

chloric acid and 1500 ml. of water. After removal of the solvents from the organic layer, the residue was recrystallized from toluene; yield 187.0 g. (40%); m.p. 153–154°.

Anal. Calcd. for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74; neut. equiv., 234.3. Found: C, 71.78; H, 7.51; neut. equiv., 235.1.

Dehydration of methyl α -phenyl- α -(2-hydroxycyclohexyl)-acetate. The methyl ester was prepared from 8.2 g. of VI, dissolved in 300 ml. of ether, by the addition of excess diazomethane, dissolved in ether, at 0°. After 2 hr. at this temperature, the solvent was removed; yield 7.9 g. (90%) after recrystallization from petroleum ether (60–75°); m.p. 94–95°.

Anal. Calcd. for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.27; H, 8.02.

The ester (12.4 g.), dissolved in 250 ml. of benzene, was added dropwise to a stirred, refluxing mixture of 20 g. of Celite, 15 g. of phosphorus pentoxide, and 750 ml. of benzene. The mixture was stirred and refluxed for 4 hr., cooled, and filtered, and the filtrate was shaken with an aqueous sodium bicarbonate solution. The solvent was removed from the dried benzene layer and the residue was distilled; yield 7.8 g. (67%); b.p. 166–170° (20 mm.). The product, which instantly decolorized solutions of potassium permanganate and bromine, may have been methyl α -phenyl- α -(1-cyclohexenyl)acetate or methyl α -phenyl- α -(2-cyclohexenyl)acetate.

Anal. Calcd. for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 77.82; H, 7.75.

Lactone of VI. A mixture of 9.3 g. of VI, 150 ml. of methanol, and 1 ml. of conc. sulfuric acid was refluxed for 4 hr. The solvent was removed, the residue was dissolved in ether, and the solution was extracted with aqueous sodium bicarbonate solution. The solvent was removed from the ether layer and the residue was recrystallized from petroleum ether (60–75°); m.p. 75–77°; yield 8.4 g. (97%).

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.75; H, 7.46. Found: C, 77.75; H, 7.45.

The same lactone was isolated in at least 90% yield when attempts were made to prepare the β -diethylaminoethyl

ester of VI by the following procedures: (a) a mixture of the silver salt of VI, β -diethylaminoethyl chloride, and acetone was stirred for 24 hr.; (b) attempted transesterification with the use of the methyl ester of the acid, β -diethylaminoethanol, sodium methoxide, and petroleum ether (60–75°).

The lactone was converted into VI in the following manner. A mixture of 8.4 g. of the lactone, 1.6 g. of potassium hydroxide, and 150 ml. of water was refluxed for 3 hr. The solution was extracted with ether. The cold aqueous layer was acidified and the precipitate (VI) was recrystallized from toluene; yield 8.8 g. (94%); m.p. and mixed m.p. 153–155°.

α -Phenyl- β -cyclopentyl- β -hydroxypropionic acids (VII). Cyclopentanecarboxaldehyde¹⁸ (31.0 g.), dissolved in 100 ml. of benzene, was added dropwise to the stirred suspension of the Ivanov reagent prepared from 43.0 g. of phenylacetic acid. The material was stirred and refluxed for 4 hr. and poured into a mixture of 53 ml. of conc. hydrochloric acid and 500 ml. of ice water. After removal of the solvent from the organic layer and recrystallization of the residue from toluene, 53.5 g. (72%) of product was obtained; m.p. 145–148° (lit.¹⁰ m.p. 145–148°). When 50 g. of this material was heated with petroleum ether (60–75°), some of the product remained undissolved. The soluble portion, obtained after removal of the solvent, was recrystallized from petroleum ether (60–75°); yield 35.5 g. (51%); m.p. 130–131°.

Anal. Calcd. for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.66; H, 7.51.

The petroleum ether-insoluble portion was recrystallized from toluene; yield 5.6 g. (8%); m.p. 161–162°.

Anal. Calcd. for $C_{14}H_{18}O_4$: C, 71.77; H, 7.74. Found: C, 71.77; H, 7.52.

ANN ARBOR, MICH.

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

Solvolysis of Dimethylcyclopentyl Halides

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The rates of solvolysis of 1,2-dimethylcyclopentyl halides are only slightly faster than those of 1-methylcyclopentyl halides. This observation implies that some reservation is necessary in considering the I-strain explanation of the relative reactivities of cyclopentyl halides.

