X-ray Structure of *trans*-4-Chloro-5-methoxymethyl-3,3-dimethyl-1,2-diphenyl-cyclopent-1-ene*

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Abstract. $C_{21}H_{23}ClO$, $M_r = 326 \cdot 8$, monoclinic, $P2_1/a$, $a = 12 \cdot 236$ (17), $b = 16 \cdot 590$ (18), $c = 9 \cdot 376$ (14) Å, $\beta = 99 \cdot 64$ (2)°, $V = 1876$ Å^3, $Z = 4$, $D_x = 1 \cdot 16$ g cm^{-3}, λ(Cu $K\alpha$) $= 1 \cdot 5418$ Å, $\mu = 17 \cdot 1$ cm^{-1}, $F(000) = 696$. $T = 293$ K. Final $R = 0 \cdot 061$ for 1467 observed reflections. This study confirms the *trans* stereochemistry of the 4-chloro and 5-methoxymethyl substituents, and shows that the Cl atom takes up a pseudoequatorial position in the cyclopentene ring. Bond lengths and angles are normal. The five-membered ring is in an envelope form.

Introduction. In a previous paper (Miller & Ullah, 1982), we described a ring-expansion route to cyclopentenes from cyclobutenes. One of the examples described was that of the tertiary chloride (1), which yielded two cyclopentenes when treated with a suspension of zinc chloride in dichloromethane. In such rearrangements it is important to know which bond migrates, since there is a precedent for both 1,2-alkyl shifts (Cargill, Jackson, Pect & Pond, 1974; Koptyug, Sheilder, Isnev, Vasil & Rezvukhin, 1971) and 1,2-vinyl shifts (Avram, Constantinescu, Dinulescu & Nenitzescu, 1969; Matsui, Thomas & White, 1981) in related systems, and to know the stereochemistry in the products.
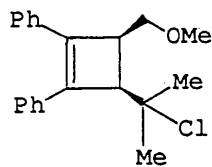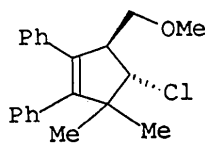
(1)   (2)

With (1), the regiochemistry of the rearrangement was readily established by proton NMR, but neither an analysis of vicinal coupling (Molander & Trost, 1981) nor of relative chemical shifts (Anteunis & Danneel,

1975; Hunter, Miller, Moore & Ullah, 1983) yielded reliable information about product stereochemistry. We report here an X-ray crystallography study of the major rearrangement product (2), and confirm that in (2) the Cl atom and the methoxymethyl group are *anti* to each other.

Experimental. Large yellow crystals were deposited from petroleum (b.p. 313–333 K)–methanol (1:1) and intensity data were collected photographically from a crystal of dimensions $0 \cdot 56 \times 0 \cdot 23 \times 0 \cdot 45$ mm mounted in turn on *b* and on *c*. Equi-inclination multifilm Weissenberg photographs of reciprocal-lattice layers $h\,0–3l$ and $0–6kl$ were scanned by use of a micro-densitometer (SERC service, Daresbury Laboratory). The merging R factor was $0 \cdot 072$ for 1467 independent data. Absorption corrections were not applied. The approximate position of the Cl atom was found from a Patterson synthesis and the structure was expanded by means of Fourier and difference-Fourier syntheses alternating with cycles of least-squares refinement. The H atoms, most of which were weakly apparent in difference syntheses, were included as 'riding' atoms in the last cycles of refinement. Block-diagonal-matrix refinement on F converged at R $0 \cdot 061$, R' $0 \cdot 061$, wR $0 \cdot 070$ with unit weights for all reflections and with anisotropic thermal parameters for all non-H atoms. The maximum excursions in the final difference map were $+0 \cdot 17$, $-0 \cdot 25$ e Å^{-3}. The *SHELX*76 program system (Sheldrick, 1976) was used in all calculations and was the source of the atomic scattering factors. Atomic parameters for the non-H atoms are given in Table 1.‡

Discussion. The crystal structure (Fig. 1) establishes that the Cl atom and the methoxymethyl group are *anti* to each other and, moreover, that the Cl is pseudoequatorial in the cyclopentene ring.

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* The crystallographic numbering scheme is different from that used to name the compound.

