Crystal and Molecular Structure of *exo*-2,*exo*-3-Dichloro-*endo*-5,6-(*o*-phenylene)norbornane

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The crystal structure of the title compound (2) has been determined from *X*-ray diffraction data collected by diffractometer. Crystals are orthorhombic, space group *Pnma*, with $Z = 4$ in a unit cell of dimensions $a = 7.503(3)$, $b = 11.022(5)$, and $c = 13.429(6)$ Å at 21 °C. The structure was refined by full-matrix least-squares to a final (conventional) *R* value of 0.083 for 928 observed reflections. The molecule has crystallographically required mirror (C_s) symmetry, and as predicted from earlier chemical studies, the chlorine atoms are in the *exo*-positions on the norbornane ring.

IN the course of a series of studies on carbocation reactions[1] we have previously studied the reaction of *endo*-5,6-(*o*-phenylene)norborn-2-ene (1,4,4a,8b-tetrahydro-1,4-methanobiphenylene) (1) with palladium chloride–copper chloride.[2] Of particular interest were the synthetic possibilities of these reactions and the study of

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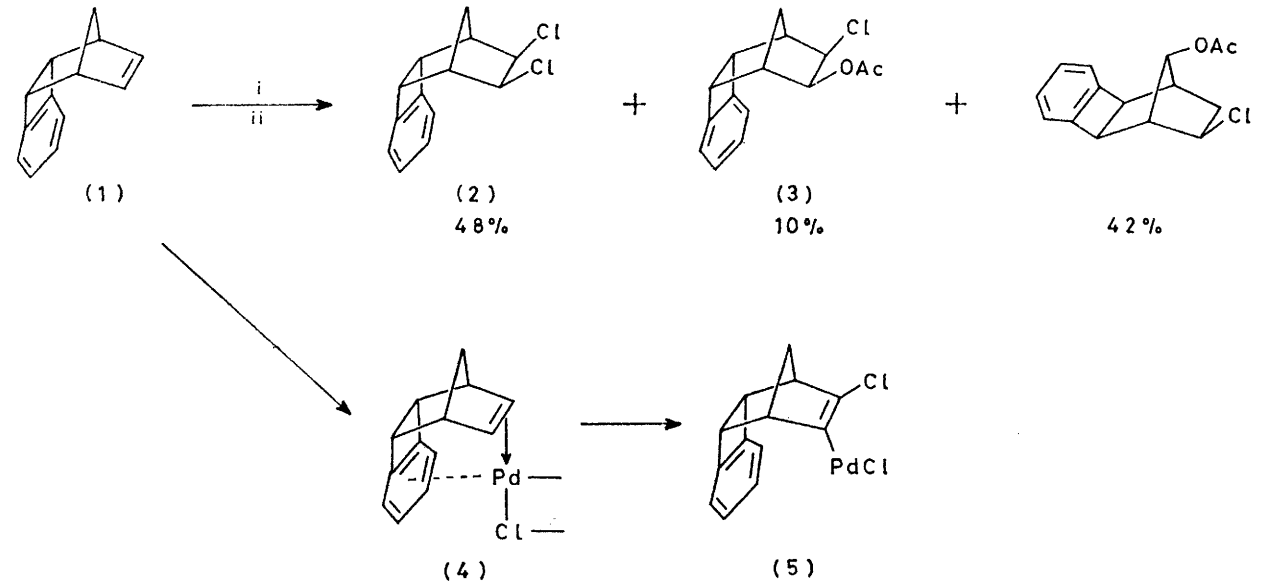
[1] R. Baker and T. J. Mason, *J.C.S. Perkin II*, 1972, 18.

[2] R. Baker and D. E. Halliday, *J.C.S. Perkin II*, 1974, 208.

the role of carbocations in them.[3] The mechanism of the reactions of olefins with palladium chloride–copper chloride has evoked considerable discussion,[4] and while it seemed apparent that the formation of the unrearranged products [Scheme (2) and (3)] could be explained by the intervention of an olefin–copper complex, the amounts of these products were much larger than expected.[2] It was suggested that this proportion could be produced *via* an *endo*-complexed intermediate (4) which, on reaction with chloride, would lead to (5), and then to (2) and (3). Since reasonable crystalline samples of (2) were available, an *X*-ray analysis was undertaken to confirm that the depicted structure was indeed correct, and so to lend support to the mechanism involving the intermediate (4).



