

pected between the dipole moments of the chloro and triazoethanols.

It should also be noted that the terminal nitrogen of a linear triazo group is separated by four atoms from the hydroxy group. The chlorine is separated from the hydroxy group by only two atoms, making it more susceptible to the inductive effect which tends to decrease the resultant moment.

The dipole moment of triazoacetone, 3.64 *D*, is the resultant of the moments of the carbonyl and the triazo groups. A theoretical dipole moment has been calculated for this molecule using the method applied to 2-triazoethanol. This calculation is based on the assumptions that: (a) The acetone molecule is Y shaped. The two branches of the Y, making an angle of 110°, represent the positions of the methyl groups. The C-C-O bond angle is 125°. (b) The carbonyl group moment is 2.7 *D*.¹⁸ (c) The C-N-N angle of the triazo group is 120°¹⁶ and the group moment is 2.12 *D*. (d) Free rotation occurs about the carbonyl carbon to triazo group carbon and C-N bonds with an equal probability for all possible positions. (e) Mutual induction effects in the triazo and carbonyl groups are negligible.

(18) Smyth, ref. 13, p. 90.

The resultant moment, 3.59 *D*, is in excellent agreement with the experimentally determined value, 3.64 *D*. Hence there is little evidence for restricted rotation or interaction between the polar groups in triazoacetone.

Summary

1. The dipole moments have been determined for a series of organic triazo compounds in benzene solution at 25°. The moments, in debye units, for the triazobenzene derivatives are: *o*-nitro, 4.46; *m*-nitro, 3.56; *p*-nitro, 2.90; *o*-chloro, 2.37; *m*-chloro, 1.45; *p*-chloro, 0.30; *o*-bromo, 2.25; *m*-bromo, 1.40; *p*-bromo, 0.32; *o*-methyl, 1.39; *m*-methyl, 1.75; *p*-methyl, 1.90. For the aliphatic compounds the dipole moments are: triazoethane, 2.12; 2-triazoethanol, 2.48; and triazoacetone, 3.64 *D*.

2. The aromatic and aliphatic triazo group moments are 1.55 and 2.12 *D*, respectively.

3. The results of the determinations are evidence in favor of a linear resonating structure for the triazo group in both aromatic and aliphatic compounds.

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I-Strain as a Factor in the Chemistry of Ring Compounds^{1,2}

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The chemistry of the cycloalkane derivatives exhibits a number of highly unusual phenomena for which no general explanation has yet been advanced. For example, both chlorocyclopropane⁶ and chlorocyclobutane⁷ are far less reactive in typical displacement reactions than are simple secondary aliphatic halides. Again, chlorocyclohexane is extraordinarily inert toward the usual nucleophilic displacements reagents,⁸ although the corresponding derivatives of cyclopentane and cycloheptane are quite reactive.⁹

On the other hand, the six-membered ring derivative, cyclohexanone, is highly reactive toward carbonyl reagents, such as cyanide ion¹⁰ and semicarbazide,¹¹ whereas cyclopentanone and cycloheptanone are surprisingly inert toward these reagents. Similarly, the reaction of perbenzoic acid with the three cyclic ketones gives the same order of reactivity.¹²

(1) Chemical Effects of Steric Strains. IV.

(2) Much of the material discussed in this paper was included in two papers presented to the Division of Organic Chemistry at Meetings of the American Chemical Society on April 10, 1946, and September 15, 1947.

(3) Department of Chemistry, Purdue University.

(4) Parke, Davis and Company Fellow at Wayne University, 1945-1947.

(5) United States Rubber Company Fellow at Wayne University, 1947-1948.

(6) Gustavson, *J. prakt. Chem.*, [2] **43**, 396 (1891).

(7) Perkin, *J. Chem. Soc.*, **65**, 950 (1894).

(8) Conant and Hussey, *This Journal*, **47**, 476 (1925).

(9) Loevenich, Utsch, Moldrickx and Schaefer, *Ber.*, **62**, 3084 (1929).

(10) (a) Lapworth and Manske, *J. Chem. Soc.*, 2533 (1928); 1976 (1930); (b) Prelog and Kobelt, *Helv. Chem. Acta*, **32**, 1187 (1949).

(11) Price and Hammett, *This Journal*, **63**, 2387 (1941).

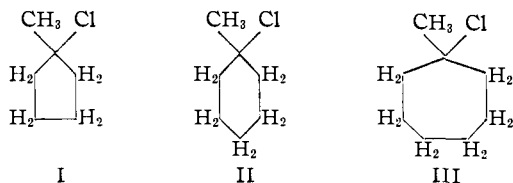
(12) Friess, *ibid.*, **71**, 2571 (1949).

The differences in reactivity between five- and seven-membered ring compounds on the one hand and the six-membered ring compounds on the other, are quite large and involve factors of the order of 100. There can be little doubt, therefore, that these differences in reactivity point to an important effect of ring size on chemical behavior.

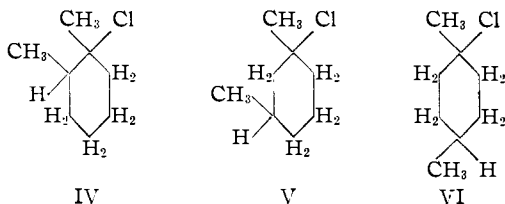
In the case of the 3- and 4-membered rings the concept of I-strain¹³ furnishes a satisfactory explanation of the inertness of chlorocyclopropane and chlorocyclobutane in bimolecular displacement reactions as well as the inertness of 1-chloro-1-methylcyclopropane and -butane in unimolecular solvolysis reactions. It is not immediately obvious that I-strain should also be an important factor in the reactions of 5-, 6- and 7-membered ring compounds. However, the I-strain hypothesis would predict that the rate of unimolecular hydrolysis of tertiary chlorides derived from these cycloalkanes should be altered by the internal strain in the ring in a manner very similar to that in which the rates of the bimolecular displacement reactions of the chlorocycloalkanes are affected. To obtain evidence on this point the rates of hydrolysis of 1-chloro-1-methylcyclopentane (I), -hexane (II) and -heptane (III) were determined.

In the course of the investigation it became of interest to observe whether methyl substituents in the cyclohexane ring would have a pronounced steric effect upon the rate of hydrolysis of the tertiary chloride (II). Accordingly, 1-chloro-1,2-(IV), 1-

(13) Brown and Gerstein, *ibid.*, **72**, 2926 (1950), and unpublished work with Mr. M. Borkowski.



chloro-1,3-(V) and 1-chloro-1,4-dimethylcyclohexane (VI) were prepared and their hydrolyses studied.



Results

The rates of hydrolysis and per cent. olefin in the product were determined by the procedures previously described.¹⁴ Rate data for a typical run are reported in Table I.

TABLE I

DATA FOR RATE OF HYDROLYSIS AND OLEFIN FORMATION FOR 1-CHLORO-1-METHYLCYCLOPENTANE IN "80% ETHANOL"^a AT 25°

Time, <i>t</i> , hr.	NaOH, ^b <i>x</i> ml.	Constant, ^c <i>k</i> ₁ , hr. ⁻¹	Na ₂ S ₂ O ₃ , ^d (<i>b</i> - <i>y</i>), ml.	<i>k</i> _E /(<i>k</i> _E + <i>k</i> _S) ^e
0	0		0	
.25	2.41	1.36		
.50	4.14	1.36	7.35	0.497
.75	5.43	1.39		
1.00	6.29	1.39		
1.50	7.40	1.42	12.86	.486
2.00	7.88	1.40	13.70	.487
∞	8.39 = <i>a</i>			

^a Density d^{25}_4 0.8496. ^b $N' = 0.03588 N$ NaOH. ^c Calculated from the expression $k_1 = 2.303/t \log a(a-x)$. ^d $N'' = 0.02009 N$ Na₂S₂O₃. ^e Olefin fraction, calculated from the expression $k_E/(k_E + k_S) = (b-y)/2x \cdot N''/N'$.