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‡ Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51607 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates* (× 10^4) *and equivalent isotropic thermal parameters* (× 10^3) *for non-H atoms with e.s.d.'s in parentheses*

	x	y	z	U_{eq}*(Å²)
Cl1	925 (2)	-247 (1)	2808 (2)	63 (1)
O1	2763 (3)	888 (3)	222 (4)	59 (1)
C1	1385 (4)	744 (3)	2412 (6)	38 (1)
C2	1048 (4)	1421 (3)	3357 (5)	36 (1)
C3	1043 (4)	2136 (3)	2352 (6)	31 (1)
C4	977 (4)	1899 (3)	980 (6)	36 (1)
C5	969 (4)	997 (3)	850 (5)	37 (1)
C6	1868 (5)	1482 (4)	4791 (6)	58 (2)
C7	-134 (5)	1324 (4)	3704 (7)	62 (2)
C8	1662 (5)	637 (4)	-218 (6)	49 (2)
C9	3473 (6)	619 (6)	-752 (8)	91 (3)
C10	992 (5)	2972 (3)	2847 (5)	37 (1)
C11	1908 (5)	3361 (4)	3638 (7)	51 (2)
C12	1843 (6)	4154 (4)	4059 (7)	61 (2)
C13	884 (6)	4587 (4)	3733 (7)	52 (2)
C14	-29 (6)	4206 (4)	2981 (7)	53 (2)
C15	10 (5)	3420 (4)	2531 (6)	45 (2)
C16	862 (5)	2411 (3)	-325 (6)	42 (2)
C17	1639 (7)	2987 (5)	-525 (9)	81 (3)
C18	1534 (9)	3434 (6)	-1746 (13)	111 (4)
C19	640 (11)	3321 (6)	-2826 (11)	106 (4)
C20	-147 (9)	2758 (6)	-2693 (8)	93 (3)
C21	-40 (6)	2295 (4)	-1429 (7)	67 (2)

* $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

Table 2. *Principal interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C1-Cl1	1.796 (6)	C11-C10	1.395 (8)
C8-O1	1.405 (7)	C15-C10	1.402 (8)
C9-O1	1.433 (9)	C12-C11	1.380 (10)
C2-C1	1.529 (8)	C13-C12	1.366 (10)
C5-C1	1.526 (7)	C14-C13	1.371 (9)
C3-C2	1.513 (8)	C15-C14	1.375 (9)
C6-C2	1.540 (7)	C17-C16	1.382 (10)
C7-C2	1.544 (8)	C21-C16	1.395 (8)
C4-C3	1.335 (8)	C18-C17	1.352 (14)
C10-C3	1.467 (8)	C19-C18	1.373 (15)
C5-C4	1.503 (8)	C20-C19	1.361 (16)
C16-C4	1.476 (8)	C21-C20	1.400 (11)
C8-C5	1.537 (8)		

C9-O1-C8	112.0 (5)	C5-C8-O1	107.4 (4)
C2-C1-C1	115.3 (4)	C11-C10-C3	122.2 (5)
C5-C1-Cl1	112.6 (4)	C15-C10-C3	121.0 (5)
C3-C2-C1	100.8 (4)	C15-C10-C11	116.8 (5)
C6-C2-C1	110.8 (4)	C12-C11-C10	121.0 (6)
C6-C2-C3	115.2 (5)	C13-C12-C11	121.7 (6)
C7-C2-C1	113.5 (5)	C14-C13-C12	118.0 (6)
C7-C2-C3	107.9 (4)	C15-C14-C13	121.8 (6)
C7-C2-C6	108.6 (5)	C14-C15-C10	120.7 (5)
C4-C3-C2	111.3 (5)	C17-C16-C4	122.5 (5)
C10-C3-C2	122.6 (5)	C21-C16-C4	119.3 (5)
C10-C3-C4	125.7 (5)	C21-C16-C17	118.1 (6)
C5-C4-C3	111.7 (5)	C18-C17-C16	121.6 (7)
C16-C4-C3	127.7 (5)	C19-C18-C17	120.1 (10)
C16-C4-C5	120.6 (5)	C20-C19-C18	121.0 (9)
C4-C5-C1	101.5 (4)	C21-C20-C19	119.1 (8)
C8-C5-C1	112.8 (4)	C20-C21-C16	120.2 (7)
C8-C5-C4	116.3 (5)		

