

in concentrated hydrochloric acid at 160° used by Braun.<sup>24</sup> A fraction (12 g.), b.p. 118.5° (14 mm.),  $n_D^{25}$  1.5167, was obtained. It was found to be 100% pure by g.l.c. analysis.

**Acknowledgment.**—The experiments involving ethylbenzene were performed by Mr. Hollis D. McBride.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

## Photochlorination of Bromocyclopentane and Chlorocyclopentane<sup>1</sup>

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The compounds mentioned in the title have been photochlorinated utilizing molecular chlorine, *t*-butyl hypochlorite, sulfuryl chloride, and trichloromethanesulfonyl chloride at 40 and -30°. A pronounced directive effect of the halogen substituent was observed in the hydrogen abstraction reaction as well as considerable stereoselectivity in the reaction of the resulting halocycloalkyl radical with the chlorinating agent. The *trans* products are always preferred. The unusually high reactivity noted for the hydrogen atoms at the 2-position in bromocyclopentane suggests that the bromine atom is participating as a neighboring group when a radical or atom attacks these hydrogen atoms. Competitive halogenations of the halocyclopentanes and halocyclohexanes with the parent hydrocarbons have also been performed.

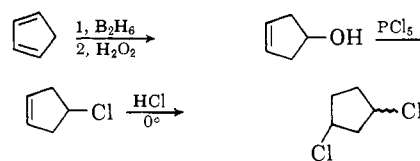
The effects of polar substituents on the position of attack of chlorine atoms on acyclic molecules have been studied.<sup>3</sup> Similar effects in cyclic compounds have been less thoroughly studied, although Nevill has reported that the major products of chlorination of cyclobutanecarboxylic acid and 1,1-cyclobutanedicarboxylic acid are the *trans*-3-chlorides.<sup>4</sup> We have investigated the chlorination of bromo- and chlorocyclopentanes and cyclohexanes<sup>5</sup> to determine the effect of the substituent in directing the attack of a chlorine atom and the stereochemical effect of the substituent in the following reaction between molecular chlorine and the halocycloalkyl radical. Closely connected with this work is the question of conformational stability of radicals derived from the cyclohexane ring system.<sup>5</sup>

### Results

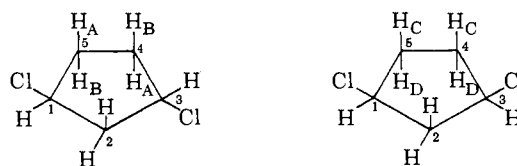
**Proof of Structure of Dihalocyclopentanes.**—The photochlorination of chlorocyclopentane produced the expected 5 isomeric dichlorocyclopentanes which could be separated by gas-liquid chromatography (g.l.c.). The photochlorination of bromocyclopentane at 40° produced *trans*-1,2-dichlorocyclopentane in addition to the 5 bromochlorocyclopentanes (see Fig. 1). All of the isomeric dihalides except the 1,3-dihalides could be obtained by standard preparative methods. Assigning the *cis*-1,3-dichlorocyclopentane structure to peak B, Fig. 1, defined the chlorination products of chlorocyclopentane and bromocyclopentane since from the g.l.c. curves of Fig. 1 it immediately follows that A must be *trans*-1,3-dichlorocyclopentane, A' must be *trans*-1,3-bromochlorocyclopentane, and B' must be *cis*-1,3-bromochlorocyclopentane. For all 5 pairs of structurally similar dichlorocyclopentanes and bromochlorocyclopentanes a constant ratio of retention times of 1:1.55 was observed.

Additional proof for the structure assignments was provided by the observation that the dichlorides corresponding to peaks A and B (Fig. 1) were the only dichlorides formed from the reaction of 4-chlorocyclo-

pentane with hydrogen chloride, although again the yields of the dichlorides were very poor.



In addition, the dichlorides corresponding to peaks A, A', B, and B' were isolated by rectifications of large scale chlorinations of chlorocyclopentane and bromocyclopentane. Analysis of the proton nuclear resonance spectra completely confirmed the assignment of structures. The spectra of each pair of isomers (A and A', B and B') were nearly identical. The spectra for the dichlorides are given in Fig. 2 and 3. The spin-spin splitting of the methylene protons attached to carbon atom 2 is particularly instructive. In the *trans* dichloride these protons are equivalent and are split by the equivalent protons on carbon atoms 1 and 3 to give the well defined triplet at  $\tau = 7.57$ ,  $J = 5.3$  c.p.s. (Fig. 2). For the *cis* isomer (Fig. 3) the protons at carbon atoms 2 are not equivalent and a complex and broad pattern is found because of the strong coupling between these two protons. Moreover, in the *cis* compound coupling between H<sub>C</sub> and H<sub>D</sub> should be weaker (because of the dihedral angle) than coupling between H<sub>A</sub> and H<sub>B</sub> in the *trans*-dichloride. Consistent with



this prediction, the separation between lines for the high field methylene protons of the *trans* isomers are greater than the corresponding separations for the *cis* isomers.<sup>6</sup>

The n.m.r. spectra of all the dichlorocyclopentanes and bromochlorocyclopentanes have been recorded.<sup>7</sup>

(1) (a) Directive Effects in Aliphatic Substitution. Part XXI. (b) This work was supported by a grant from the Petroleum Research Fund, administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

(2) Alfred P. Sloan Foundation Fellow, 1959-1963.

(3) H. C. Brown and A. B. Ash, *J. Am. Chem. Soc.*, **77**, 4019 (1955); P. S. Fredricks and J. M. Tedder, *J. Chem. Soc.*, 918 (1959); 3520 (1961); L. Horner and L. Schläfer, *Ann.*, **635**, 31 (1960).

(4) W. A. Nevill, D. S. Frank, and R. D. Trepka, *J. Org. Chem.*, **27**, 422 (1962).

(5) G. A. Russell, A. Ito, and R. Konaka, *J. Am. Chem. Soc.*, **85**, 2988, (1963).

(6) These arguments apply strictly when eclipsed methylene groups are considered (F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961)). In cyclopentane the methylene groups are not completely eclipsed (K. S. Pitzer and W. E. Donath, *J. Am. Chem. Soc.*, **81**, 3213 (1959); F. V. Brutcher, T. Roberts, S. J. Barr, and N. Pearson, *ibid.*, **81**, 4915 (1959)) and in very flexible 5-membered rings, particularly those containing a hetero atom, the coupling constants of *trans*-hydrogen atoms can actually exceed those of *cis*-hydrogen atoms (F. A. L. Anet, *ibid.*, **84**, 747 (1962)).

