Crystal Structure of *syn*-8,8-Dichloro-4-phenyl-3,5-dioxabicyclo[5,1,0]-octane

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The crystal and molecular structure of the title compound has been determined from three-dimensional *X*-ray diffraction data. Crystals are monoclinic, space group $P2_1/c$, with Z = 8 in a unit cell of dimensions a = 21·231(6), b = 6·047(2), c = 19·408(5) Å, and β = 106·90(2)°. The structure was solved by direct methods and refined by least-squares techniques to R 0·089 for 1672 observed reflections obtained by diffractometer. The two molecules in the asymmetric unit have nearly identical geometries, with the seven-membered ring in the chair conformation. The phenyl group is equatorial and the dichloromethylene group is oriented to give the *syn*-isomer. The addition of the dihalogenocarbene to the parent olefin appears to be sterically rather than electronically controlled. The distances and angles in the molecule are as expected.

THE steric factors which influence Simmons–Smith cyclopropanations of oxygen-containing olefins are reasonably well understood.[1] Unfortunately, similar generalizations for additions involving dihalogenocarbenes are not available and in no case has the geometry of the reaction product been studied by diffraction techniques. Therefore, when the addition of dichlorocarbene to 1,3-dioxa-2-phenyl-5-cycloheptene proceeded in a highly selective manner, the nature of the isomer could not be unequivocally established. Our study of 8,8-dichloro-4-phenyl-3,5-dioxabicyclo[5,1,0]octane has shown that the *syn*-isomer is formed and that the addition is determined by steric factors and not by the directing influence of the oxygen atoms.[2]

EXPERIMENTAL

Crystals from ethyl acetate were clear needles, and were shown by preliminary Weissenberg and precession photographs to be monoclinic.

Crystal Data.—$C_{12}H_{12}O_2Cl_2$, M = 259·1. Monoclinic, a = 21·231 ± 0·006, b = 6·047 ± 0·002, c = 19·408 ± 0·005 Å, β = 106·90 ± 0·02°, U = 2384·1 Å^3, D_m (by flotation) = 1·43 g cm^{-3}, Z = 8, D_c = 1·443, F(000) = 1072. Cu-K_α

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[1] C. D. Poulter, E. C. Friedrich, and S. Winstein, *J. Amer. Chem. Soc.*, 1969, **91**, 6892 and references therein.

[2] G. R. Clark, B. Fraser-Reid, and G. J. Palenik, *Chem. Comm.*, 1970, 1641.

radiation, $\lambda = 1{\cdot}5418$ Å; $\mu(\text{Cu-}K_\alpha) = 48{\cdot}8\ \text{cm}^{-1}$. Systematic absences, $h0l$ if $l = 2n + 1$ and $0k0$ if $k = 2n + 1$, indicate space group $P2_1/c$ (C_{2h}^5).

The crystal used for the intensity measurements had dimensions 0·21 × 0·15 × 0·10 mm. Intensity data were measured by use of the stationary-crystal–stationary-counter technique, with Cu-K_α radiation and a nickel foil (0·70 mil) at the counter window. 4 Standard reflections were measured after every 100 reflections to monitor the crystal alignment and stability in the X-ray beam. After *ca.* 4000 reflections had been measured within the limit $2\theta \lesssim 120°$, the intensities of these 4 had decreased by *ca.* 25%. The crystal alignment was unchanged, and the decrease in intensities was therefore attributed to crystal decomposition and the data collection was terminated. A background curve was determined by measurement of the background in areas of reciprocal space which were free from streaking or reflections. After correction for the background, the data was placed on a common scale by using the intensities of the standard reflections. A total of 3384 independent reflections had been measured of which the 1672 reflections $\geqslant 1{\cdot}2$ times the appropriate background were considered as observed. The remaining 1712 reflections were entered as 0·1 times the appropriate background count and were flagged with a minus sign. The reflections were then corrected for the $\alpha_1 - \alpha_2$ splitting and converted to a set of structure amplitudes on an arbitrary scale by multiplication by Lorentz-polarization corrections. No absorption correction was made since the variation of intensity as a function of ϕ (at $\chi = 90°$) was $< 15\%$.