Table 3. *Torsion angles* (°) *(e.s.d.'s 0.5–0.7°)*

C1-C2-C3-C4	19.3	C3-C4-C5-C8	-138.9
C2-C3-C4-C5	-2.1	C9-O1-C8-C5	-176.9
C3-C4-C5-C1	-16.1	Cl1-C1-C5-C8	-80.3
C2-C1-C5-C4	27.6	Cl1-C1-C2-C7	-38.7
C5-C1-C2-C3	-28.5	Cl1-C1-C2-C6	83.8
Cl1-C1-C2-C3	-153.8	Cl1-C1-C5-C4	154.5

All the bond angles and bond lengths, given in Table 2, show that all C—H, C—C, C=C, C—O and C—Cl bond lengths are normal. Torsional angles (Table 3) between planes C2–C1–C5–C4 = 27.6° and C5–C1–C2–C3 = 28.5°, showing that the cyclopentene ring is considerably puckered, with C(1) out of plane. These angles are higher than that reported for 1,2-diphenylcyclopentene (17.2°) (Bernstein, 1975) but are
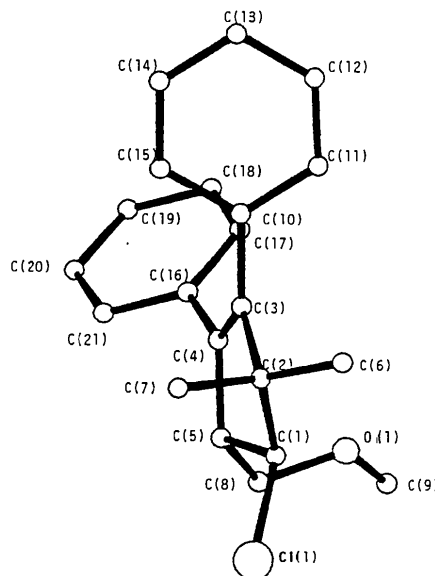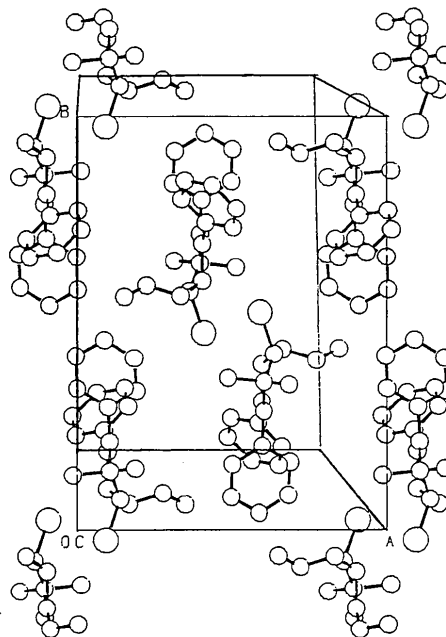

Fig. 1. Perspective view of the molecule.

Fig. 2. Molecular packing in the unit cell of the molecule viewed down the *c* axis.

Table 4. *Distances of atoms from mean planes* (Å)
(*e.s.d.'s* 0·0006–0·0011 Å)

The planes are defined by the starred atoms.

Plane (1)	C1	C2*	C3*	C4*	C5*	C10	C16
	0·455	−0·006	0·011	−0·011	0·006	−0·086	−0·110
Plane (2)	C3	C10*	C11*	C12*	C13*	C14*	C15*
	−0·034	−0·006	0·006	0	−0·006	0·007	−0·001
Plane (3)	C4	C16*	C17*	C18*	C19*	C20*	C21*
	−0·036	0·003	−0·003	0	0·003	−0·003	0

Dihedral angles (°) between normals to planes (e.s.d.'s 0·5–0·7°)

Plane (1)/plane (2)	107·6
Plane (1)/plane (3)	123·2
Plane (2)/plane (3)	66·6

consistent with that determined by electron diffraction in cyclopentene [29·0 ± 2·5°] (Davis & Muecke, 1970).

The dihedral angles between the normals to the planes, listed in Table 4, show that both phenyl rings are out of the plane of the C=C bond. Fig. 1 shows the molecule and gives the atomic numbering scheme. Fig. 2 shows the molecular packing.