The results of the rate studies are summarized in Table II. It will be observed that the rates of hydrolysis of both 1-chloro-1-methylcyclopentane and 1-chloro-1-methylcycloheptane are much faster than the hydrolysis of typical open-chain tertiary chlorides, such as diethylmethylcarbinyl chloride, whereas the corresponding tertiary chloride derived from cyclohexane is considerably slower. The olefin formed in the hydrolysis also shows a marked difference in the cyclohexyl derivative (72% of the product) as compared with the other cyclic (49%) and open-chain (16-41%) halides.

The introduction of a methyl group in the 2-, 3- or 4-position of the 1-chloro-1-methylcyclohexane results in relatively minor changes in the first order rate constant. Certainly, the effect of the methyl substituent is very small contrasted with the very large effect observed as the cyclohexane ring is either increased or decreased by one carbon atom.

The opportunity for geometrical isomerism in these compounds raised a possible complication in the rate studies involving these tertiary chlorides. However, it has been shown that the presence of two

(14) Brown and Fletcher, *THIS JOURNAL*, **71**, 1845 (1949); *ibid.*, **2**, 1223 (1950).

TABLE II

SUMMARY OF RATE DATA FOR THE HYDROLYSIS OF THE 1-CHLORO-1-METHYLCYCLOALKANES IN "80% ETHANOL" AT 25°

Compound	<i>k</i> ₁ , hr. ⁻¹	<i>k</i> _E /(<i>k</i> _E + <i>k</i> _S)
(CH ₃) ₂ CClCH ₃	0.0330	0.16
(CH ₃)(C ₂ H ₅)CClCH ₃	.055	.34
(C ₂ H ₅) ₂ CClCH ₃	.086	.41
CH ₂ (CH ₂) ₃ CClCH ₃	1.38	.49
CH ₂ (CH ₂) ₄ CClCH ₃	0.0114	.72
CH ₂ (CH ₂) ₅ CClCH ₃	1.05	.49
CH ₃ HC-(CH ₂) ₂ -CClCH ₃	0.0098 ^a	
CH ₃ HC-(CH ₂) ₃ -CClCH ₃	.0107 ^a	
CH ₃ HC-(CH ₂) ₄ -CClCH ₃	.0168 ^a	

^a Density of solvent d^{25}_4 0.8538; for all other rate data in this table density of solvent d^{25}_4 0.8496. The rate of hydrolysis of *t*-butyl chloride in the more aqueous solvent was 0.0384 hr.⁻¹. Therefore, to be strictly comparable with the other rate constants the last three values should be reduced by approximately 14% (0.0330/0.0384 = 0.86).

tertiary chlorides which hydrolyze at different rates can be demonstrated by analysis of the rate data.¹⁵ Thus, in the present investigation the hydrolysis of 1-chloro-1-methylcycloheptane indicated the presence of a few per cent. of a tertiary chloride which hydrolyzed at a much slower rate, in the neighborhood of those observed for the chlorodimethylcyclohexanes. It is believed that the reaction of hydrogen chloride with 1-methylcycloheptanol results in the formation of a small quantity of rearranged product, presumably one of the cyclohexyl derivatives.¹⁶

The hydrolysis of the 1-chloro-1,2-, 1-chloro-1,3- and 1-chloro-1,4-dimethylcyclohexanes proceeded in a simple manner with no indication of the presence of two chlorides which hydrolyze at different rates. In order to investigate the possible effects of geometrical isomerism, 1,3-dimethylcyclohexanol was fractionated in an efficient column and separated into fractions which contained predominantly the *cis* and the *trans* isomers.¹⁷ These fractions were separately treated with hydrogen chloride at 0° to convert them to the tertiary chloride. Portions of the products, without purification, were removed and immediately used for hydrolysis studies. No significant difference in rate was observed for the two fractions ($k_1 = 0.0109 \pm 0.0007$ hr.⁻¹).

The two products were then separately fractionated through a Vigreux column under reduced pressure and separated into several fractions. Each of these fractions was then individually hydrolyzed and the rates determined. Again the rate constants were essentially the same for all fractions ($k_1 = 0.0106 \pm 0.0008$ hr.⁻¹).

Further work on this phase of the problem is desirable and is planned. However, it appears safe to conclude from these results either that the two geo-

(15) Reference 14 and unpublished work with Mrs. Fletcher.

(16) This phenomenon is under investigation with Mr. M. Borkowski.

(17) Chiurdoglu, *Bull. soc. chim. Belg.*, **47**, 241 (1938).

metrical isomers, if present, must hydrolyze at essentially the same rates, or that one of the isomers is much more stable than the other and is preferentially formed from both the *cis* and the *trans* tertiary alcohol.

Discussion

I-Strain in Small Rings.—In the case of the 3- and 4-membered ring compounds the application of the I-strain hypothesis is relatively simple and straightforward.¹⁸ I-Strain is that change in internal strain which results from change in coordination number of a ring atom involved in chemical reaction. Thus, in chlorocyclopropane the strain at the carbon atom holding the chlorine substituent may be considered to be that involved in distorting the bonds of the carbon atom from the normal tetrahedral value of 109.5° to the 60° value required by the geometry of the 3-membered ring (Fig. 1). The con-

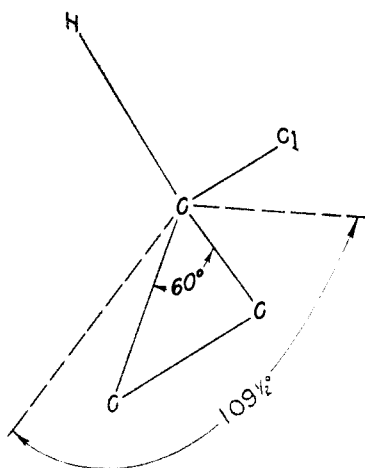


Fig. 1.—Diagram of a cyclopropyl derivative, showing distortion of angle from 109.5 to 60° .

figuration of the transition complex of a carbon compound undergoing a typical bimolecular displacement reaction is believed to be that of a trigonal bipyramid, with the preferred bond angles (R-C-R) of the three groups not participating in the displacement being 120° (Fig. 2). Thus, in the

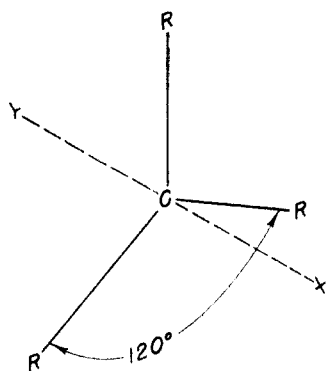


Fig. 2.—Diagram of the transition complex in a displacement reaction (S_N2).

transition complex involving the cyclopropane ring, there will be an increase in the internal strain: the strain at the carbon atom undergoing displacement will be that involved in bending the bond angle

from its preferred value of 120° to the approximately 60° value required in the ring (Fig. 3). Therefore, the angle is deformed 49.5° in the parent compound (109.5 to 60°) and 60° in the transition complex (120 to 60°). Formation of the transition complex will involve an increase in energy over and above that which would be involved in the formation of a similar transition complex from an open-chain compound.

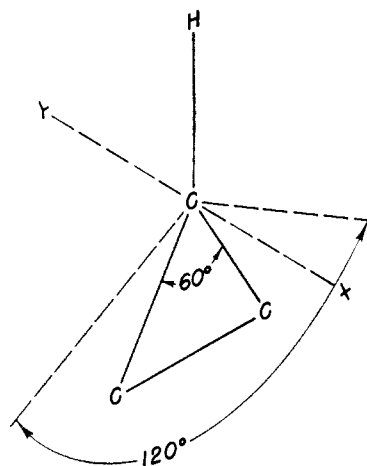


Fig. 3.—Diagram of the transition complex of a cyclopropyl derivative, showing distortion of angle from 120 to 60° .

