# Geometry of Dihalogenocarbene Additions to Heterocyclic Olefiins: an *X*-Ray Crystallographic Study

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*Summary* The crystal structure of the product of addition of dichlorocarbene to 2-phenyl-1,3-dioxacyclohept-5-ene shows that the *syn*-isomer is formed.

THE nature of stereoelectronic control in Simmons–Smith cyclopropanation of oxygen-containing olefins now seems reasonably well understood.[1] However, analogous additions of dihalogenocarbenes have received so little attention that no generalisations exist. Therefore, it was impossible to determine on theoretical grounds whether the single product obtained from the addition of dihalogenocarbene to 2-phenyl-1,3-dioxacyclohept-5-ene was the *syn*- or *anti*-isomer.[2] Routine techniques† could not establish the molecular geometry unequivocally, and hence an *X*-ray analysis was undertaken. Our study of the adduct 8,8-dichloro-4-phenyl-3,5-dioxabicyclo[5,1,0]octane is the first structural determination of an adduct of a dihalogenocarbene with an oxygen-containing olefin, and demonstrates that the dichlorocarbene addition does not follow the path expected by a consideration of the directive influence of the oxygen atoms.[1]

Colourless crystals, from ethyl acetate, were studied by *X*-ray diffraction using Cu-$K_\alpha$ radiation: $C_{12}H_{12}O_2Cl_2$, $M = 259{\cdot}1$; monoclinic, space group $P2_1/c$ (No. 14), $a = 21{\cdot}231(6)$, $b = 6{\cdot}047(2)$, $c = 19{\cdot}408(5)$ Å, $\beta = 106{\cdot}90(2)^\circ$, $U = 2384{\cdot}1$ Å$^3$, $D_m = 1{\cdot}43$ g/cm$^3$, $Z = 8$, $D_c = 1{\cdot}443$ g/cm$^3$.

The intensities of 3384 (1672 non-zero) independent reflections with $2\theta < 135^\circ$ were measured using a General Electric diffractometer. The four chlorine atoms were located in an *E*-map calculated with signs determined by the symbolic addition method. The light atoms were located in Fourier syntheses. The structure was refined by least-squares methods using anisotropic thermal parameters to an *R*, the usual residual, of 0·093. The hydrogen atoms have not been included in these calculations.

The two crystallographically independent molecules have nearly identical geometries. The chemically equivalent bond distances and angles are equal within their estimated standard deviations (typical deviations are $\pm 0{\cdot}016$ Å in bond lengths and $\pm 0{\cdot}9^\circ$ in bond angles). The molecular stereochemistry is shown in the Figure together with the atomic numbering and average bond distances. The dichloromethylene group is directed to the upper side of the molecule and thus establishes that the compound is the *syn*-epimer.

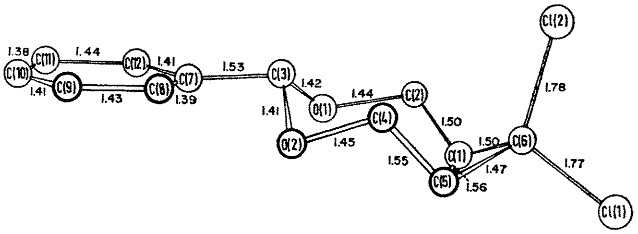

FIGURE. *Atomic numbering and average bond distances in* 8,8-*dichloro*-4-*phenyl*-3,5-*dioxabicyclo*[5,1,0]*octane. The average bond angles in the seven-membered heterocyclic ring system are* C(2)–O(1)–C(3) *of* 114°, C(3)–O(2)–C(4) *of* 113°, C(2)–C(1)–C(5) *of* 119°, C(1)–C(5)–C(4) *of* 117°, C(1)–C(2)–O(1) *of* 110°, C(5)–C(4)–O(2) of 108°, *and* O(1)–C(3)–O(2) *of* 120°.

The carbon–chlorine bonds average 1·771 Å, in excellent agreement with the average distance of 1·772 Å in methylene chloride.[3] Both C–Cl bond lengths are similar to the values found in monochloro-compounds such as methyl chloride (1·781 Å)[4] and 2-chloropropane (1·798 Å)[5] but are longer than the value in cyclopropyl chloride (1·740 Å).[6] The Cl–C–Cl angle averages 108·6° which is smaller than the angle of 111·8° found in methylene chloride.[3] The

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† The n.m.r. spectrum of the adduct shows an AA′,BB′,XX′ system.

average C–C bond distances in the cyclopropyl ring are less regular than in compounds where the ring has fewer substituents. The average C–C bond lengths are 1·510 Å in cyclopropane,[7] 1·514 Å in cyclopropyl chloride,[6] and 1·518 Å in *cis*-1,2,3-tricyanocyclopropane.[8] The shortening of the C–C bonds involving C(6) is similar to that of 1·451 Å found in tri-isopropylidenecyclopropane.[9] The distortions in the cyclopropane ring may be related to the fused ring system and the long C(1)–C(5) distance of 1·556 Å. The shortening of the C(6)–C(1) and C(6)–C(5) bonds and the lengthening of the C(6)–Cl distances relative to cyclopropyl chloride are consistent with the long C(1)–C(5) bond distance.

The seven-membered ring is in the chair conformation (as expected from a comparison with cycloheptene),[10] with the phenyl ring in the equatorial position. The formation of the *syn*-isomer suggests that the lone-pair electrons of the oxygen atoms do *not* exert a *cis*-directing influence on the dichlorocarbene addition. Furthermore, the addition of the dihalogenocarbene to the olefin appears to be controlled mainly by steric considerations, in contrast to the situation when methylene is the electrophile.[11] The results are in agreement with recent observations on the addition of dichlorocarbene to 3-methoxycyclohexene.[12]

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[1] C. D. Porter, E. C. Friedrich, and S. Winstein, *J. Amer. Chem. Soc.*, 1969, **91**, 6892 and references cited therein.
[2] B. Fraser-Reid, R. Li-Jiun Sun, and J. T. Brewer, *Tetrahedron Letters*, 1969, 2775.
[3] R. J. Myers and W. D. Gwinn, *J. Chem. Phys.*, 1952, **20**, 1420.
[4] S. L. Miller, L. C. Aamodt, G. Dousmanis, C. H. Townes, and J. Kraitchman, *J. Chem. Phys.*, 1952, **20**, 1112.
[5] F. L. Tobiason and R. H. Schwendeman, *J. Chem. Phys.*, 1964, **40**, 1014.
[6] R. H. Schwendeman, G. D. Jacobs, and T. M. Krigas, *J. Chem. Phys.*, 1964, **40**, 1022.
[7] O. Bastiansen, F. N. Fritsch, and K. Hedberg, *Acta Cryst.*, 1964, **17**, 538.
[8] A. Hartman and F. L. Hirschfeld, *Acta Cryst.*, 1966, **20**, 80.
[9] V. H. Dietrich, *Acta Cryst.*, 1970, **B26**, 44.
[10] N. L. Allinger and W. Szkrybalo, *J. Org. Chem.*, 1962, **27**, 722.
[11] S. Winstein, J. Sonnenberg, and J. de Vrimes, *J. Amer. Chem. Soc.*, 1959, **81**, 6523; E. J. Corey and R. L. Dawson, *ibid.*, 1963, **85**, 1782; W. G. Dauben and G. H. Berezin, *ibid.*, p. 468.
[12] M. A. Tobias and B. E. Johnston, *Tetrahedron Letters*, 1970, 2703.