References

ANTEUNIS, M. & DANNEEL, D. (1975). *Org. Magn. Reson.* **7**, 345–348.

AVRAM, M., CONSTANTINESCU, D., DINULESCU, G. & NENITZESCU, C. D. (1969). *Tetrahedron Lett.* **59**, 5215–5218.

BERNSTEIN, J. (1975). *Acta Cryst.* B**31**, 418–422.

CARGILL, R. L., JACKSON, T. E., PECT. N. P. & POND, D. M. (1974). *Acc. Chem. Res.* pp. 106–113.

DAVIS, M. I. & MUECKE, T. W. (1970). *J. Phys. Chem.* **74**, 1104–1108.

HUNTER, G., MILLER, J. A., MOORE, M. & ULLAH, G. M. (1983). *Org. Magn. Reson.* **21**, 275–278.

KOPTYUG, V. A., SHEILDER, I. A., ISNEV, I. S., VASIL, L. V. & REZVUKHIN, A. I. (1971). *Zh. Org. Khim.* **6**, 1089–1096.

MATSUI, T., THOMAS, J. A. & WHITE, J. D. (1981). *J. Org. Chem.* **46**, 3376–3378.

MILLER, J. A. & ULLAH, G. M. (1982). *J. Chem. Soc. Chem. Commun.* pp. 874–875.

MOLANDER, G. A. & TROST, B. M. (1981). *J. Am. Chem. Soc.* **103**, 5969–5972.

SHELDRICK, G. M. (1976). *SHELX76.* Program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1989). C**45**, 780–782

Structure of 2-Imidazolidinone Hemihydrate

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Abstract. $C_3H_6N_2O.\frac{1}{2}H_2O$, $M_r = 95\cdot103$, tetragonal, $P\bar{4}2_1c$ (No. 114), $a = 9\cdot686$ (3), $c = 10\cdot034$ (3) Å, $V = 941\cdot4$ Å^3, $Z = 8$, $D_x = 1\cdot342$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0\cdot71069$ Å, $\mu = 0\cdot100$ mm^{-1}, $F(000) = 408$, room temperature, $R = 0\cdot049$, $wR = 0\cdot053$ for 419 observed reflections $[F_o \geq 3\sigma(F_o)]$. The 2-imidazolidinone (ethyleneurea) molecules are located on general positions with the water molecules situated on twofold axes along **c** at $(0,\frac{1}{2},z)$. The five-membered imidazolidine ring assumes an envelope conformation. The structure is characterized by extensive hydrogen bonding. Each $C_3H_6N_2O$ molecule is hydrogen bonded to two adjacent molecules and this arrangement leads to the formation of tetramers. Each water of crystallization is hydrogen bonded to four ethyleneurea molecules each belonging to a different tetramer.

Introduction. The crystal structures of several ethyleneurea complexes with cadmium, mercury and copper have been described (Brown, Pierce & Trefonas, 1972; Majeste & Trefonas, 1972, 1974). A careful search of the Cambridge Structural Database revealed that the structure of the uncomplexed ethyleneurea molecule was not known. We now report the structure of ethyleneurea hemihydrate.

Experimental. Crystals in the form of transparent spheres, ~0·3 mm in diameter. Intensity data collected on a Philips PW 1100 four-circle diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, $\omega/2\theta$ scan mode, scan speed 2°ωmin^{-1}, scan width 1·20°ω, $5 \leq 2\theta \leq 50°$, 994 unique reflections (h 0→11, k 0→11, l 0→11) of which 424 with $F_o \geq 3\sigma(F_o)$. Cell parameters by least squares from 25 reflections with $5\cdot8 \leq 2\theta \leq 25\cdot3°$. No significant intensity variation for 3 standards (002, 112, 040) measured every 2 h. Corrections for Lorentz and polarization applied. Structure solved by *SHELXS*86 (Sheldrick, 1986) and refinement performed using the *SHELX*77 system of programs (Sheldrick, 1977). Full-matrix least squares, 87 parameters refined (scale factor, atomic coordinates, anisotropic temperature factors for non-hydrogen atoms and isotropic temperature factors for hydrogens). Function minimized $\sum w(|F_o| - |F_c|)^2$.