A similar treatment leads to the conclusion that I-strain will also be a factor in the reactions of the 4-membered ring compounds. Here the deformation of the bond angles will be 19.5° in the parent compound (109.5 to 90°) and 30° in the transition complex (120 to 90°).

The argument can be generalized to the statement that in three- and four-membered carbon rings, a chemical change involving a change in coordination number of one of the ring atoms from four to five will result in an increase in internal strain (positive I-strain) which will be unfavorable for the chemical change.

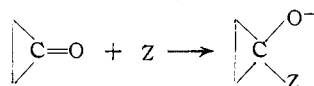
The solvolysis of a tertiary chloride in hydroxylic solvents is believed to proceed through the ionization of the halide in the rate-determining step.¹⁸ The carbonium ion is presumably planar with R-C-R bond angles of 120° . The formation of the carbonium ion will also result in increased internal strain in the case of cyclopropyl and cyclobutyl derivatives (Fig. 4). The general conclusion may be reached that the I-strain predicted for bimolecular

(18) The evidence is summarized by Hughes, *J. Chem. Soc.*, 968 (1946). Swain, *THIS JOURNAL*, **70**, 1119 (1948), has proposed that the solvolysis of tertiary halides is a termolecular reaction which involves both a "pull" by a solvent molecule on the halogen being substituted and a "push" by another solvent molecule attacking the carbon atom undergoing substitution. According to this interpretation there would be no important difference in the nature of the intermediates involved in the two reaction types which Hughes and Ingold have termed unimolecular and bimolecular. Fortunately for the simplicity of the present discussion the application of the I-strain concept to either interpretation leads to the same answer. Either intermediate, the carbonium ion (Hughes and Ingold) with the central carbon having coordination number three, or the activated complex (Swain) with the central carbon having coordination number five, will have configurations with preferred R-C-R bond angles of 120° . Since Swain has not yet shown how his interpretation can explain the large number of phenomena so nicely accounted for by Hughes and Ingold, the latter's approach has been adopted here.

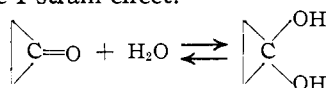
displacement reactions in cyclopropyl and cyclobutyl compounds will be paralleled in the unimolecular reactions of these small rings. This prediction has been verified in the unimolecular hydrolysis of 1-chloro-1-methylcyclopropane and 1-chloro-1-methylcyclobutane. Both of these tertiary chlorides hydrolyze at a much slower rate than do open-chain tertiary chlorides.¹³

The generalization previously proposed may then be extended. Reactions of 3- and 4-membered carbon rings requiring in the rate-determining stage a change in the coordination number of one of the ring atoms from four to five or from four to three will result in positive I-strain and in decreased reaction rates.

The same concept predicts that reactions of small rings involving a change in coordination number of a ring atom from three to four should involve a decrease in internal strain (negative I-strain).



Reactions of this type should be strongly favored in the 3- or 4-membered rings. Thus, the I-strain concept predicts that the reactions of cyclopropanone and cyclobutanone with typical carbonyl reagents should be very rapid¹⁹ and equilibria involving addition to the carbonyl group of small ring compounds should be strongly favored. Reactions of this type do not appear to have been studied quantitatively. However, cyclopropanone has been obtained only as the hydrate.²⁰ It may be considered that the addition of water to the carbonyl group is a reaction of this type and in cyclopropanone the usual equilibrium between a ketone and its hydrate is strongly shifted to the right as a result of the I-strain effect.



Reactivity of the Common²¹ Ring Compounds.—Application of the I-strain concept to the 5-, 6-

(19) For this statement to be valid the reaction should involve as the rate-determining step the coordination of the reagent with the carbonyl carbon. Most reactions involving carbonyl groups which have received careful attention appear to be of this type. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 329. However, cyclopropanone has been isolated only in the form of its hydrate and cyclobutanone is probably also strongly hydrated in aqueous solutions. Carbonyl reactions of these cyclic ketones may well involve some other reaction in the rate-determining step than the simple coordination of the reagent with the carbonyl group. In such a case, the high reactivity predicted for the small ring ketones would be observed only in non-hydroxylic solvents where prior reaction of the solvent with the carbonyl group would not interfere with the rate of the carbonyl reaction.

(20) Lipp, Buchkremer and Sees, *Ann.*, **499**, 1 (1932).

(21) In discussing the chemistry of ring compounds, it is convenient to possess terms to designate individual groups of rings of specified number of ring members. Such groups should contain ring systems which possess well recognized general characteristics. As a result of correspondence with Professor V. Prelog of the Institute of Technology in Zürich, the following classification is suggested.

- Small rings: 3- and 4- members
- Common rings: 5-, 6-, and 7- members
- Medium rings: 8- to 12- members
- Large rings: 13- members and larger

Professor Korubium of Purdue University has suggested the title, the classical rings, as a generic term to include the first two groups. The last two groups together would continue to be termed the many-membered rings.

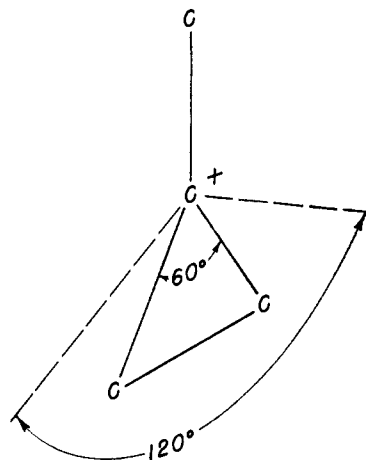


Fig. 4.—Diagram of the carbonium ion of a cyclopropyl derivative, showing distortion of angle from 120 to 60°.

and 7-membered ring compounds is not as direct as in the small rings. In the common rings the bond angles are presumably not far from the normal tetrahedral values.²² Any strains present in these rings presumably arise from torsional forces about carbon-carbon single bonds which result in the molecules assuming constellations²³ to minimize the energy.²⁴ Calculation of the various interactions and the resulting energies of the ring compounds is quite involved and is not yet on a precise quantitative basis.²⁴

Relative small differences in internal strain can have very large effects upon the rates and equilibria of reactions of these ring compounds. It therefore appears desirable to adopt here an empirical approach to the question of the importance of I-strain in the chemistry of the common ring compounds. Thus, an examination of the effect of ring size on reaction rates and equilibria should demonstrate whether the reactions are affected in a consistent, systematic manner as the coordination number of a ring atom is altered during the reaction from (a) four to five (SN2), (b) four to three (SN1), and (c) three to four (carbonyl reactions).

Data concerning such reactions of the common ring compounds are summarized in Table III.

The data for bimolecular displacement reactions (reactions 1-3) are fragmentary and largely qualitative in nature. However, they do indicate that in such reactions the 6-membered rings are much less reactive than the 5- and 7-membered rings. Moreover, in reactions 4-6, where the reaction involves an ionization of one of the atoms on the ring carbon, it is evident that here also the 6-membered ring compounds are less reactive than simple open-chain and 5- and 7-membered ring derivatives. Finally, in reactions 7-11, which involve addition to the carbonyl group, and in reaction 12, which involves addition to the semicarbazone group,





(22) Sachse, *Z. physik. Chem.*, **10**, 203 (1892); Mohr, *J. prakt. Chem.*, [2] **98**, 315 (1918).

(23) Prelog, *J. Chem. Soc.*, 424 (1950).