(7) A. Ito, Ph.D. Thesis, Iowa State University Library, Ames, Iowa.

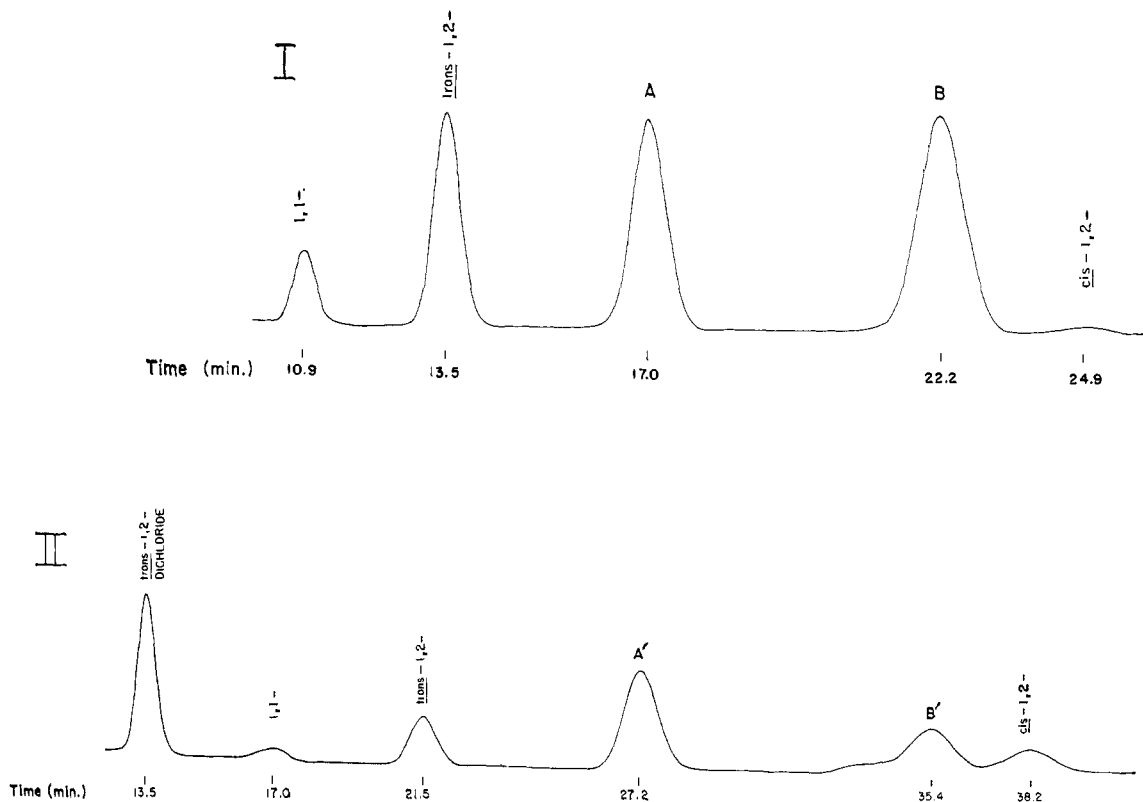


Fig. 1.—Products of the photochlorination of chlorocyclopentane (I) and bromocyclopentane (II) at 40° in carbon tetrachloride. The poorly resolved peak at ~33 min. in II is probably *trans*-1,2-dibromocyclopentane.

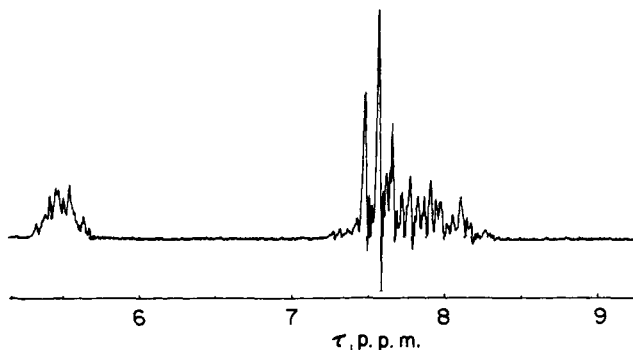
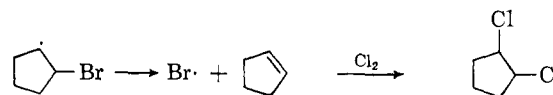


Fig. 2.—Proton magnetic resonance spectrum of A (*trans*-1,3-dichlorocyclopentane) at 60 Mc./sec. in carbon tetrachloride.

**Products of Chlorination.**—Table I summarizes the results of the chlorination of chlorocyclopentane and bromocyclopentane. The data of Table I indicate that the ratio of the isomeric dihalocyclopentanes isolated is independent of the percentage chlorination. The ratio of dichlorides detected is therefore a fair measure of the initial reaction products. Relative reactivities calculated from the ratio of dihalides, given in Table I on a per hydrogen basis, indicate a strong polar effect in the attack of chlorine atoms on chlorocyclopentane. The *cis-trans* ratios for the 1,2- and 1,3-dihalides indicate a pronounced stereoselectivity in the reaction of the resulting halocycloalkyl radical with molecular chlorine.

Chlorination of bromocyclopentane at 40° produced significant amounts of *trans*-1,2-dichlorocyclopentane in addition to the five expected bromochlorocyclopentanes. The dichloride which constituted 26% of the total dihalocyclopentanes and over 50% of the products of attack at the 2-carbon atom undoubtedly result from the following reaction.<sup>8</sup>

(8) A. B. Ash and H. C. Brown, *Record Chem. Progr. (Kresge-Hooker Sci. Lib.)*, **9**, 81 (1948).



To avoid this decomposition reaction the temperature was lowered until the amount of dichlorocyclopentane formed became less than 2% of the total bromochlorocyclopentanes. Such was the case when the photochlorination was performed at -30° in carbon tetrachloride solution.

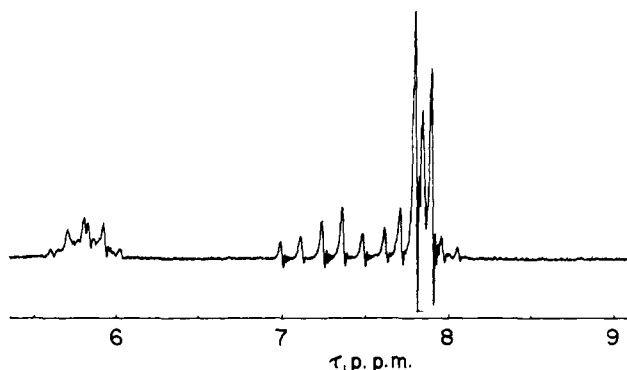


Fig. 3.—Proton magnetic resonance spectrum of B (*cis*-1,3-dichlorocyclopentane) at 60 Mc./sec. in carbon tetrachloride.