In connection with another study,³ the rates of solvolysis of mixtures of *cis*- and *trans*-1,2-dimethylcyclopentyl bromides and chlorides were measured. As a matter of collateral interest the rates of solvolysis of 1-methylcyclopentyl bromide and chloride were determined under comparable conditions.

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RESULTS

The first-order rate constants for solvolysis of various cyclopentyl halides are summarized in Table I and Table II. All rates were measured at $25.00 \pm 0.02^\circ$ in ethanol solutions containing 0.100*N* lithium perchlorate.

Scrutiny of the data shows that the rates measured for various samples of dimethylcyclopentyl halides were not as consistent as might be desired. This was shown to be not readily resolvable into two rates because of different reactivities of *cis* and *trans* isomers. Samples prepared from dimethylcyclopentene known to be relatively rich in the *cis* isomer³ (ca. 30%) were solvolyzed and the data

TABLE I
RATES OF SOLVOLYSIS OF CYCLOPENTYL BROMIDES IN ABSOLUTE ETHANOL
(25.0°, 0.1N LiClO₄)

Bromide	Source ^a	% Solvolysis Followed	$k_1 \times 10^4 \text{ sec.}^{-1}$
1,2-Dimethylcyclopentyl	1,2-Dimethylcyclopentene	99	11.3
1,2-Dimethylcyclopentyl	1,2-Dimethylcyclopentene	85	11.2
1,2-Dimethylcyclopentyl	1,2-Dimethylcyclopentene	86	9.2
1,2-Dimethylcyclopentyl	1,2-Dimethylcyclopentene	93	9.0
1,2-Dimethylcyclopentyl	1,2-Dimethylcyclopentene	93	7.3
1,2-Dimethylcyclopentyl	1,2-Dimethylcyclopentene	97	7.5
1,2-Dimethylcyclopentyl	<i>cis</i> -1,2-Dimethylcyclopentene	98	9.7
1,2-Dimethylcyclopentyl	<i>cis</i> -1,2-Dimethylcyclopentanol	92	11.2
1,2-Dimethylcyclopentyl	<i>trans</i> -1,2-Dimethylcyclopentanol	90	12.0
1,2-Dimethylcyclopentyl	<i>trans</i> -1,2-Dimethylcyclopentanol	89	8.3
1-Methylcyclopentyl	1-Methylcyclopentene	99	5.8
1-Methylcyclopentyl	1-Methylcyclopentene	97	5.2
1-Methylcyclopentyl	1-Methylcyclopentene	94	5.0
1-Methylcyclopentyl	1-Methylcyclopentene	76	4.2

^a Compound from which bromide was prepared by reaction with hydrogen bromide.

TABLE II
RATES OF SOLVOLYSIS OF CYCLOPENTYL CHLORIDES IN ABSOLUTE ETHANOL
(25.0°, 0.1N LiClO₄)

Chloride	Source ^a	% Solvolysis Followed	$k_1 \times 10^6 \text{ sec.}^{-1}$
1,2-Dimethylcyclopentyl	1,2-Dimethylcyclopentene	92	15.3
1,2-Dimethylcyclopentyl	1,2-Dimethylcyclopentene	80	13.5
1,2-Dimethylcyclopentyl	<i>cis</i> -1,2-Dimethylcyclopentanol	91	19.5
1,2-Dimethylcyclopentyl	<i>cis</i> -1,2-Dimethylcyclopentanol	95	16.0
1,2-Dimethylcyclopentyl	<i>trans</i> -1,2-Dimethylcyclopentanol	91	16.5
1-Methylcyclopentyl	1-Methylcyclopentene	69	8.7
1-Methylcyclopentyl	1-Methylcyclopentene	79	8.3

^a Material from which chloride was prepared by reaction with hydrogen chloride.