(24) Pitzer, *Science*, **101**, 672 (1945); Kilpatrick, Pitzer and Spitzer, *This Journal*, **69**, 2483 (1947); Beckett, Pitzer and Spitzer, *ibid.*, **69**, 2488 (1947). These torsional forces are usually attributed to hydrogen-hydrogen repulsion terms which stabilize the "staggered" as compared to the "opposed" constellation.

TABLE III

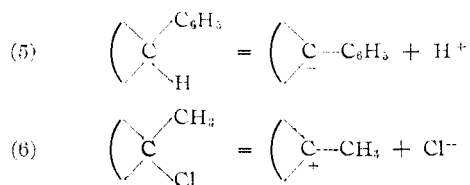
EFFECT OF RING SIZE ON REACTION RATE AND EQUILIBRIA OF FIVE-, SIX- AND SEVEN-MEMBERED RING COMPOUNDS

Reaction	Conditions	Constant	Compound				Ref
							
1 $\begin{array}{c} \text{H} \\ \\ \text{C} \\ \\ \text{Br} \end{array} + \delta\text{-C}_6\text{H}_7\text{NH}_2 = \begin{array}{c} \text{H} \\ \\ \text{C} \\ \\ \text{NHCH}_2\text{H}_7 \end{array} + \text{C}_6\text{H}_6$	Reflux 1 hr., no solvent	% Br ⁻ produced	83.6	18.6	73.4	^a	
2 $\begin{array}{c} \text{H} \\ \\ \text{C} \\ \\ \text{Br} \end{array} + \text{K}_2\text{CO}_3 = \text{olefin} + \text{alcohol}$	Reflux 24 hr., 28.5% aq. K ₂ CO ₃	% Br ⁻ produced	81.4	10.1	35.2	^a	
3 $\begin{array}{c} \text{H} \\ \\ \text{C} \\ \\ \text{Cl} \end{array} + \text{I}^- = \begin{array}{c} \text{H} \\ \\ \text{C} \\ \\ \text{I} \end{array} + \text{Cl}^-$	Acetone, 60°	<i>k</i> ₂ (l. mole ⁻¹ hr. ⁻¹)	0.0015		0.0001	^b	
4 $\begin{array}{c} \text{H} \\ \\ \text{C} \\ \\ \text{Br} \end{array} + \text{Hg}^{2+} = \begin{array}{c} \text{H} \\ \\ \text{C} \\ \\ \text{HgBr} \end{array}$	70% dioxane, 25°	<i>k</i> ₂ (l. mole ⁻¹ min. ⁻¹)	30.5		8.15	^c	
5 $\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{C} \\ \\ \text{H} \end{array} + \text{R}^+\text{K}^- = \begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{C} \\ \\ \text{K}^- \end{array} + \text{RH}$	Ether, 25°	Relative acid. at equil.	Med.	High	Low	^d	
6 $\begin{array}{c} \text{CH}_3 \\ \\ \text{C} \\ \\ \text{Cl} \end{array} = \begin{array}{c} \text{C} \\ \\ \text{CH}_3 \end{array} + \text{Cl}^-$	80% alc, 25°	<i>k</i> ₁ (hr. ⁻¹)	0.6330	1.38	6.0114	1.05	^e
7 $\text{C}=\text{O} + \text{CN}^- = \begin{array}{c} \text{O}^- \\ \\ \text{C} \\ \\ \text{CN} \end{array}$	Equil. 20°, 96% alc.	<i>K</i> (l. mole ⁻¹)	32.8	67.1	1087	14.6	^f
8 $\text{C}=\text{O} + \text{CN}^- = \begin{array}{c} \text{O}^- \\ \\ \text{C} \\ \\ \text{CN} \end{array}$	Equil. 22-23°, 100% alc.	<i>K</i> (l. mole ⁻¹)	14.3 ^g	47.6	1000	7.69	
9 $\text{C}=\text{O} + \text{H}_2\text{NNHCONH}_2 = \begin{array}{c} \text{C}=\text{NNHCONH}_2 \\ \\ \text{O} \end{array} + \text{H}_2\text{O}$	Buffer pH 7.0, 25°	<i>k</i> ₂ (l. mole ⁻¹ sec. ⁻¹)	0.0861	0.0153	0.512		^h
10 $\text{C}=\text{O} + \text{C}_6\text{H}_5\text{CO}_2\text{H} = \begin{array}{c} \text{O}^- \\ \\ \text{C}=\text{O} + \text{C}_6\text{H}_5\text{CO}_2\text{H} \end{array}$	Moist chloroform, dark, 27°	<i>k</i> ₂ (l. mole ⁻¹ sec. ⁻¹) × 10 ⁶	12.3 ⁱ	17.3	106	1.69	ⁱ
11 $\text{C}=\text{O} + \text{H}_2 = \begin{array}{c} \text{H} \\ \\ \text{C} \\ \\ \text{OH} \end{array}$	Equilibrium, gas phase, 200°	<i>K</i> (l. mole ⁻¹) ΔH_{98}° (cal.)	0.848 ^j -12,960 ^j	0.918 -12,260	6.6 -15,233		^j
12 $\text{C}=\text{NNHCOCH}_2\text{N}^+(\text{CH}_3)_3 + 2e + 2\text{H}^+ = \text{CHNHNHCOCH}_2\text{N}^+(\text{CH}_3)_3$	Polarographic redn. at pH 8.2	Half-wave potential, v.	-1.56	-1.58	-1.51	-1.61	^k

^a Loevenich, Utsch, Moldrickx and Schaefer, *Ber.*, **62**, 3084 (1929). ^b Conant and Hussey, *THIS JOURNAL*, **47**, 476 (1925). ^c Benfey, *ibid.*, **70**, 2163 (1948). ^d Kleene and Wheland, *ibid.*, **63**, 3321 (1941). ^e Present investigation. ^f Lapworth and Manske, *J. Chem. Soc.*, 2533 (1928); 1976 (1930). ^g Prelog and Kobelt, *Helv. Chim. Acta*, **32**, 1187 (1949). The figure for the open-chain compound refers to di-*n*-octyl ketone. ^h Price and Hammett, *THIS JOURNAL*, **63**, 2387 (1941). ⁱ Friess, *ibid.*, **71**, 2571 (1949). The value for the open-chain compound is for methyl isopropyl ketone (private communication). ^j Cubberley and Mueller, *ibid.*, **68**, 1149 (1946); **69**, 1535 (1947). The data for the open-chain compound is for 2-butanone. ^k Prelog and Häfner, *Helv. Chim. Acta*, **32**, 2088 (1949).

it is observed that reactions involving the 6-membered ring are highly favored over the corresponding reactions of open-chain and 5- and 7-membered ring compounds.

Reactions 5 and 6 strongly support the position that the cause of these differences in reactivity must be steric, rather than polar, in origin. Thus, reaction 5 involves, in effect, the separation of a positive hydrogen ion from the cycloalkane ring; reaction 6 involves the separation of a negative chloride ion



The similarity of the structural effects in the two reactions emphasizes that we must be dealing with a steric effect of some kind and not an unusual polar effect of cyclic systems.

The Inertness of Cyclohexyl Halides.—The inertness of cyclohexyl halides in displacement

reactions has been noted frequently in the literature.^{8,9,25} The sluggish reactions of cyclohexyl halides have usually been considered to be due to a steric effect in which the puckering of the ring hindered the approach of the attacking reagent. Thus Bartlett and Rosen^{25a} state: "The resistance of cyclohexyl halides to bimolecular displacement reactions might be accounted for on steric grounds, as involving shielding by the unreacting portion of the strainless ring. . ."