Photochlorination with sulfuryl chloride, trichloromethanesulfonyl chloride,<sup>9</sup> or *t*-butyl hypochlorite gave results qualitatively similar to photochlorination but with significant quantitative differences in both the position of attack and the *cis-trans* ratios of the resulting dichlorides.

To ascertain the extent of the polar effect of the chlorine substituent upon the 3-position in chlorocyclopentane and in the 4-position in chlorocyclohexane,<sup>5</sup> the competitive chlorinations summarized in Table II were performed.

(9) E. S. Huyser, *J. Am. Chem. Soc.*, **82**, 5246 (1960).

TABLE I  
 PHOTOCHEMICAL CHLORINATION OF 1 M CHLOROCYCLOPENTANE AT 40°

Solvent	Chlorination, %	Dihalocyclopentanes <sup>a</sup>					cis-trans ratios		Rel. react. <sup>b</sup> 1:2:3-positions
		1,1-	cis-1,2-	trans-1,2-	cis-1,3-	trans-1,3-	2-Attack	3-Attack	
CCl <sub>4</sub>	15	4.5	<sup>c</sup>	31.5	25.6	38.4	...	0.66	0.21:0.36:0.75 <sup>d</sup>
CCl <sub>4</sub>	27	4.7	0.5	31.3	25.6	37.9	0.016	.68	.20:0.38:0.75 <sup>d</sup>
CCl <sub>4</sub>	47	4.5	.5	30.9	25.8	38.2	.016	.68	.21:0.37:0.75 <sup>d</sup>
CCl <sub>4</sub>	50	4.4	.5	30.6	26.0	38.4	.016	.68	.20:0.36:0.75 <sup>d</sup>
CH <sub>3</sub> CN	15	3.1	1.3	28.1	30.8	36.7	.046	.84	.14:0.33:0.75 <sup>d</sup>
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	15	4.4	1.2	26.9	30.7	36.7	.045	.84	.19:0.31:0.75 <sup>d</sup>
C <sub>6</sub> H <sub>6</sub>	15	5.8	0.8	27.4	27.3	38.7	.029	.71	.26:0.32:0.75 <sup>d</sup>
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> O	15	7.9	<sup>c</sup>	25.2	29.6	37.3	...	.79	.35:0.38:0.75 <sup>d</sup>
CS <sub>2</sub>	15	9.4	1.0	28.6	25.2	35.7	0.035	.71	.46:0.36:0.75 <sup>d</sup>
CCl <sub>4</sub> <sup>e</sup>	15	4.2	<sup>c</sup>	28.7	29.5	37.6	...	.79	.18:0.32:0.75 <sup>d</sup>
CCl <sub>4</sub> <sup>f</sup>	15	3.4	<sup>c</sup>	43.3	23.2	30.1	...	.77	.17:0.54:0.66 <sup>d</sup>
CS <sub>2</sub> <sup>f</sup>	15	6.0	<sup>c</sup>	44.5	20.9	28.7	...	.73	.48:0.89:1.0 <sup>h</sup>
CCl <sub>4</sub>	35 <sup>g</sup>	6.4	1.4	31.6	14.2	46.4	0.044	.31	.42:0.54:1.0 <sup>h</sup>
CCl <sub>4</sub>	35 <sup>i</sup>	14.3	2.1	29.2	11.4	42.6	0.072	.27	1.06:0.58:1.0 <sup>h</sup>
CCl <sub>4</sub>	35 <sup>j</sup>	25.0	<sup>c</sup>	33.6	9.3	32.2	...	.29	2.41:0.81:1.0 <sup>h</sup>
CCl <sub>4</sub> <sup>f</sup>	35 <sup>j</sup>	8.9	<sup>c</sup>	51.0	9.8	30.3	...	.32	0.88:1.3:1.0 <sup>h</sup>

<sup>a</sup> Percentage of total dihalides. <sup>b</sup> Per hydrogen atom. <sup>c</sup> Too small to measure. <sup>d</sup> Relative to cyclohexane; see Table II. <sup>e</sup> -30°. <sup>f</sup> Bromocyclopentane, -30°. <sup>g</sup> Sulfuryl chloride, 80°. <sup>h</sup> Assumed. <sup>i</sup> Trichloromethanesulfonyl chloride, 80°. <sup>j</sup> *t*-Butyl hypochlorite.

 TABLE II  
 COMPETITIVE CHLORINATIONS INVOLVING HALOCYCLOALKANES

Halocycloalkane (A)	Reference hydrocarbon (B)	Temp., °C.	Solvent	[A] <sub>0</sub>	[A] <sub>t</sub>	[B] <sub>0</sub>	[B] <sub>t</sub>	<i>k</i> <sub>γ</sub> / <i>k</i> <sub>α</sub> <sup>a</sup>	<i>k</i> <sub>δ</sub> / <i>k</i> <sub>α</sub> <sup>a</sup>
Chlorocyclopentane	Cyclohexane	40	CCl <sub>4</sub>	1.00	0.726	0.16	0.073	0.75	...
Chlorocyclopentane	Cyclohexane	40	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	1.00	.861	.17	.115	.75	...
Chlorocyclohexane	Cycloheptane <sup>b</sup>	40	CCl <sub>4</sub>	1.00	.842	.52	.358	.81	1.0
Bromocyclopentane	Cyclopentane <sup>b</sup>	-30	CCl <sub>4</sub>	1.00	.858	.21	.154	.66	...
Chlorocyclopentane	Bromocyclopentane <sup>c</sup>	-30	CCl <sub>4</sub>	1.00	.641	1.00	.607	.73 <sup>c</sup>	...

<sup>a</sup> Relative reactivity of a hydrogen in the γ- or δ-position of A relative to a cyclohexane hydrogen atom. <sup>b</sup> Cycloheptane and cyclopentane hydrogen atoms taken as 1.11 and 1.05 times as reactive as a cyclohexane hydrogen atom, respectively [G. A. Russell, *J. Am. Chem. Soc.*, **80**, 4997 (1958)]. <sup>c</sup> The γ-hydrogens of bromocyclopentane assumed to have a relative reactivity of 0.66.