TABLE 1

Final parameters ($\times 10^4$) for the non-hydrogen atoms. The temperature factor is in the form exp ($- \beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}hk - \beta_{13}hl - \beta_{23}kl$). For each atom the upper line gives the parameters for molecule A and the lower line for molecule B

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl(1)	4461(2)	5576(8)	4194(2)	28(1)	641(19)	22(1)	9(7)	−4(2)	−24(8)
	9532(2)	5778(8)	3669(2)	35(1)	592(18)	27(1)	17(8)	−5(2)	−4(8)
Cl(2)	4608(2)	7035(7)	2836(2)	25(1)	443(14)	36(1)	−60(6)	17(2)	−3(7)
	9551(2)	7313(6)	2272(2)	23(1)	255(11)	56(2)	−25(5)	10(2)	38(7)
O(1)	2466(3)	6213(14)	1907(4)	19(2)	268(28)	31(3)	28(12)	−2(4)	−45(16)
	7467(3)	6016(13)	1438(4)	25(2)	249(23)	31(3)	27(12)	10(4)	−48(14)
O(2)	2926(4)	2790(14)	1748(4)	22(2)	156(26)	34(3)	−2(13)	−1(4)	1(15)
	7979(4)	2710(13)	1278(4)	32(3)	155(24)	36(3)	20(13)	12(5)	−4(15)
C(1)	3359(5)	6042(22)	3011(6)	15(3)	358(46)	35(4)	−26(20)	7(6)	−46(26)
	8366(6)	5985(24)	2541(7)	21(3)	381(51)	35(4)	10(21)	−2(6)	−24(27)
C(2)	3033(6)	7374(21)	2351(7)	29(4)	240(40)	34(4)	−11(21)	−6(7)	−54(24)
	8001(6)	7306(22)	1880(7)	29(4)	217(40)	47(5)	−2(21)	−11(7)	−92(26)
C(3)	2628(5)	4756(18)	1410(6)	27(3)	172(35)	27(4)	8(19)	9(6)	−57(20)
	7656(5)	4604(20)	949(6)	22(3)	241(39)	30(4)	−8(18)	2(6)	−17(22)
C(4)	3618(5)	3078(21)	2154(6)	25(3)	285(43)	27(4)	15(20)	6(6)	−58(23)
	8661(5)	3120(21)	1673(6)	21(3)	280(43)	31(4)	−22(19)	−7(6)	62(23)
C(5)	3653(5)	3794(21)	2916(7)	22(3)	255(42)	35(4)	−18(19)	−10(6)	6(24)
	8704(5)	3842(21)	2434(6)	21(3)	286(43)	33(4)	18(19)	0(6)	2(24)
C(6)	4072(5)	5679(24)	3252(6)	19(3)	455(54)	25(4)	−39(22)	24(5)	37(26)
	9106(6)	5824(22)	2734(6)	26(4)	325(46)	27(4)	−1(22)	12(6)	47(24)
C(7)	1983(6)	4106(19)	864(5)	33(4)	207(36)	17(3)	−34(20)	14(6)	17(20)
	7024(6)	3939(21)	377(6)	24(3)	278(41)	30(4)	−21(20)	23(6)	31(23)
C(8)	1915(7)	2059(25)	531(6)	41(4)	434(55)	24(4)	−100(27)	35(7)	−29(25)
	6984(6)	1852(22)	57(6)	39(4)	345(50)	18(3)	−103(24)	21(6)	−26(22)
C(9)	1326(7)	1606(24)	−31(7)	50(5)	348(51)	30(5)	−128(28)	16(8)	−29(26)
	6434(7)	1337(23)	−509(6)	48(5)	344(50)	21(4)	−37(26)	20(7)	10(24)
C(10)	843(7)	3232(28)	−232(7)	39(5)	558(68)	27(4)	−74(29)	8(7)	57(29)
	5904(7)	2826(25)	−747(7)	39(4)	426(57)	31(5)	−133(28)	5(7)	−5(28)
C(11)	922(7)	5272(26)	88(7)	35(4)	430(59)	36(5)	−27(27)	16(7)	4(29)
	5950(7)	4886(27)	−425(7)	38(5)	498(6)	32(5)	−62(28)	19(7)	14(29)
C(12)	1506(6)	5744(24)	646(6)	24(3)	426(53)	24(4)	−4(23)	8(6)	22(26)
	6504(6)	5465(23)	154(6)	28(4)	366(49)	26(4)	3(22)	11(6)	28(25)