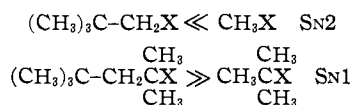
There are a number of difficulties with this interpretation. First, cyclohexanone is highly reactive toward carbonyl group reagents. If steric hindrance were an important factor in the displacement reactions of cyclohexyl halides, it should also markedly affect the approach of these reagents to the carbonyl group. Certainly, in the aliphatic series, large bulky groups which markedly reduce the displacement reactions also reduce the rates of carbonyl group reactions.

Second, cycloheptyl halides appear to be highly reactive in displacement reactions. Examination of the molecular models, Figs. 5 and 6, do not in-

(25a) Bartlett and Rosen, *THIS JOURNAL*, **64**, 543 (1942); (b) Solomon and Thomas, *ibid.*, **72**, 2028 (1950).

dicating any marked steric differences in the approach to one of the ring atoms.

Third, the inertness of cyclohexane derivatives in displacement reactions is reflected in the slow unimolecular hydrolysis of 1-chloro-1-methylcyclohexane. However, in other instances large bulky groups, which markedly hinder bimolecular displacement reactions of alkyl halides, markedly favor the unimolecular solvolysis of such tertiary halides.^{14,25a} Thus, the replacement of an α -hydrogen in methyl and *t*-butyl halides has pronounced opposite effects.



If the inertness of cyclohexyl halides were due to the large steric requirements of the bulky puckered ring, it would have been anticipated that these requirements would have favored the unimolecular reaction of the tertiary halide.

Finally, the introduction of a methyl group in the 2-, 3- or 4-position of the cyclohexane ring has little effect either on the reactions of cyclohexanone^{10a} or on the reactions of 1-chloro-1-methylcyclohexane (Table II). Certainly, if the reactions of the parent cyclohexane derivatives were already strongly hindered sterically, their reactions would be expected to be markedly affected by the presence of methyl groups in the ring. The absence of marked effects of this kind, suggest that such steric hindrance effects are not a major factor in the reactions of cyclohexane derivatives.^{25b}

We are thus forced to the conclusion that the inertness of cyclohexane derivatives relative to open-chain and 5- and 7-membered ring compounds must be due to a steric effect, but cannot be the result of classical steric hindrance effects.

I-Strain in the Common Rings.—It is proposed that the unusual changes in reactivity observed in the 5-, 6- and 7-membered ring compounds are primarily due to I-strain. Consider how the peculiar changes in reactivity may be simply correlated and systematized with the aid of this concept.

The data in Table III are fragmentary and of variable quality. Although more complete and more precise data on the reactions of cyclic compounds are desirable, the following conclusions appear to be in substantial accord with the available information.

Reactions involving a change in coordination number of the ring atom from four to five (No. 1-3) and four to three (No. 4-6) are strongly favored in the 5- and 7-ring compounds relative to the 6-ring derivatives. Reactions involving a change in coordination number of the ring atom from three to four (No. 7-12) are strongly favored in the 6-ring derivatives relative to the 5- and 7-ring compounds. There must be an important factor which in a cyclohexane ring atom strongly favors the change in coordination number from three to four and opposes the change from four to five or four to three.

The cyclohexane ring with six tetrahedral carbon atoms is highly symmetrical and stable, with

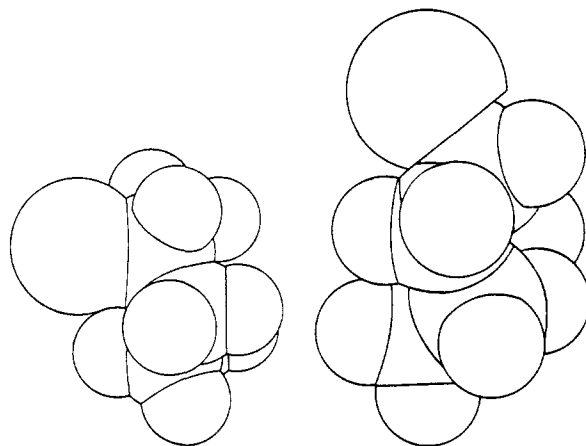


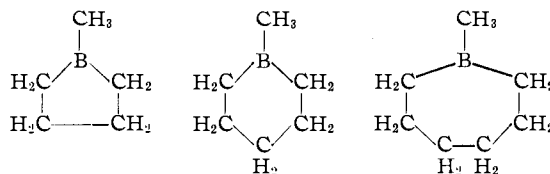
Fig. 5.—Molecular model of cyclohexyl bromide. Fig. 6.—Molecular model of cycloheptyl bromide.

hydrogen-hydrogen repulsions reduced to a minimum in the chair form as a result of the fully staggered constellation permitted by this form.²⁴ Enlargement of one of the ring ($\text{C}-\text{C}-\text{C}$) angles will decrease the symmetry, decrease the puckering, and increase the hydrogen-hydrogen repulsions. The increase in the angle will lead to an *increase* in internal strain (positive I-strain). Therefore, in cyclohexane derivatives I-strain will oppose reactions of cyclohexane derivatives involving a change in covalency of a ring atom from either four to five or four to three. Conversely, in these compounds a change in covalency from three to four will involve a *decrease* in internal strain (negative I-strain). Such reactions will be strongly favored.

On the other hand, 5- and 7-membered rings are appreciably strained, primarily as a result of the torsional forces about carbon-carbon single bonds.^{23,24,26} It is proposed that the introduction of an atom with a preferred 120° angle leads to a decrease in internal strain. Therefore, I-strain will favor reactions involving changes in coordination number from four to five or four to three and oppose reactions involving covalency changes from three to four.

Justification for the concept is furnished by the observation that both 5- and 7-membered carbon rings are under considerable strain, whereas 6-membered rings are relatively strain-free.

Thus Spitzer and Huffman²⁶ report heats of combustion per methylene group for cyclopentane 158.7, cyclohexane 157.4 and cycloheptane 158.3 kcal. One might attempt to present theoretical arguments to justify the proposed changes in I-strain in ring compounds with changes in coordination number of a ring atom.²⁷ However, at the



(26) Spitzer and Huffman, *THIS JOURNAL*, **69**, 211 (1947).

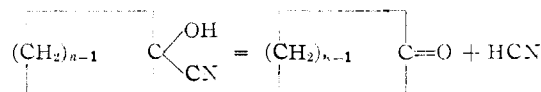
(27) In this connection it would be of interest to have the heats of formation of the heterocyclic boron compounds to compare with those of the alicyclic derivatives.

present time a more satisfactory test of the value of the concept would appear to be furnished by its utility in correlating the change in reactivities of the common ring compounds with ring size. A thoroughly satisfactory test will require much more extensive and precise data on rates of reactions and energies of activation, equilibrium constants and heats of reaction, than are now available (Table III). It is hoped that workers in other laboratories will assist in gathering precise quantitative data on a number of representative reactions of these ring compounds and thereby permit a rigorous test of the value of the I-strain concept in the common ring derivatives.²⁸

It should be emphasized that many other factors, such as steric hindrance or F-strain, entropy effects, etc., will affect the relative rates of reactions of the cycloalkane derivatives. It is here proposed only that I-strain is a highly important factor which may be expected to strongly influence all of the reactions of cyclic compounds in the manner indicated, and in cases where it is the predominant factor affecting reactivity, I-strain should lead to

a very simple and predictable order of reactivity for cyclic derivatives.

I-Strain in the Medium Rings.²⁹—Rings in the range of 8- to 12-members are relatively difficult to form by either the classical Ruzicka technique³⁰ or by Ziegler's high dilution technique.³¹ Moreover, many physical properties of the cyclanes and their derivatives show extreme values in this range. Prelog²⁹ has pointed out that extreme values of chemical properties are also observed in rings of this range. Thus, for the reaction



he reports³² the following dissociation constants:

n	5	6	7	8	9	10
$K \times 10^2$	2.1	0.1	13	86	170	large
n	11	12	13	14	16	20
$K \times 10^2$	112	31	26	6	9	7

Prelog points out that in these reactions that reaction component is stabilized which contains a more nucleophilic oxygen (or nitrogen). He suggests that rings in this range can exist in two extreme constellations, which he terms "O-outside" and "O-inside" (Figs. 7, 8). The "O-inside" constellation presumably is stabilized by interaction with the carbon-hydrogen bonds (weak hydrogen bonding). He therefore proposes that reactions which would decrease the nucleophilic properties of the substituent atom (oxygen in the case of the cyclanones) would be opposed by the energy involved in such hydrogen bonding.