The data of Table II show that the deactivating effect of a halogen substituent extends to the 3-position in both cyclopentane and cyclohexane but that there is no appreciable deactivation in the 4-position of cyclohexane. In the present examples the 3- and 4-halocycloalkyl radicals have the same number of hyperconjugative resonance structures and the difference in reactivity between the hydrogen atoms at the 3- and 4-positions cannot be explained in terms of hyperconjugation as has been suggested by Fredricks and Tedder for several acyclic examples of the polar effect.<sup>10</sup>

### Discussion

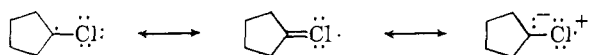
The polar effects of the chlorine substituents in chlorocyclopentane and chlorocyclohexane are essentially the same. In photochlorination with molecular chlorine in carbon tetrachloride solution at -30° the relative reactivities of the hydrogen atoms at the 1-, 2-, and 3-positions of chlorocyclopentane are 0.18:0.32:0.75, whereas for chlorocyclohexane the relative reactivities are 0.25:0.31:0.79.<sup>b</sup> This is somewhat surprising in view of the fact that cyclopentane is a fairly rigid ring while cyclohexane is a flexible system. It would seem quite reasonable to conclude that a chlorine atom attacks axial and equatorial hydrogen atoms with equal facility.<sup>11</sup>

(10) P. S. Fredricks and J. M. Tedder, *Chem. Ind. (London)*, 490 (1959).

(11) However, an alternative explanation can be advanced. Chlorocyclohexane exists mainly in the conformation wherein chlorine occupies an equatorial position in carbon disulfide solution (L. W. Reeves and K. O. Stromme, *Can. J. Chem.*, **38**, 1241 (1960)). It is reported that this conformation is preferred over the axial conformation by 0.41 kcal./mole. At 40° the ratio of equatorial to axial conformations should be 1.94. Attack on axial or equatorial hydrogen atoms could be preferred if  $k_c = k_e(0.34) + k_a(0.66)$  where  $k_c$ ,  $k_e$ , and  $k_a$  are the rate constants for attack of a chlorine atom at a given hydrogen atom in chlorocyclopentane ( $k_c$ ) and the equatorial ( $k_e$ ) and axial ( $k_a$ ) hydrogen atoms at the same position of chlorocyclohexane.

The effect of solvents in altering the position of attack of chlorine atoms upon chlorocyclopentane seems reasonable. Nitrobenzene has no effect whereas benzene, and to a greater extent carbon disulfide, increases the amount of attack at the 1-position, the relative reactivities of hydrogen atoms at the 1-, 2-, and 3-positions being 0.19:0.31:0.75 in nitrobenzene, 0.26:0.32:0.75 in benzene; and 0.45:0.37:0.75 in carbon disulfide. There is no significant change between the reactivities of the hydrogen atoms β and γ to the chlorine substituent as the solvent is changed. The difference in reactivity between these hydrogen atoms is determined solely by the inductive effect of the chlorine substituent and it has been previously established that complexing the chlorine atom with aromatic solvents has no effect on such relative reactivities.<sup>12</sup> On the other hand, the reactivity of the α-hydrogen atom relative to the β- or γ-hydrogen atoms increases as the solvent is changed from nitrobenzene to benzene to carbon disulfide. This is consistent with the conclusion that the weakest carbon-hydrogen bond in the system is that at the α-position but that this position undergoes powerful deactivation by the inductive effect of the chloro substituent. By complexing the chlorine atom,<sup>12</sup> the importance of bond-dissociation energy in determining reactivity is emphasized and the reactivity of the α-hydrogen atom increased. In carbon disulfide solution the α-hydrogen atom is actually more reactive than the β-hydrogen atom. The lower bond-dissociation energy of the α-carbon-hydrogen bond is undoubtedly due to resonance stabilization of the 1-chlorocyclopentyl radical. The stability of this radical, relative to its 2- and 3-isomers, is seen when sulfuryl chloride, trichloromethanesulfonyl chloride, or *t*-butyl hypo-

(12) (a) G. A. Russell, *Tetrahedron*, **8**, 101 (1960); (b) G. A. Russell, *J. Am. Chem. Soc.*, **80**, 4987, 5002 (1958).



chlorite are used as chlorinating agents. In Table III the sensitivity of the attacking radical to inductive effects is given as measured by the relative reactivities of the  $\beta$ - and  $\gamma$ -hydrogen atoms of chlorocyclopentane.

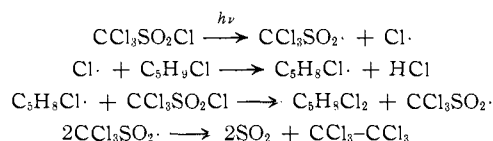
TABLE III

POLAR AND RESONANCE EFFECTS IN ATTACK OF RADICALS UPON CHLOROCYCLOPENTANE

Chlorinating agent	Attacking radical	Sensitivity to polar effect, $k_\beta/k_\gamma$	Sensitivity to bond disson. energy, $k_\alpha/k_\gamma^a$
$\text{Cl}_2\text{-CCl}_4$	$\text{Cl}\cdot$	0.50	0.29
$\text{Cl}_2\text{-C}_6\text{H}_6$	$\text{C}_6\text{H}_5\cdot \rightarrow \text{Cl}\cdot$	.43	.36
$\text{SO}_2\text{Cl}_2$	$\text{SO}_2\text{Cl}\cdot$ and $\text{Cl}\cdot$	.54	.42 <sup>b</sup>
$\text{Cl}_2\text{-CS}_2$	$\text{CS}_2\text{Cl}\cdot$	.48	.61
$\text{CCl}_3\text{SO}_2\text{Cl}$	$\text{CCl}_3\text{SO}_2\cdot$	.58	1.1 <sup>b</sup>
$(\text{CH}_3)_3\text{COCl}$	$(\text{CH}_3)_3\text{CO}\cdot$	.81	2.4

<sup>a</sup> Per hydrogen atom, 40°. <sup>b</sup> 80°.