Structure Analysis.—The four chlorine atoms in the unit cell were located by comparing the Patterson function with E maps obtained by the symbolic-addition procedure. A Fourier synthesis was calculated with phases determined by the chlorine atoms and the remaining non-hydrogen atoms were easily located. Two full-matrix least-squares cycles were calculated by use of isotropic thermal parameters and with all non-chlorine atoms treated as carbon atoms. At this point the four atoms in positions expected to be ring oxygen atoms all had low thermal parameters. These atoms were then treated as oxygen atoms in subsequent calculations. Three additional least-squares cycles reduced R to 0·14. The quantity $\Sigma w(F_o - F_c)^2$ was minimized in all the least-squares calculations. The weighting scheme used was $\sqrt{w} = F_o/F_{\text{low}}$ if $F_o < F_{\text{low}}$, $\sqrt{w} = 1$ if $F_{\text{low}} \leqslant F_o \leqslant F_{\text{upper}}$, and $\sqrt{w} = F_{\text{upper}}/F_o$ if $F_o > F_{\text{upper}}$, where $F_{\text{low}} = 25{\cdot}0$ and $F_{\text{upper}} = 200{\cdot}0$. Scattering factors were from ref. 3.

A difference-Fourier synthesis verified the correctness of the basic structure and also indicated anisotropic motion for a number of the atoms. Refinement was continued with anisotropic thermal parameters and a block-diagonal approximation to the full matrix. After 12 cycles, no parameter shifted by $> 0{\cdot}1\sigma$ and R was 0·093. A difference-Fourier synthesis did not yield unambiguous positions for the hydrogen atoms, and their contributions were therefore not included in further calculations. The value of F_{low} was changed to 10·0 and F_{upper} to 40·0 and three additional least-squares cycles were computed. There were only a few parameters which shifted *ca.* 1σ and only three positional parameters shifted by 2 or more σ. The final R was 0·089 and the refinement was terminated. The final positional

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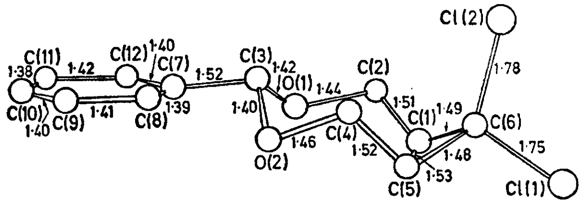
[3] H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 1964, **17**, 1040.

and thermal parameters for the non-hydrogen atoms are given in Table 1. Observed and calculated structure factors are listed in Supplementary Publication No SUP 20529 (4 pp., 1 microfiche).†

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The two crystallographically independent molecules in the asymmetric unit are related by a translation of *ca.* 0·5 in *x*. Consequently, the *hk*0 reflections were all unobservable in the preliminary photographic study, giving rise to an apparent systematic absence which does not correspond to a known space group. The two molecules have nearly identical geometries and the conformation is shown in the Figure, together with the mean bond distances and the atomic numbering. The individual bond distances are given in Table 2, with the individual bond angles given in Table 3.



The atomic numbering and mean bond distances. The molecule is shown in the correct conformation

TABLE 2

Bond lengths (Å) in the two molecules in the asymmetric unit *

	Molecule *A*	Molecule *B*
Cl(1)–C(6)	1·78	1·78
Cl(2)–C(6)	1·78	1·73
O(1)–C(2)	1·44	1·44
O(1)–C(3)	1·42	1·42
O(2)–C(3)	1·41	1·39
O(2)–C(4)	1·46	1·45
C(1)–C(2)	1·50	1·52
C(1)–C(5)	1·53	1·53
C(1)–C(6)	1·46	1·51
C(3)–C(7)	1·52	1·52
C(4)–C(5)	1·52	1·52
C(5)–C(6)	1·48	1·49
C(7)–C(8)	1·38	1·40
C(7)–C(12)	1·39	1·41
C(8)–C(9)	1·43	1·39
C(9)–C(10)	1·39	1·41
C(10)–C(11)	1·37	1·38
C(11)–C(12)	1·42	1·41

* Estimated standard deviations are 0·02 Å except for Cl(1)–C(6) and Cl(2)–C(6) which are 0·01 Å.

The seven-membered ring is in a chair conformation with the phenyl group in the equatorial position. The chair form was not unexpected since cycloheptene is also in this conformation.[4] The dichloromethylene group is directed to the upper side of the molecule giving the *syn*-epimer. The formation of the *syn*-isomer suggests that the lone-pair electrons on the oxygen atoms do not exert the same *cis*-directing influence on the approaching dihalogenocarbene as they do in normal Simmons–Smith cyclopropanations. In fact, the addition appears to have occurred by the least-sterically restricted path. Whether this is a common feature of dihalogenocarbene additions cannot be answered without further structural studies.