There is one apparent difficulty with this interpretation. If the "O-inside" constellation is markedly stabilized by the interaction of the nucleophilic substituent with carbon-hydrogen bonds as postulated, it is not entirely clear why this factor does not also serve to stabilize the "O-inside" configuration in the larger rings in the 14 to 18 range. Yet the reactions of these ring compounds are entirely normal and do not differ markedly from those of simple open-chain derivatives. Certainly, in the open-chain derivatives with relatively short chains, such carbon-hydrogen interaction must be negligible.

The I-strain concept is capable of explaining the same observations without the necessity of assuming specific constellations for the ring systems. All the evidence points to considerable internal strain in the 8- to 12-membered rings, strains due primarily to carbon-hydrogen repulsion. Reactions involving a change in coordination number from four to five or four to three would involve a decrease in strain and would proceed with ease. Reactions involving a change in coordination number from three to four would involve an increase in strain and such reactions would be hindered. All known facts about the 8- to 12-membered rings are readily explained in terms of this

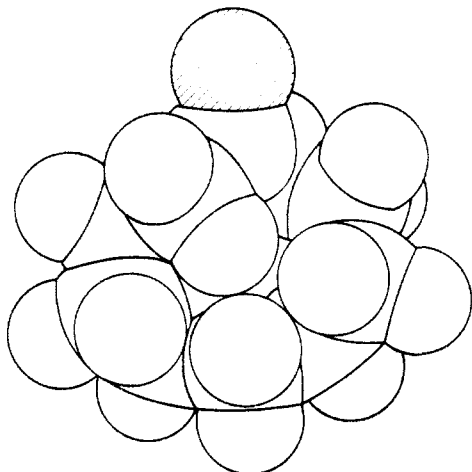


Fig. 7.—Molecular model of cyclodecanone "O-outside" structure.

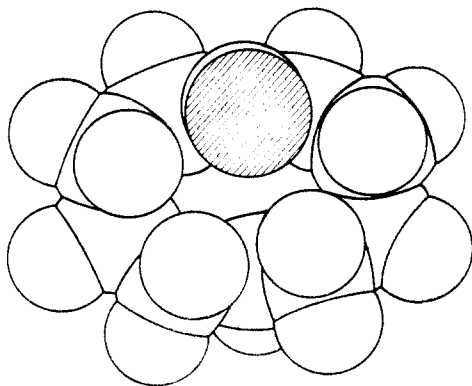


Fig. 8.—Molecular model of cyclodecanone "O-inside" structure.

(28) At present we are engaged in studies of the hydrolysis of the 1-chloro-1-methylcycloalkanes (3- to many-membered rings), the displacement reactions of the cycloalkyl halides, and the chlorination of the cycloalkanes. No other studies in this field are contemplated in the near future.

(29) For an excellent review of the subject, see Prelog, *J. Chem. Soc.*, 420 (1950).

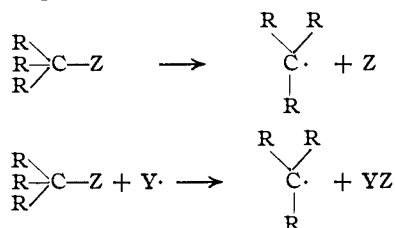
(30) Ruzicka, Brögger, Pfeiffer, Schinz and Stoll, *Helv. Chim. Acta*, 9, 499 (1926).

(31) Ziegler, Eberle and Ohlinger, *Ann.*, 504, 94 (1933).

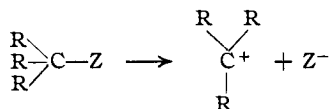
(32) Prelog and Kobelt, *Helv. Chim. Acta*, 32, 1187 (1949).

concept. We are at present seeking an experimental test of the relative advantages of the two alternative methods of correlating the data. However, the I-strain concept does appear to be of wider utility, since it is applicable to rings of all sizes, whereas Prelog's interpretation does not appear to be directly applicable to the small and to the common rings.

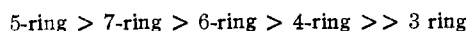
I-Strain in Free-Radical Reactions of Ring Compounds.³³—Reactions involving homolysis of an electron-pair bond as the rate-determining step are also susceptible to analysis in terms of the I-strain concept. Such reactions as



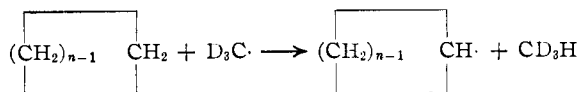
involve the formation of a free radical in which the central carbon atom possesses coordination number three. The free radical is believed to be planar with R-C-R bond angles of 120°. Therefore, the changes in internal strain accompanying homolysis of the C-Z bond should closely parallel the changes in internal strain accompanying heterolysis of the C-Z bond, as in the reaction



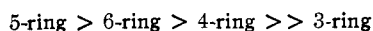
It may therefore be predicted that homolysis of the C-Z bond in ring compounds should exhibit the order of reaction rates



However, data to test this prediction were not available in the literature at the time this paper was prepared and it did not appear desirable to include a discussion of this point. Fortunately, at the Symposium on Anomalies in Reaction Kinetics, held at the University of Minnesota on June 19-21, 1950, under the auspices of the Division of Physical and Inorganic Chemistry of the American Chemical Society, data were presented which support this prediction. Drs. Trotman-Dickenson and Steacie of the National Research Council, Ottawa, Canada reported that they had studied the reaction



and had observed the order for the relative reaction rates



The energies of activation for the reaction parallel these reactivities with 10.3 kcal. for cyclopropane, 9.3 for cyclobutane and 8.3 kcal. for cyclopentane.³⁴

(33) Added to manuscript July 15, 1950.

(34) The authors wish to express their deep appreciation to Drs. Trotman-Dickenson and Steacie for their kind permission to mention their unpublished results.

It would be highly desirable to have cycloheptane and the higher cycloalkanes studied in this reaction. However, the observed order gives strong support to the utility of the I-strain concept.

Conclusion

The available information on the reactions of cycloalkanes and their derivatives can be correlated and systematized in terms of the change in internal strain accompanying a change in coordination number of the ring atom participating in the reaction (I-strain). This approach to the reactions of cyclic compounds appears to be highly promising in clarifying the unusual chemistry of these compounds.

Experimental Part

Materials.—The solvent used for the hydrolyses was an ethanol-water mixture, approximately 80% ethanol by volume. Two separate batches were made up and used. The density of each batch is recorded in Table II, together with information as to which solvent was used for each kinetic study.

The starting materials for the synthesis of the tertiary chlorides were cyclic ketones. Cyclohexanone and 3- and 4-methylcyclohexanone were Eastman Kodak Co. chemicals. Cyclopentanone was prepared from adipic acid.³⁵ Cycloheptanone was prepared from cyclohexanone by treatment with nitrosomethylurethan in the presence of an alkaline catalyst.³⁶ 2-Methylcyclohexanone was prepared from 2-methylcyclohexanol by dichromate oxidation.³⁷ The physical constants of the cyclic ketones used agreed satisfactorily with literature values.