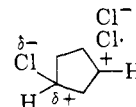
As Table III shows, all the radicals involved appear to have rather similar sensitivities to polar effects. If this is the case, then  $k_\alpha/k_\gamma$  should be a measure of the sensitivity of atoms or radicals to the strength of the carbon hydrogen bonds being broken. Column 4 in Table III indicates a sensitivity to bond dissociation energy of  $\text{Cl}\cdot < \text{Cl}\cdot\leftarrow\text{C}_6\text{H}_5 \sim \text{SO}_2\text{Cl}\cdot < \text{CS}_2\text{Cl}\cdot < \text{CCl}_3\text{SO}_2\cdot < (\text{CH}_3)_3\text{CO}\cdot$ . The interpretation of the result using trichloromethanesulfonyl chloride may be erroneous because of the very short kinetic chain involved in this chlorination as evidenced by the formation of 0.4 mole of hexachloroethane for each mole of dichlorocyclopentane. A significant amount of hydrogen abstraction may have occurred by the chlorine atom. The absence of pentachloroethane or tetra-



chloroethylene in the chlorination products indicates that hexachloroethane was not the actual chlorinating agent in this process.<sup>13</sup>

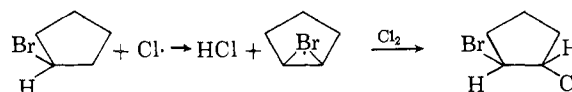
The ratios of *cis*- to *trans*-dichlorides formed as a result of hydrogen abstraction from the 2- and 3-carbon atoms of chlorocyclopentane form a consistent picture with a greater predominance of the *trans* isomer for 2- than for 3-attack. One would expect that abstraction of a hydrogen atom either *cis* or *trans* to the chlorine substituent would produce the same cycloalkyl radical with a planar  $\text{sp}^2$  configuration since this configuration will relieve eclipsing strains in the cyclopentyl system. Reaction of the 3-chlorocyclopentyl radical with molecular chlorine in carbon tetrachloride, benzene, or carbon disulfide solution gives a *cis-trans* ratio of 1,3-dichlorocyclopentanes of 0.67, 0.71, and 0.71, respectively. The *cis-trans* ratio of 1,2-dichlorides shows somewhat greater variation, possibly owing to the experimental uncertainties involved in measuring the small amounts of *cis*-1,2-dichlorocyclopentane formed. The *cis-trans* ratios for the 1,2-dichlorides in these solvents are in the range 0.03 to 0.015. The preference for the *trans*-dichlorides can be due to a steric effect and/or due to dipole-dipole interactions in the transition state for the reaction of the chlorine molecule with the cycloalkyl radical. Evidence for a simple steric effect would appear to be furnished by the lower value observed for the *cis-trans* ratio of 1,3-dichlorides obtained in chlorination with sulfonyl chloride (0.31),

trichloromethanesulfonyl chloride (0.27), and *t*-butyl hypochlorite (0.29). Evidence for dipole-dipole interaction being involved in determining the ratio of *cis* to *trans* products is furnished by the ability of solvents with high dielectric constants to favor the formation of *cis* compounds. Acetonitrile and nitrobenzene increase the *cis-trans* ratio of 1,3-dichlorides in photochlorination with molecular chlorine from 0.67-0.71 to 0.84. A larger effect is found when the effect of dielectric constant upon the ratio of *cis*- and *trans*-1,2-dichlorocyclopentanes is considered. It is believed that the effect of an increase in the dielectric constant of the solvent is to cause a decrease in the dipole-dipole interactions by dissipation of the effective charges in transition states of the type



It is interesting that solvents which could form a complex with molecular chlorine, such as benzene, do not have any appreciable effect on the ratio of *cis*- to *trans*-dichlorides.

When compared to chlorocyclopentane, bromocyclopentane has an abnormally high reactivity at the 2-position in photochlorination with molecular chlorine. At 30° the relative reactivities (all relative to a hydrogen atom of cyclohexane) of the hydrogen atoms at the 1-, 2-, and 3-positions of chlorocyclopentane and bromocyclopentane ( $\text{C}_5\text{H}_9\text{Cl}/\text{C}_5\text{H}_9\text{Br}$ ) are 0.18/0.17:0.32/0.54:0.73/0.66, respectively. The bromine substituent appears to have a slightly stronger polar deactivating influence than the chlorine substituent for hydrogen atoms at the 1- and 3-positions but not at the 2-position. This may well be connected with neighboring group participation by the bromine substituent but not by the chlorine substituent. Photochlorination of



bromocyclopentane at -30° in carbon disulfide solution increased the reactivity of the 1-hydrogen atom relative to the 2- or 3-position but did not appreciably alter the relative reactivities at the 2- and 3-positions from the value found in carbon tetrachloride solution. This result does not appear to be in accord with the postulated participation by the neighboring bromine atom. However, when chlorinations with *t*-butyl hypochlorite are considered, further support for an anomalous reactivity at the 2-position of bromocyclopentane is found since a hydrogen atom at the 2-position is 1.3 and 1.5 times as reactive as hydrogen atoms at the 3- and 1-positions, respectively.

### Experimental

**Chlorination Procedure.**—Photochlorinations using molecular chlorine were performed in a reaction bath mounted in a  $40 \pm 0.1^\circ$  thermostat. The apparatus has been described previously.<sup>14</sup> For photochlorinations performed at -30° the reaction vessel was immersed in an acetone bath maintained at  $-30 \pm 1^\circ$  by adding small pieces of Dry Ice. Photochlorinations utilizing *t*-butyl hypochlorite at 40° were performed in the same apparatus used for photochlorinations with molecular chlorine. For sulfonyl chloride chlorinations the reaction mixture was placed in a Pyrex glass tube equipped with a water condenser. The reaction mixture was illuminated by a 200-watt unfrosted tungsten light bulb mounted approximately 5 cm. from the reaction flask. The solution was heated by a gas flame so that gentle boiling of the solution occurred during the 3-hr. reaction period. The temperature of the reaction mixture was measured by an Anschütz thermometer suspended by a platinum wire. For trichloromethanesulfonyl chloride chlorinations a quartz reaction

(13) J. P. West and L. Schmerling, *J. Am. Chem. Soc.*, **72**, 3525 (1950).

(14) G. A. Russell, A. Ito, and D. G. Hendry, *ibid.*, **85**, 2976 (1963).

vessel was used. The reaction mixture was illuminated with a General Electric UA-2 lamp during the 5-hr. reaction period. Otherwise the reaction apparatus was the same as that used for sulfonyl chloride chlorinations.