TABLE 3

Bond angles (deg.) in the two molecules in the asymmetric unit *

	Molecule *A*	Molecule *B*
C(2)–O(1)–C(3)	113	114
C(3)–O(2)–C(4)	113	113
C(2)–C(1)–C(5)	119	119
C(2)–C(1)–C(6)	122	119
C(5)–C(1)–C(6)	59	59
O(1)–C(2)–C(1)	110	110
O(1)–C(3)–O(2)	112	113
O(1)–C(3)–C(7)	107	107
O(2)–C(3)–C(7)	107	109
O(2)–C(4)–C(5)	108	109
C(1)–C(5)–C(4)	118	119
C(1)–C(5)–C(6)	58	60
C(4)–C(5)–C(6)	120	119
Cl(1)–C(6)–Cl(2)	108	110
Cl(1)–C(6)–C(1)	118	116
Cl(1)–C(6)–C(5)	118	117
Cl(2)–C(6)–C(1)	122	122
Cl(2)–C(6)–C(5)	123	124
C(1)–C(6)–C(5)	63	61
C(3)–C(7)–C(8)	121	119
C(3)–C(7)–C(12)	117	120
C(8)–C(7)–C(12)	122	121
C(7)–C(8)–C(9)	119	119
C(8)–C(9)–C(10)	119	122
C(9)–C(10)–C(11)	122	119
C(10)–C(11)–C(12)	120	121
C(7)–C(12)–C(11)	119	119

* Estimated standard deviations are 1°.

The mean C–Cl distances [1·77(1) Å] are not significantly different from the values [1·759(3) and 1·762(3) Å] found in a similar dichlorocarbene adduct.[5] Similarly, the bond lengths in the cyclopropane ring [1·53(2), 1·48(2), and 1·48(2) Å] are also identical with the more precise values of 1·520(4), 1·489(4), and 1·490(4) Å.[5] The dimensions in the cyclopropane ring differ from those found in dichlorocyclopropane (1·532 and 1·534 Å) by a microwave study[6] and in cyclopropanecarboxamide (1·507 and 1·481 Å).[7] Furthermore, the various studies differ in that the fused systems have the long distance opposite the substituted carbon atom although dichlorocyclopropane is essentially an equilateral triangle. In cyclopropanecarboxamide, the bond opposite the substituted carbon atom is the shortest. These results suggest that the dimensions in a cyclopropane ring are dependent upon both the nature of the substituents as well as whether or not the three-membered ring is part of a fused system. Unfortunately, the lack of precise data on cyclopropane rings precludes any definitive correlation.

The mean C–O bonds in the seven-membered ring are

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† For details of Supplementary Publications, see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. will be supplied as full size copies).

[4] N. L. Allinger and W. Szkrybalo, *J. Org. Chem.*, 1962, **27**, 722.

[5] J. A. Deyrup, M. Betkouski, W. Szabo, M. Mathew, and G. J. Palenik, *J. Amer. Chem. Soc.*, 1972, **94**, 2147.

[6] W. H. Flygare, A. Narath, and W. D. Gwinn, *J. Chem. Phys.*, 1962, **36**, 200.

[7] R. E. Long, H. Maddox, and K. N. Trueblood, *Acta Cryst.*, 1969, *B*, **25**, 2083.

1·43 Å although the C(3)–O bonds appear slightly shorter (mean 1·41 Å) compared with the C(1)–O and C(5)–O bond distances (mean 1·45 Å). While this difference is not significant, the difference could be rationalized on the basis of *s* character arguments.[8] Since C(3) is bonded to only one hydrogen atom and a phenyl group, compared with two hydrogen atoms and an sp^3 carbon atom for C(4), the *s* character in the C(4)–O bond is expected to be less than in the C(3)–O bonds. The mean C–O distance (1·43 Å) is in agreement with the usually accepted value for an O(ether)–C(Me) bond length. Similarly, the mean C–C distances and C–C–C angles in the phenyl ring show no unexpected deviations.

There appear to be no abnormal intermolecular interactions between molecules. The shortest intermolecular distance is 3·37 Å between Cl(1) at x, y, z, and Cl(1′) at $-x, -y, -z$. All other distances exceed 3·4 Å and are not considered to be significant.

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[8] H. A. Bent, *Chem. Rev.*, 1961, **61**, 275.