The desired tertiary alcohols were prepared by reaction of methylmagnesium iodide with the cyclic ketones. The tertiary alcohols were purified by fractional distillation, and were converted to the tertiary chlorides as described previously.¹⁴ The dimethylcyclohexanols and the dimethylchlorocyclohexanes distilled over a relatively wide temperature range. The substances presumably consisted of a mixture of *cis*- and *trans*-derivatives. However, in this phase of the investigation no attempt was made to separate the substances into their individual isomers. (However, see below for 1,3-dimethylcyclohexanol and chloride.) Physical constants of the tertiary alcohols and chlorides are listed in Table IV.

TABLE IV

PROPERTIES OF CYCLIC ALCOHOLS AND CHLORIDES

	B. p., °C.	Mm.	n_D^{20}
1-Methylcyclopentanol	133-136	745	M. p. 32-34°
1-Methylcyclohexanol	66.5-67.5	20	1.4605
1-Methylcycloheptanol	91.5-92.5	46	1.4653
1,2-Dimethylcyclohexanol	80-90	41	1.4565-1.4588
1,3-Dimethylcyclohexanol	69-79	18	1.4495-1.4532
1,4-Dimethylcyclohexanol	155-170	740	Solid
1-Chloro-1-methylcyclopentane	69.0-69.2	127	1.4446
1-Chloro-1-methylcyclohexane	65.2-65.5	44	1.4559
1-Chloro-1-methylcycloheptane ^a	88.0-89.0	40	1.4681
1-Chloro-1,2-dimethylcyclohexane	54-63	17	1.4601
1-Chloro-1,3-dimethylcyclohexane	56-58	16	1.4524
1-Chloro-1,4-dimethylcyclohexane	52-58	17	1.4503

^a New compound: 1.215 millimoles of chloride required 1.198 millimoles of standard sodium hydroxide.

Kinetic Studies.—The rates of hydrolysis and amount of olefin formation were measured in 80% ethanol as described in a previous paper.¹⁴ The alcohol used for the dimethylchlorocyclohexane hydrolyses had a slightly higher water content than did that used for the remaining chlorides. By studying the rate for *t*-butyl chloride in both solvents, it was

(35) Thorpe and Kon, "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 192.

(36) Kohler, Tishler, Potter and Thompson, *THIS JOURNAL*, **61**, 1057 (1939).

(37) The procedure described for the oxidation of menthol to menthone was used: Sandborn, ref. 35, p. 340.

ascertained that the more aqueous solvent gave rates some 14% higher. This correction has not been applied to the results reported in Table II, but is relatively small compared to the magnitude of the effects observed.

For all the halides reported in this paper, good first-order rate constants were obtained, except in the case of 1-chloro-1-methylcycloheptane (Table V). In this case the calculated rate constants showed a decrease with time, indicating the presence in the tertiary chloride of a few per cent. of a tertiary chloride which hydrolyzes at a relatively slow rate.¹⁴ A complete analysis of the data was attempted, but the amount of the slow hydrolyzing component is so small that the results were not very satisfactory.

TABLE V

RATE DATA FOR HYDROLYSIS OF 1-CHLORO-1-METHYL-CYCLOHEPTANE

Time, t hr.	NaOH, ^a x ml.	Constant, k_1 , hr. ⁻¹	$\text{Na}_2\text{S}_2\text{O}_8$, ^b $(b - y)$, ml.	$k_E/(k_E + k_S)$
0	0		0	
0.25	1.71	1.06		
.50	3.02	1.05	5.47	.501
.75	4.02	1.05		
1.00	4.76	1.04		
1.50	5.73	1.00	10.22	.493
2.00	6.25	0.942	11.13	.493
2.50	6.54	.874		
3.00	6.72	.810	11.92	.491
3.50	6.81	.736		
4.00	6.85	.663	12.14	.490
∞	7.37 = a			

^a $N' = 0.03620$ N NaOH. ^b $N'' = 0.02003$ N $\text{Na}_2\text{S}_2\text{O}_8$.

The excellent first order rate constants obtained for the three methyl derivatives of 1-chloro-1-methylcyclohexane, illustrated in Table VI for the 1,3-dimethyl compound, indicate the absence of two components which hydrolyze at markedly different rates.

TABLE VI

RATE DATA FOR HYDROLYSIS OF 1-CHLORO-1,3-DIMETHYL-CYCLOHEXANE

Time, hr.	0	2.0	4.0	6.0	8.0	24.0	28.0
$a - x$, ml.	6.74	6.59	6.45	6.33	6.20	5.20	4.99
k_1 , hr. ⁻¹		0.0110	0.0110	0.0101	0.0105	0.0108	0.0107

Preparation and Hydrolysis of Chlorides from *cis*- and *trans*-1,3-Dimethylcyclohexanol.—The tertiary alcohol from the action of methylmagnesium iodide on 3-methylcyclohexanone was repeatedly distilled under reduced pressure through a short column of 15 theoretical plates until two major fractions were obtained: a *trans*-rich fraction, b.p. 66.3–70.6 (19 mm.), m.p. 6–10° and a *cis*-rich fraction, b.p. 68.0–71.0 (15.2 mm.), m.p. 23–27°.¹⁵

The *cis*-rich and *trans*-rich fractions were individually

TABLE VII

SUMMARY OF RATE CONSTANTS FOR 1-CHLORO-1,3-DIMETHYL-CYCLOHEXANE

Chloride	k_1 , hr. ⁻¹
Chloride from mixture of isomeric alcohols (Table VI)	0.0107
Chloride from <i>cis</i> -rich alcohol fraction	
Before distillation	.0106
Fraction No. 1	.0101
Fraction No. 2	.0101
Fraction No. 3	.0111
Chloride from <i>trans</i> -rich alcohol fraction	
Before distillation	.0113
Fraction No. 1	.0108
Fraction No. 2	.0110
Fraction No. 3	.0105

(38) Chiurdoglu, *Bull. soc. chim. Belg.*, **47**, 241 (1938), reports a m. p. of 13.5° for the pure *trans* isomer and 27° for the pure *cis* compound.

treated with hydrogen chloride at 0° to convert the alcohols to the tertiary chlorides. The organic layers were quickly separated from the lower aqueous layer and dissolved hydrogen chloride removed from the organic layer by a short exposure to a vacuum. Samples were removed and the rates of hydrolysis determined.

The two samples of tertiary chlorides were then distilled individually under vacuum (21 mm.) through a Vigreux column and three fractions each collected. The rates of hydrolysis of each fraction were then determined. The results are summarized in Table VII.

The individual fractions show only slight differences in the first order rate constant. It must be concluded either that the isomeric tertiary chlorides hydrolyze at practically the same rate or that one of the isomeric tertiary chlorides is markedly more stable than the other isomer and is formed preferentially, to the practical exclusion of the less stable isomer.

Acknowledgment.—A preliminary investigation of the problem was carried out in 1945 with the aid of financial assistance from Grants 710 and 776 of the Penrose Fund of the American Philosophical Society. This assistance as well as the assistance afforded by graduate fellowships supported by Parke, Davis and Company and by the United States Rubber Company is gratefully acknowledged. The authors also wish to express their appreciation for valuable comments and assistance obtained in discussions and correspondence with Professor V. Prelog (Technical Institute, Zürich), Dr. D. H. R. Barton (Birkbeck College, London) and Dr. D. M. Wepster (Delft Technical University, Holland).

Summary

1. Rates of hydrolysis at 25° in 80% ethanol have been measured for 1-chloro-1-methylcyclopentane, -hexane, -heptane, 1-chloro-1,2-, 1-chloro-1,3- and 1-chloro-1,4-dimethylcyclohexane. *cis*- and *trans*-rich fractions of 1,3-dimethylcyclohexanol have been converted to chlorides at 0° and the rates of hydrolysis of the individual products measured.

2. Olefin formation is high for the cyclohexane derivative and is considerably lower for the 5-ring and 7-ring tertiary chlorides.