**Analytical Procedures.**—Isomeric dihalocycloalkanes formed in the chlorination reactions were analyzed by gas-liquid chromatography (g.l.c.) in an instrument using a hot wire thermal conductivity gage. Analysis of dichlorocyclopentanes and bromochlorocyclopentanes were made using a 3 ft.  $\times$  0.25 in. column of di-2-ethyl sebacate on firebrick at 140°. Under these conditions the order of elution and relative retention times were: chlorocyclopentane (1.0), 1,1-dichlorocyclopentane (1.76), *trans*-1,2-dichlorocyclopentane (2.18), *trans*-1,3-dichlorocyclopentane (2.74), *cis*-1,3-dichlorocyclopentane (3.58), *cis*-1,2-dichlorocyclopentane (4.02); bromocyclopentane (1.58), 1-bromo-1-chlorocyclopentane (2.74), *trans*-1-bromo-3-chlorocyclopentane (5.71), and *cis*-1-bromo-2-chlorocyclopentane (6.16). For dichlorides resulting from chlorinations utilizing sulfonyl chloride and trichloromethanesulfonyl chloride a 300 ft.  $\times$  1/16 in. copper Goly column packed with polypropylene glycol was employed at 75°. Under these conditions relative retention times were: chlorocyclopentane (1.0), 1,1-dichlorocyclopentane (1.28), *trans*-1,2-dichlorocyclopentane (1.51), *trans*-1,3-dichlorocyclopentane (1.94), *cis*-1,3-dichlorocyclopentane (2.55), *cis*-1,2-dichlorocyclopentane (2.91), and hexachloroethane (3.20).

It was assumed that the isomeric dichlorocyclopentanes and bromochlorocyclopentanes had similar thermal conductivities. In the case of 1,1- and *trans*-1,2-dichlorocyclopentane, which were available in a high state of purity, the area ratio and the mole ratio differed from each other by less than 3%. For competitive chlorinations correction factors to correct area ratios to mole ratios were measured. *trans*-1,2-Dichlorocyclopentane was measured in the chlorination product of bromocyclopentane by an experimentally determined calibration factor with *trans*-1-bromo-2-chlorocyclopentane as the standard using a 2-m. di-2-ethylhexyl sebacate column at 140°.

Determination of the reactivity of chlorocyclopentane *vs.* cyclohexane in carbon tetrachloride solution was made by measuring the disappearance of the reactants using a 3 ft.  $\times$  0.25 in.  $\beta$ , $\beta$ '-oxydipropionitrile (20%) on firebrick column at 90° with bromobenzene as an internal standard. Relative reactivities were calculated from the expression

$$k_A/k_B = \frac{\log ([A]_t/[A]_0)}{\log ([B]_t/[B]_0)}$$

Relative reactivities of chlorocyclopentane and cyclohexane in nitrobenzene solution were determined by using a 2-m. di-2-ethylhexyl sebacate column at 140° utilizing the nitrobenzene as an internal standard. The relative reactivity of chlorocyclohexane and cycloheptane was determined using the same column at 140° with chlorobenzene as the internal standard. The relative reactivities of bromocyclopentane *vs.* cyclopentane and chlorocyclopentane were determined by utilizing a 1-m. polypropylene glycol, 20% on Chromosorb W, at 87° with bromobenzene as the internal standard.

**Reagents.**—Sulfonyl chloride (Eastman, practical grade) was distilled through a Vigreux column immediately before use. Trichloromethanesulfonyl chloride (Eastman, practical grade) was used as received. *t*-Butyl hypochlorite was prepared according to the procedure of Teeter and Bell.<sup>15</sup> Chlorocyclopentane (Matheson Coleman and Bell) was found to have a purity of 99.5% by g.l.c. and was not further purified. Chlorocyclohexane (Eastman) was found to have a purity of 99.8% by g.l.c. and was not further purified. Bromocyclopentane (Chem. Intermediates and Res. Lab., Inc.) was rectified in a Todd column packed with glass helices at 50 mm. and had a purity of 99.5% by g.l.c. Cyclopentane (Phillips, 99 mole % minimum) was washed with fuming sulfuric acid and distilled. Its purity was established to be 99.9% by g.l.c. Cyclohexane (Eastman, spectrograde) was used. It contained no detectable impurities. The cycloheptane used was 99.9% pure by g.l.c. Its preparation has been described previously.<sup>12</sup> Reagent grade carbon tetrachloride was passed through silica gel and stored over Molecular Sieves (Linde Co.) Nitrobenzene was distilled through a Vigreux column and the center fraction passed over silica gel and stored over molecular sieves. Acetonitrile, carbon disulfide, and benzene were passed through silica gel before use. All reagents were tested for possible impurities that might interfere in g.l.c. analyses.

**1,1-Dichlorocyclopentane.**—From 170 g. of cyclopentanone and 400 g. of phosphorus pentachloride, following the procedure of Braude and Forbes,<sup>16</sup> 54 g. of 1-chlorocyclopentane, b.p. 102–106° at 740 mm., and 66 g. of 1,1-dichlorocyclopentane, b.p. 132–140° at 740 mm., were obtained by a rapid distillation through a 30-cm. Dufton column. After rectification through a Todd column packed with glass helices, 1,1-dichlorocyclopentane, b.p. 141–141.2° at 746 mm.,  $n_D^{20}$  1.3709, was obtained.

(15) H. M. Teeter and E. W. Bell, *Org. Syn.*, **32**, 20 (1952).

(16) E. A. Braude and W. F. Forbes, *J. Chem. Soc.*, 1755 (1951).

***cis*-1,2-Dichlorocyclopentane.**—*trans*-2-Chlorocyclopentanol, b.p. 83–84.5° at 18 mm., was prepared by the method of Donahoe and VanderWerf.<sup>17</sup> The chlorohydrin (15 g.) was mixed with 29 g. of freshly distilled pyridine in a dropping funnel. This mixture was dropped slowly onto 42 g. of thionyl chloride contained in a 500-ml. three-necked flask equipped with a stirrer, thermometer, and condenser and maintained at 70–80°. After 2 hr. the excess thionyl chloride was destroyed by the addition of 65 ml. of ice-water and the organic layer separated and washed three times with 6-ml. portions of 10% aqueous sodium carbonate. The product was steam distilled, dried over calcium chloride, and then rectified at 20 mm. The yield of the fraction boiling at 71–74° was 1.4 g. or 8%. This fraction was found by g.l.c. to consist of 75% *cis*-1,2-dichlorocyclopentane and 25% of the *trans* isomer. Purification by preparative g.l.c. gave material 97% pure by g.l.c.,  $n_D^{20}$  1.4822.