SCHEME

Reagents: i, $CuCl_2$–$PdCl_2$; ii, AcOH–AcONa

EXPERIMENTAL

exo-2,*exo*-3-Dichloro-*endo*-5,6-(*o*-phenylene)norbornane was prepared as previously described.[2] Transparent crystals having a pronounced acicular habit and suitable for *X*-ray analysis were sealed into 0.3 mm diameter Lindemann glass capillaries to prevent decomposition.

Crystal Data.—$C_{13}H_{12}Cl_2$, $M = 239.1$. Orthorhombic, $a = 7.503(3)$, $b = 11.022(5)$, $c = 13.429(6)$ Å, $U = 1\,110.5$ Å^3, $D_m = 1.41(3)$ g cm^{-3} (by flotation), $Z = 4$, $D_c = 1.43$ g cm^{-3}, $F(000) = 496$. Laue symmetry *mmm*. Systematic absences, $hk0$ for $h \neq 2n$ and $0kl$ for $k + l \neq 2n$ are consistent with space groups $Pnma$ or $Pn2_1a$ (alternative setting of $Pna2_1$). Mo-K_α radiation, $\lambda = 0.710\,7$ Å; μ(Mo-K_α) = 3.72 cm^{-1}.

A well formed crystal, of length 0.43 mm, was oriented with the (100) direction approximately coincident with the ϕ axis of an Enraf–Nonius CAD 3 diffractometer. Accurate unit-cell dimensions were determined from least-squares refinement of the angular settings for sixteen accurately centred, high-angle reflections, obtained by use of the program SETANG supplied with the diffractometer. The integrated intensities of a total of 1 433 reflections within the sphere $0° < 2\theta \leqslant 48°$ (1 033 independent) were measured at an instrument take-off angle of 2.5° by the θ—2θ scan method at a scan rate of 10° min^{-1}. A scan range $\Delta(2\theta) = (0.6 + 0.2 \tan \theta)$ centred about the average peak position was used and the net intensities were calculated as $I = P - (B_1 + B_2)F/n_s$ where P, B_1, and B_2 are peak and stationary background counts, the latter being measured for one half the scan time, F is a filter factor, and n_s the number of scans of the reflection. On the basis of this formula, 928 reflections had a non-zero net count and were used in all stages of the analysis.[5] Instrumental and crystal stability were monitored by the measurement of two standards every 30 reflections. No deviation $> 2\sigma(I)$ was observed. Intensity data were assigned standard deviations according to the formula $\sigma(I) = [(P + B_1 + B_2)(F/n_s)^2 + (cI)^2]^{\frac{1}{2}}$, with c having the value 0.05. The eight crystal faces were indexed and measured for an absorption correction, although the transmission factors, which were calculated neglecting the presence of the capillary, ranged from only 0.89 to 0.92, indicating that such corrections could have been neglected.

Structure Solution.—Computations were carried out on a CDC 6600 computer, using local modifications of Zalkin's FORDAP Fourier Program, Prewitt's SFLS5 full-matrix least-squares program, and locally written absorption correction and data reduction routines. Scattering factors for chlorine and carbon were taken from ref. 6, that for hydrogen from ref. 7. In all least squares refinements the quantity minimised was $\Sigma w(|F_o| - |F_c|)^2$, the weights being evaluated as $w^{\frac{1}{2}} = 2LpF_o/\sigma(I)$.

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[3] W. C. Baird, *J. Org. Chem.*, 1969, **31**, 2411.

[4] P. M. Maitlis, 'The Organic Chemistry of Palladium,' Academic Press, New York, 1971.

[5] F. L. Hirshfeld and D. Rabinowich, *Acta Cryst.*, 1973, **A29**, 510.

[6] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[7] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

The solution of the structure was straightforward in space group *Pnma*, proceeding *via* the location of the chlorine atom in a Patterson map and the subsequent location and isotropic refinement of all non-hydrogen atoms, to R 0.154 and R' 0.133 $\{R' = [\Sigma w)|F_o| - |F_c|)^2/\Sigma(F_o)^2]^{\frac{1}{2}}\}$. Variable weight anisotropic refinement (2 cycles) followed by further refinement including the hydrogen atoms with isotropic thermal parameters led to final residuals for all reflections of R 0.083 and R' 0.079 at convergence. The residual for those reflections with $I \geqslant 3\sigma(I)$ was 0.041. A final difference-Fourier map indicated no residual peak >0.3 eÅ^{-3}, which is <0.5 peak height assigned to hydrogen atoms. Shifts in all parameters in the final least-squares cycle were all $<0.1\sigma$. Positional parameters are listed in Table 1. Observed and calculated structure factors and thermal parameters are available as Supplementary Publication No. SUP 22270 (10 pp., 1 microfiche).*