3. The first order rate constant for the solvolysis is quite small for the cyclohexane derivative and very large for the cyclopentane and cycloheptane derivatives. The introduction of a methyl group in the 2-, 3- and 4-positions of the cyclohexane ring has relatively little effect upon the rate of hydrolysis of the tertiary chloride derived from cyclohexane.

4. It is pointed out that this relative reactivity of the ring systems is also observed in the bimolecular reactions of the cycloalkyl halides. However, in the cycloalkanones the opposite is observed, cyclohexanone being much more reactive than the 5- and 7-membered ring derivatives.

5. The inertness of cyclohexyl halides in displacement reactions is usually attributed to steric hindrance afforded by the puckered ring. This explanation is not in accord with the high reactivity of cyclohexanone toward carbonyl reagents, the high reactivity of cycloheptyl halides in displacement reactions, the marked inertness of 1-chloro-1-methylcyclohexane in solvolytic reactions and the negligible effect of methyl substituents on the rates of such reactions.

6. The peculiar changes in reactivity with ring

size are attributed to changes in internal strain accompanying the change in coordination number of a ring atom (I-strain). The I-strain concept permits the chemistry of the small rings (3-, 4-

members), the common rings (5-, 6-, 7) and the medium rings (8- to 12-) to be correlated and systematized.

LAFAYETTE, INDIANA

RECEIVED JUNE 16, 1950

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF OKLAHOMA]

Chromyl Chloride Oxidation of Methylcyclohexane

BY ALBERT TILLOTSON AND BRUCE HOUSTON

The Étard reaction which has been extensively studied as a means of introducing the carbonyl group into side chains on aromatic rings and into olefinic compounds appears to have received little attention as an oxidizing agent with saturated hydrocarbons.

Étard¹ reported the formation of chlorinated ketones from pentane and from hexane. He did not establish the structures of these or give the yields obtained. Crook² obtained high yields of an addition product by the action of chromyl chloride on 2,7-dimethyloctane whose analysis corresponded to $C_{10}H_{22}(CrO_2Cl_2)_4$. He obtained on hydrolysis of this product small amounts of material which gave aldehydic reactions with semicarbazide and with Schiff reagent but which were not further identified.

We have now found that methylcyclohexane shows little tendency to react with chromyl chloride in carbon tetrachloride solution at 35°. However, the addition of less than 1% of an olefin initiated a moderately rapid reaction. This resulted in the formation of an 85% yield of a solid addition product. The chromium content of this material indicated a formula of $C_6H_{11}CH_3(CrO_2Cl_2)_2$ and on hydrolysis gave a 25% yield of hexahydrobenzaldehyde. No other organic product of the hydrolytic reactions was identified.

This observation on the effect of olefins is in accord with that of Kishner³ who observed that 2,6-dimethyloctane was moderately stable to permanganate at 100° but was oxidized rather rapidly at 50° in the presence of menthene. The authors have made similar observations on the effect of olefins on the oxidation of methylcyclohexane with lead tetraacetate, although in this case the character of the resulting products appears to be very different from those obtained with chromyl chloride.

Experimental

Materials.—The methylcyclohexane was Phillips Petroleum Co. "Pure Grade," guaranteed to be not less than 99% pure with the most likely impurities listed as ethylcyclopentane. The chromyl chloride was prepared by the method of Law and Perkin.⁴

Étard Addition Product.—Preliminary tests were run by placing in each of five test-tubes 3 ml. of methylcyclohexane and 0.3 ml. of chromyl chloride in 7 ml. of carbon tetrachloride. One drop of an olefin was added to each of the first three tubes, and a drop of benzene to the fourth. The olefins used were cyclohexene, 2-methyl-2-butene and pi-

nene. Immediate red-brown precipitates were noted in each of the tubes with added olefins. The tube with the benzene underwent a gradual darkening as it stood, whereas no change was noted in the tube without olefins or aromatic until twenty minutes had elapsed. Then it became slowly darker but no filterable material was noted after several hours.

A solution of 77.5 g. (0.5 mole) of chromyl chloride in 2 volumes of carbon tetrachloride was slowly added to 49 g. of methylcyclohexane in 2 volumes of carbon tetrachloride. The temperature was maintained between 83° and 38°. At the end of 15 minutes after starting the addition of chromyl chloride, no sign of reaction was noted and 0.3 ml. of 2-methylbutene was added. Precipitation began immediately. The chromyl chloride addition required 5 hours. The precipitate was then filtered and washed with carbon tetrachloride. After 4 days a further quantity of solid had precipitated from the filtrate and it was added to the solid previously obtained. About two-thirds of the total yield came down during the first 5-hour period. On drying *in vacuo* 87 g. of a fine, red-brown hygroscopic powder was obtained. Gravimetric analyses for chromium were made. *Anal.* Calcd. for $C_6H_{11}CH_3(CrO_2Cl_2)_2$: Cr, 25.49. Found: Cr, 26.09.

When some of the addition product was added to cold water, considerable heat was evolved and gave what appeared to be a true solution.

Hexahydrobenzaldehyde.—Two hundred ml. of crushed ice and water and 50 ml. of ether were placed in a separatory funnel. One-tenth mole (40.8 g.) of the addition product was added a few grams at a time with vigorous shaking after each addition. The water layer was extracted with two more portions of ether and the extracts dried over magnesium sulfate. The ether was then removed under reduced pressure and from the crude residue 2.8 g. of a liquid boiling between 75 and 80° at 20 mm. was collected. Eight-tenths gram of a black residue remained in the flask which would not distil at 150° at 20 mm. Darzens and Lefebure⁵ reported a boiling point of 75–78° at 20 mm. for hexahydrobenzaldehyde. The compound obtained here also gave the Schiff aldehyde test and the derivatives subsequently described.

Attempts to improve the yield of recoverable oxidation product were made by: (a) decomposing the addition product in a water solution of sodium bisulfite instead of water; (b) using benzene in place of ether as an extracting agent; (c) converting the aldehyde to the hexahydrobenzoic acid and steam distilling this. None of these resulted in a measurable gain of product.

Hexahydrobenzaldehyde Semicarbazone.—This was prepared in the usual manner. After 2 recrystallizations from 50% alcohol, the melting point was 178°. Bouveault⁶ reported a m.p. of 176°. *Anal.* Calcd. for $C_6H_{11}CHN-NH-CO-NH_2$: N, 24.83. Found: N, 24.83.⁷

Hexahydrobenzoic Acid.—Twice the calculated volume of hydrogen peroxide solution was added to 1 g. of hexahydrobenzaldehyde. The water was removed by evaporation at 2 mm. pressure; a solid melting between 26 and 30°. Hiers and Adams⁸ reported the m.p. of hexahydrobenzoic acid to be 29–30°.

Summary

Methylcyclohexane gave a good yield of a solid addition product with chromyl chloride in the

(1) Étard, *Compt. rend.*, **84**, 951 (1877).
 (2) K. E. Crook, M.S. Thesis, University of Oklahoma, 1926.
 (3) Kishner, *J. Russ. Phys.-Chem. Soc.*, **45**, 1788 (1913); Brooks, "The Non-Benzenoid Hydrocarbons," Chemical Catalog Co., Reinhold Publishing Corp., New York, N. Y., 1922, p. 57.
 (4) Law and Perkin, *J. Chem. Soc.*, **91**, 191 (1907).

(5) Darzens and Lefebure, *Compt. rend.*, **142**, 715 (1906).
 (6) Bouveault, *Chem. Centr.*, **74**, II, 1437 (1903).
 (7) Micro-Dumas analysis by Mr. C. C. Hobbs of this Laboratory.
 (8) Hiers with Adams, *THIS JOURNAL*, **48**, 2392 (1926).