***trans*-1,2-Dichlorocyclopentane** prepared by the method of Goering and McCarron<sup>18</sup> had a b.p. of 50.0–50.5° at 20 mm.,  $n_D^{20}$  1.4781.

***cis*- and *trans*-1,3-Dichlorocyclopentane.**—Reaction of hydrogen chloride with *trans*-1,3-cyclopentanediol<sup>19</sup> gave mainly tar, whereas reaction of the diol with thionyl chloride and pyridine yielded a small amount of an impure oil containing 9% of *trans*-1,2-dichlorocyclopentane, 52% of *trans*-1,3-dichlorocyclopentane, and 39% of *cis*-1,3-dichlorocyclopentane. Reaction of the di-*p*-toluenesulfonate prepared from *trans*-1,3-cyclopentanediol (m.p. 90.0–92.5°) with lithium chloride in ethanol at 80° yielded a small amount of dichloride whose most predominant g.l.c. peak was identical with *cis*-1,3-dichlorocyclopentane. Reaction of hydrogen chloride with 4-chlorocyclopentene in petroleum ether occurred slowly at 0°. By g.l.c. analysis, only *cis*- and *trans*-1,3-dichlorocyclopentane were formed.

***cis*-1,3-Dichlorocyclopentane** was isolated from a chlorination of 150 g. of chlorocyclopentane in 500 ml. of a 1:1 mixture of carbon tetrachloride and benzene at –10°. After the addition of 40 g. of chlorine vapor, the solvent was removed using a simple distillation head. The isomeric dichlorocyclopentanes were rectified in a Todd column packed with glass helices at 70 mm. The fraction, b.p. 102.6° at 70 mm.,  $n_D^{20}$  1.4868,  $n_D^{25}$  1.4839, was proved to be *cis*-1,3-dichlorocyclopentane by n.m.r. Purity of this fraction was determined by g.l.c. to be 96.4% *cis*-1,3-dichlorocyclopentane, 0.5% *trans*-1,3-dichlorocyclopentane, and 3.1% *cis*-1,2-dichlorocyclopentane.

***trans*-1,3-Dichlorocyclopentane** was isolated in high purity from the photochlorination of chlorocyclopentane. The n.m.r. spectrum confirmed the structure of the fraction, b.p. 89.2° at 70 mm.,  $n_D^{20}$  1.4822,  $n_D^{25}$  1.4800, as that of *trans*-1,3-dichlorocyclopentane.

**1-Bromo-1-chlorocyclopentane.**—A method similar to that reported by Goering and Sims was employed.<sup>20</sup> Reaction of anhydrous hydrogen bromide with 1-chlorocyclopentene gave material boiling at 75–79° at 14 mm. which consisted of 83% of 1-bromo-1-chlorocyclopentane and 13% of 1-chlorocyclopentene by g.l.c. analysis.

***trans*-1-Bromo-2-chlorocyclopentane.**—The method of Goering and Sims was employed utilizing the reaction of hydrogen chloride in chloroform solution with 60 g. of cyclopentene and 165 g. of *N*-bromosuccinimide.<sup>20</sup> Distillation gave 79 g. of material, b.p. 55–67° at 12 mm. Rectification in a Todd column packed with glass helices gave pure *trans*-1-bromo-2-chlorocyclopentane, b.p. 78° at 38 mm.,  $n_D^{20}$  1.5123,  $n_D^{25}$  1.5100.

***cis*-1-Bromo-1-chlorocyclopentane.**—1-Chlorocyclopentene<sup>21</sup> (49.1 g.) in 1500 ml. of pentane was illuminated with a quartz tube mercury vapor lamp directly immersed in the solution at 0° while hydrogen bromide was passed through the solution for a period of 1 hr. Rapid distillation gave 45 ml. of material, b.p. 50–66° at 4 mm. Rectification through a 30-cm. Dufton column gave 52 g. of *cis*-1-bromo-2-chlorocyclopentane, b.p. 63.9–64.5° at 4 mm.,  $n_D^{20}$  1.5227.

***cis*- and *trans*-1-Bromo-3-chlorocyclopentane.**—The reaction of anhydrous hydrogen bromide with 3-chlorocyclopentene<sup>22</sup> at room temperature in the presence of cyclohexenyl hydroperoxide or benzoyl peroxide failed to produce either of the desired products. Reaction of 4-chlorocyclopentene with anhydrous hydrogen bromide in petroleum ether gave a product which by g.l.c. indicated the presence of both *cis*- and *trans*-1-bromo-3-chlorocyclopentane but no other bromochlorocyclopentane.

A solution of 157 g. of bromocyclopentane in 500 ml. of carbon tetrachloride was photochlorinated at –10° with 43 g. of chlorine. The reaction product was rectified in a Todd column at

(17) H. B. Donahoe and C. A. VanderWerf, *Org. Syn.*, **30**, 24 (1950).

(18) H. L. Goering and F. H. McCarron, *J. Am. Chem. Soc.*, **78**, 2270 (1956).

(19) A. C. Darby, H. B. Henbest, and I. McClenaghan, *Chem. Ind. (London)*, 462 (1962); G. Zweifel and H. C. Brown, *J. Am. Chem. Soc.*, **85**, 2066 (1963).

(20) H. A. Goering and L. L. Sims, *ibid.*, **77**, 3465 (1955).

(21) N. A. Domin and L. I. Khova, *Zh. Obshchei Khim.*, **21**, 522 (1951).

(22) R. B. Moffett, *Org. Syn.*, **32**, 41 (1952).

18.5 mm. Practically pure *trans*-1-bromo-3-chlorocyclopentane,  $n_D^{20}$  1.5147, and 91.7% *cis*-1-bromo-3-chlorocyclopentane contaminated by 1.9% *trans*-1-bromo-3-chlorocyclopentane and 6.4% of *cis*-1-bromo-2-chlorocyclopentane and an unknown compound were obtained. The n.m.r. spectra of the above fractions support the assignment of structure.

