids defined by the principal axes of thermal vibration and scaled to include 50 % probability.

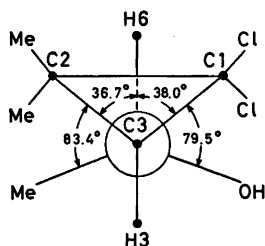


Fig. 2. Newman projection of the molecule viewed along the C3–C6 bond.

carbon atom adjacent to each other ($\angle \text{C1} - \text{C3} - \text{C6} - \text{O} = 79.5^\circ$). The consequences for the understanding of the mechanism of addition of dihalocarbenes to allylic alcohols under two-phase conditions will be discussed elsewhere.¹

The $\text{C}_{\text{methyl}} - \text{C}_{\text{ring}}$ distance (mean value 1.519 Å) as well as the C3–C6 bond length (1.498 Å) correspond approximately to the sum of single bond radii for sp^2 and sp^3 hybridized carbon atoms (1.505 Å). The Cl– C_{ring} bond length (mean value 1.761 Å) is found to be the same as in 2,2,2',2'-tetrachloro-3,3,3',3'-tetramethylbicyclopropyl (3) (1.763 Å)³ and, within the accuracy of the determinations, as in 1,1-dichloro-2,2-diphenylcyclopropane (4) (1.754 Å)² whereas it is slightly longer than the Cl–C bond in 1,1-dichlorocyclopropane (5) (1.734 Å).⁸ The $\text{C}_{\text{methyl}} - \text{C}_{\text{ring}} - \text{C}_{\text{methyl}}$ and Cl–C–Cl angles are 113.0(4) and 110.5(2)°, respectively, and these values are as found for tetra-

chloride 3 (113.1(2) and 110.2(1)°, respectively);³ the corresponding angles in dichloride 4 are 113.9 and 110.9°, respectively.²

A comparison of bond lengths observed in substituted cyclopropanes is given in Ref. 2. The ring bond lengths are obviously influenced by the type of substituents, the observations ranging from 1.44 to 1.56 Å. According to Ibers the main reason for this variation is a difference between substituents which can interact through a π -orbital system, *e.g.* phenyl, and substituents which can only interact through σ orbitals, *e.g.* halogens and which will affect all bond lengths equally. In 1-(2,2-dichloro-3,3-dimethylcyclopropyl)ethanol the cyclopropane ring has substituents of the latter type and consequently the ring should be an equilateral triangle. This, however, is not the case; the bond lengths and the angles of the ring are similar to those found for 1,1-dichloro-2,2-diphenylcyclopropane² and nearly the same as those found for 2,2,2',2'-tetrachloro-3,3,3',3'-tetramethylbicyclopropyl³ (Table 4). However, a discussion of this finding must await further investigations of similar compounds.

Correction for riding motion did not change the C6–O bond, which is of normal length. However, the C6–C7 bond distance increased from 1.495 to 1.551 Å; this indicates that this bond may in fact be of normal length.

Each molecule is hydrogen bonded to two neighbouring molecules; the length of the hydrogen bonds is 2.72 Å. Other intermolecular

Table 4. A comparison of bond lengths (Å) and angles (°) within substituted cyclopropane rings.

Compound	$\text{R}_2\text{C} - \text{CCl}_2$	$\text{Cl}_2\text{C} - \text{CHR}'$	$\text{R}_2\text{C} - \text{CHR}'$	Internal angles		Ref.
				$\text{C}(\text{Cl}_2)$	$\text{C}(\text{R}_2)$	
1-(2,2-Dichloro-3,3-dimethylcyclopropyl)-ethanol (2) ^a	1.515	1.498	1.527	61.1	58.9	This work
1,1-Dichloro-2,2-diphenylcyclopropane (4) ^b	1.520	1.490	1.529	61.1	58.5	2
2,2,2',2'-Tetrachloro-3,3,3',3'-tetramethylbicyclopropyl (3) ^a	1.512	1.507	1.541	61.4	59.2	3

^a R=Me. ^b R=Ph.

separations are as normal for van der Waals contact.

REFERENCES

1. Kleveland, K., Skattebøl, L. and Sydnes, L. K. *To be published*.
2. Lauher, J. W. and Ibers, J. A. *J. Am. Chem. Soc.* **97** (1975) 561.
3. Rømming, C. and Sydnes, L. K. *Acta Chem. Scand. B* **30** (1976) 963.
4. Doyle, P. A. and Turner, P. S. *Acta Crystallogr. A* **24** (1968) 390.
5. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* **42** (1965) 3175.
6. Germain, G., Main, P. and Woolfson, M. M. *Acta Crystallogr. A* **27** (1971) 368.
7. Groth, P. *Acta Chem. Scand.* **27** (1973) 1837.
8. Flygare, W. H., Narath, A. and Gwinn, W. D. *J. Chem. Phys.* **36** (1962) 200.

Received August 31, 1976.