TABLE 1

Fractional atomic co-ordinates for (2), with estimated standard deviations in parenthesrs

Atom	x	y	z
Cl	0.555 84(15)	0.109 87(9)	0.397 38(9)
C(1)	0.171 6(9)	$\frac{1}{4}$	0.347 8(5)
C(2)	0.379 5(5)	0.179 3(3)	0.468 1(3)
C(3)	0.195 5(5)	0.147 4(4)	0.425 1(3)
C(4)	0.050 8(6)	0.177 9(4)	0.501 0(3)
C(5)	0.089 7(5)	0.186 3(4)	0.612 4(3)
C(6)	0.116 4(5)	0.119 9(4)	0.698 5(3)
C(7)	0.144 0(6)	0.187 3(4)	0.785 4(3)
H(1)	0.052 1(94)	$\frac{1}{4}$	0.341 1(57)
H(2)	0.256 1(68)	$\frac{1}{4}$	0.287 8(37)
H(3)	0.386 2(44)	0.151 0(32)	0.528 8(27)
H(4)	0.169 7(54)	0.075 0(40)	0.402 6(27)
H(5)	−0.048 7(48)	0.143 1(32)	0.483 7(26)
H(6)	0.095 4(50)	0.023 2(41)	0.691 5(31)
H(7)	0.171 7(56)	0.142 0(38)	0.839 3(33)

TABLE 2

Bond distances (Å) and angles (°) in (2), with estimated standard deviations in parentheses

(*a*) Distances

C(1)–C(3)	1.546(6)	C(2)–C(3)	1.537(6)
C(2)–C(2′)	1.561(5)	C(3)–C(4)	1.526(6)
C(4)–C(4′)	1.589(6)	C(4)–C(5)	1.528(6)
C(5)–C(5′)	1.404(6)	C(5)–C(6)	1.381(6)
C(7)–C(7′)	1.381(6)	C(6)–C(7)	1.398(6)
C(2)–Cl	1.800(4)	C(2)–H(3)	0.89(4)
C(1)–H(1)	0.90(7)	C(1)–H(2)	1.02(5)
C(3)–H(4)	0.89(4)	C(4)–H(5)	0.86(4)
C(6)–H(6)	1.05(5)	C(7)–H(7)	0.95(5)

(*b*) Angles

C(3)–C(1)–C(3)	94.11(0.42)	H(1)–C(1)–H(2)	124.0(4.9)
H(1)–C(1)–C(3)	99.7(4.2)	H(1)–C(1)–C(3)	116.9(2.2)
C(1)–C(3)–C(2)	100.94(0.36)	C(1)–C(3)–C(4)	101.79(0.35)
C(2)–C(3)–H(4)	121.6(2.3)	C(4)–C(3)–H(4)	106.5(2.4)
C(1)–C(3)–H(4)	114.6(2.7)	C(2)–C(3)–C(4)	109.68(0.33)
C(3)–C(2)–Cl	111.40(0.26)	C(2′)–C(2)–Cl	115.13(0.27)
C(3)–C(2)–H(3)	109.0(2.4)	C(2′)–C(2)–H(3)	110.8(2.40)
Cl–C(2)–H(3)	107.3(2.4)	C(2′)–C(2)–C(3)	103.20(0.30)
C(3)–C(4)–C(4′)	102.75(0.36)	C(4′)–C(4)–H(5)	118.8(2.5)
C(5)–C(4)–C(4′)	86.52(0.34)	C(3)–C(4)–H(5)	109.7(2.4)
C(3)–C(4)–C(5)	122.18(0.36)	C(5)–C(4)–H(5)	116.3(2.3)
C(4)–C(5)–C(5′)	93.48(0.33)	C(5′)–C(5)–C(6)	121.90(0.40)
C(4)–C(5)–C(6)	114.60(0.41)	C(5)–C(6)–C(7)	116.05(0.42)
C(6)–C(7)–C(7′)	122.05(0.45)	C(5)–C(6)–H(6)	115.3(2.5)
C(7)–C(6)–H(6)	128.1(2.5)	C(6)–C(7)–H(7)	114.1(3.2)
C(7′)–C(7)–H(7)	123.7(3.1)		

(*c*) Least-squares plane

Atoms: C(4)—(6), C(4′)—(6′)
Equation: * $-0.983\,8X + 0.179\,5Z = 0.824\,9$
Distances (Å × 10^3): C(4) 0.7, C(5) −1.36, C(6) −0.9, C(7) 4.8, H(6) 140, H(7) −62

* Equation in the form $lX + mY + nZ = d$, where X, Y, and Z are orthogonal Å co-ordinates.