**4-Chlorocyclopentene.**—3-Cyclopenten-1-ol<sup>23</sup> (29.4 g.) in 85 ml. of petroleum ether was added dropwise to a mixture of phosphorus pentachloride (39 g.) and 85 ml. of petroleum ether. The temperature was maintained at  $-10^\circ$  during the addition

(23) E. L. Alfred, J. Sonnenberg, and S. Winstein, *J. Org. Chem.*, **25**, 26 (1960).

and allowed to slowly reach room temperature during an additional 10 hr. of stirring. The mixture was treated with ice, the organic layer washed with 10% sodium carbonate, and fractionated with a Vigreux column under reduced pressure. Pure 4-chlorocyclopentene, 2.6 g., b.p.  $39^\circ$  at 60 mm., was obtained. The n.m.r. spectrum was consistent with this structure. Reaction of 3-cyclopenten-1-ol with concentrated hydrochloric acid under reflux or with thionyl chloride and pyridine at  $40$ – $50^\circ$  failed to produce 4-chlorocyclopentene.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

## Photochlorination of Chlorocyclohexane and Bromocyclohexane<sup>1</sup>

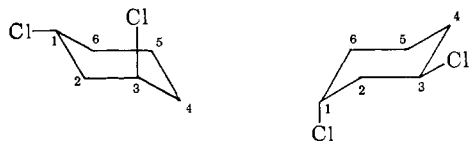
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Bromo- and chlorocyclohexane have been chlorinated at  $40$  and  $-30^\circ$  using molecular chlorine in carbon tetrachloride or carbon disulfide solution as well as *t*-butyl hypochlorite as the chlorinating agent. The seven dihalocyclohexanes have been analyzed by gas-liquid chromatography with appropriate structure proof by n.m.r. spectroscopy. A deactivating polar effect by halogen substituent was observed which became more pronounced at the lower temperature. Reaction of the  $\beta$ -,  $\gamma$ -, or  $\delta$ -halocyclohexyl radical with chlorine or *t*-butyl hypochlorite gave in all instances a preferential formation of the *trans*-dihalide.

In a continuation of a study of directive effects in the chlorination of the halocycloalkanes,<sup>3</sup> the products of chlorination of chloro- and bromocyclohexane were determined. The photochlorination of chlorocyclohexane produced the 7 expected dichlorocyclohexanes which could be separated by gas-liquid chromatography (g.l.c.). Chlorination of bromocyclohexane produced 7 isomeric bromochlorocycloalkanes in addition to *trans*-1,2-dichlorocyclohexane. Of the dichlorides, 5 were obtainable by conventional methods. For the 1,3-dichlorocyclohexanes no stereoselective syntheses could be found. By elimination, two peaks in the g.l.c. curve of the chlorination products of chlorocyclohexane could be assigned to *cis*- and *trans*-1,3-dichlorocyclohexane. These same two dichlorides were the predominant products (46 and 32% of the total dichlorides) produced in the ferric chloride-catalyzed addition of hydrogen chloride to 3-chlorocyclohexene. The dichlorides were separated from this reaction product by g.l.c. and their structures established by n.m.r. The compound with the shortest retention time in g.l.c. was assigned the *trans* structure on the basis of the spectrum given in Fig. 1. The spectrum of the isomer, considered to be *cis*-1,3-dichlorocyclohexane, is given in Fig. 2.

For the *trans* compound two equivalent conformations exist and if the rate of interconversion is rapid, protons attached to carbon atom 2 (as well as carbon atom 5),



should be equivalent and the hydrogen atoms at carbon atom 4 (or 6) should be nearly equivalent. In the *cis* compound the two possible conformations may not be present at equal concentrations or the preferred conformation may be essentially frozen. In any event the protons of the methylene groups should not be magnetically equivalent in the *cis* compound and a complex

spectrum should be expected. In view of this analysis, Fig. 1 obviously represents the *trans* compound and Fig. 2, the *cis* isomer. In the *trans* compound the methylene protons at the 2-position and the methine protons at carbon atoms 1 and 3 form an  $A_2X_2$  system giving rise to a triplet (methylene protons) at  $\tau = 7.81$  with  $J_{AX} = 5.4$  c.p.s., while the absorption due to the methine protons centered at  $\tau = 5.68$  appears to be approximately a triplet of triplets with coupling constants in the range of 5 to 5.5 c.p.s.

For the *cis* isomer the methylene protons of carbon atom 2 are non-equivalent and are strongly coupled to give approximately an AB system. The doublet centered at  $\tau = 7.3$  may well be due to half of an AB system with  $J_{AB} = 12.5$  c.p.s. A similar situation can be found in the spectrum of  $\beta$ -D-xylopyranose tetraacetate<sup>4a</sup> and 6-methyl-3-piperidinol.<sup>4b</sup> The peak at  $\tau = 6.30$  in the spectrum for *cis*-1,3-dichlorocyclohexane is due to the methine protons. Since it is at higher field than the methine protons of the *trans* compound, it appears that the preferred conformation of *cis*-1,3-dichlorocyclohexane is the diequatorial form.<sup>5</sup>

It is interesting to compare the n.m.r. spectra of the 1,4-dichlorocyclohexanes with those of the 1,3-isomers. As expected, the *cis* compound now having two equivalent conformations gives the simpler spectrum. The methine peak of the *trans* compound occurs at a slightly lower field ( $\tau = 5.82$ ) than for the *cis* compound ( $\tau = 5.94$ ), a fact which supports the reported predominance of the diaxial conformation for *trans*-1,4-dichlorocyclohexane in carbon tetrachloride solution.<sup>6</sup>

The n.m.r. spectrum of all the isomeric dichlorocyclohexanes have been recorded.<sup>7</sup>

The bromochlorocyclohexanes formed upon chlorination of bromocyclohexane were assigned structures on the basis of retention times in g.l.c. The bromo-

(4) (a) R. V. Lemieux, R. K. Kulling, H. J. Bernstein, and W. G. Schneider, *ibid.*, **79**, 1005 (1957); (b) B. Belleau and Y.-K. Au-Young, *ibid.*, **85**, 64 (1963).

(5) Since axial protons are more shielded than equatorial protons a difference in  $\tau$ -values of 0.4 is expected (L. M. Jackman, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 117. See also E. L. Eliel and M. N. Gianni, *Tetrahedron Letters*, 97 (1962)).

(6) The mole fraction of diaxial conformer is reported to be 0.75 (presumably at room temperature) on the basis of Raman spectroscopy (K. Kozima and T. Yoshino, *J. Am. Chem. Soc.*, **75**, 166 (1953)).

(7) A. Ito, Ph.D. Thesis, Iowa State University Library, 1963.

(1) (a) Directive Effects in Aliphatic Substitutions. XXII. (b) This work was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

(2) Alfred P. Sloan Foundation Fellow, 1959-1963.

(3) G. A. Russell and A. Ito, *J. Am. Chem. Soc.*, **85**, 2983 (1963).