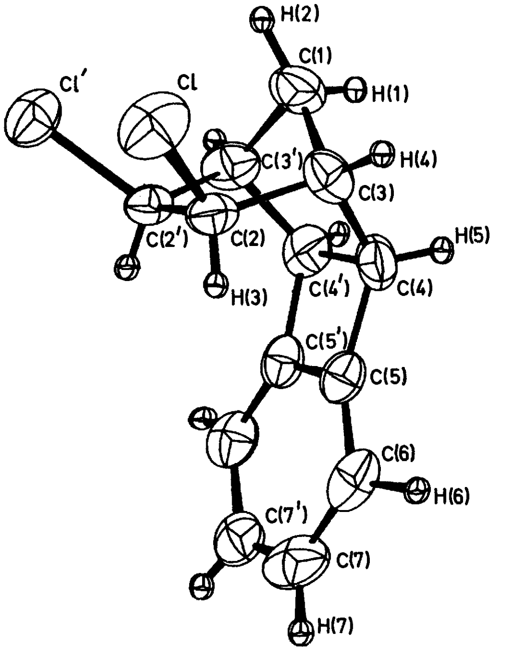

FIGURE 1 Perspective view of the structure of (2) showing the atom numbering scheme

RESULTS AND DISCUSSION

Table 2 contains the pertinent structural information for the title molecule which has crystallographically imposed mirror symmetry. Figure 1 gives a perspective view of the molecule, while Figure 2 illustrates the molecular packing and shows the molecules viewed normal to their planes of symmetry. None of the van der Waals non-bonded distances appears to be unusual, the shortest chlorine–hydrogen contacts being: Cl · · · H(2^{II}) 3.28, Cl′ · · · H(3^{I}) 3.04, and Cl · · · H(7^{III}),

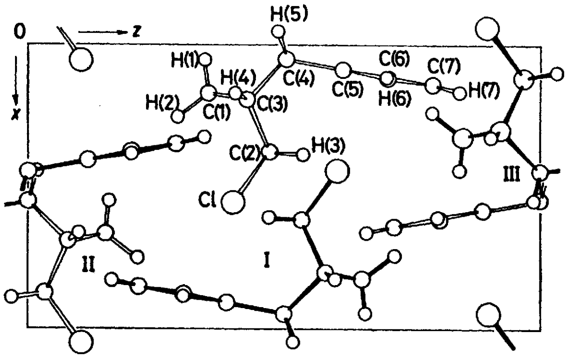

FIGURE 2 Projection of the contents of one unit cell on the (010) plane. Numbered molecules are as follows: in the following positions relative to the reference molecule at x,y,z: I $-x, \frac{1}{2} + y, -z$; II $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$; and III $\frac{1}{2} - x, -y, \frac{1}{2} + z$

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1977, Index issue.

3.38 Å. The contacts involving H(1) all appear to be rather long, the H(2) • • • H(1^{II}) distance being 2.85 Å.

All bond distances and angles in the norbornane fragment appear to be in accord with reported values, with the angle at the bridgehead carbon being appreciably smaller than the tetrahedral value.[8-10] The angles at C(4) also depart appreciably from the tetrahedral value and together with the rather long C(4)–C(4′) distance are presumably indicative of the presence of the strain in the four-membered ring.

The two H–C(1)–C(3) angles differ appreciably; the larger, involving H(2), reflecting the intramolecular contact of 3.106 Å with the chlorine atom in the *exo*-position. Equivalent angles would produce a Cl • • • H(2) distance less than the sum of van der Waals radii. The Cl • • • Cl′ distance is 3.087 Å. The distances and angles in the benzo-ring indicate a small deviation from six-fold to three-fold symmetry, which is significant in the case of the angles, and scarcely so in the case of the distances. The phenylene grouping is planar, and the dihedral angle between this plane and that defined by C(3), C(4), C(3′), and C(4′) is 126.5°. The dihedral angles between the plane containing C(1) and the bridgehead carbon atom, and the other two planes of the norbornane fragment are 122.6 and 123.2° respectively.

[7/1118 *Received, 27th June*, 1977]

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