TABLE III
SOLVOLYSIS RATES OF CYCLOALKYL HALIDES

Compounds	k^{25} 80% C ₂ H ₅ OH sec. ⁻¹	k^{25} 98% C ₂ H ₅ OH sec. ⁻¹	k^{25} C ₂ H ₅ OH sec. ⁻¹
1-Chloro-1-methylcyclohexane	$3.22 \times 10^{-6}{}^a$		$2.93 \times 10^{-8}{}^b$
1-Bromo-1-methylcyclohexane		$6.85 \times 10^{-6}{}^c$	$3.30 \times 10^{-6}{}^d$
1-Chloro-1,2-dimethylcyclohexane	$4.00 \times 10^{-6}{}^a$		$3.72 \times 10^{-8}{}^b$
1-Bromo-1,2-dimethylcyclohexane		$7.50 \times 10^{-6}{}^c$	$3.61 \times 10^{-6}{}^d$
1-Chloro-1-methylcyclopentane	$3.83 \times 10^{-4}{}^a$		$3.55 \times 10^{-6}{}^b$
1-Chloro-1-methylcyclopentane			$8.50 \times 10^{-6}{}^e$
1-Bromo-1-methylcyclopentane			$5.00 \times 10^{-4}{}^e$
1-Chloro-1,2-dimethylcyclopentane			$1.56 \times 10^{-5}{}^e$
1-Bromo-1,2-dimethylcyclopentane			$9.33 \times 10^{-4}{}^e$

^a From Brown *et al.*⁷ ^b Calculated using $m = 1$. ^c From Nevitt and Hammond.⁸ ^d Calculated using $m = 0.9$. ^e This paper.

were treated by the differential kinetic method.⁴ The rates could not be resolved into two components by this procedure. However, it is still possible that some of the differences are due to variations in the reactivities of the two isomers which are too small to be resolved by the mathematical analysis or to interconversion of the isomers under solvolysis conditions. If this is the case, it

must be assumed that the *cis* isomer reacts more slowly than the *trans* compound by less than a factor of two.

Table III shows comparisons among the rates of solvolysis of various tertiary cycloalkyl halides. Data collected under different reaction conditions are extrapolated to absolute ethanol by means of the Grunwald-Winstein equation:⁵

(4) J. S. Fritz and G. S. Hammond, *Quantitative Organic Analysis*, John Wiley and Sons, New York (1957), p. 158.

(5) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948).

$$\log \frac{k}{k_0} = mY$$

The Y values used were those recently reported by Fainberg and Winstein⁶ and *m* values were estimated by comparison with structurally similar tertiary halides.⁵

The data show that, for cyclohexyl compounds, bromides are faster than chlorides by a factor of 100 and that in the cyclopentyl series the bromides are faster by a factor of 60. As an average, cyclopentyl compounds react about 250 times as fast as the corresponding cyclohexyl compounds.

Brown⁷ has attributed the difference in reactivity between cyclopentyl and cyclohexyl compounds to I-strain. Steric strain is believed to be increased in the conversion of an *sp*³ cyclohexyl carbon atom to an *sp*² transition state. In contrast, strain due to interactions between eclipsed *cis* groups in cyclopentanes should be relieved by passing to a transition state in which a ring member is assuming a planar configuration.

The data now available are not easily understood in terms of the most straightforward application of the theory of I-strain. If 1-methylcyclopentyl halides are seriously strained because of the nearly eclipsed relationship between the methyl group, halogen atoms and the hydrogens on adjacent carbon atoms, this strain should be increased by replacement of one of the adjacent hydrogens by another methyl group. If this were the case, one should expect that ionization of 1,2-dimethylcyclopentyl halides should relieve more strain than is the case with 1-methylcyclopentyl compounds. The data show that introduction of the second methyl group increases solvolysis rates by a factor of two or less.

There is no very good way of estimating the magnitude of the effects to be expected. The fully eclipsed form of *cis*-1,2-dimethylcyclopentyl halides contains one methyl-methyl interaction similar to that in the fully eclipsed form of *n*-butane.⁹ Comparison of the *n*-butane barriers with that in ethane indicates that methyl-methyl eclipsing should increase strain by 0.5–0.8 kcal. per mole in comparison with hydrogen-methyl eclipsing. One would ordinarily expect less than faithful reflection of such a small energy difference in the rates of solvolysis. However, if the I-strain theory is right, a considerable amount of the eclipsing strain in cyclopentyl halides is released in the transition stages for solvolysis. We have been unable to find data satisfactory for estimation of the added strain in *trans*-1,2-dimethylcyclopentyl halides. However, as solvolysis of samples known to be mixtures of *cis*

and *trans* halides does not give kinetically resolvable rates, the reactivity of the two isomers must be very similar. Data for the mixtures may therefore be taken as representative of the *cis* compounds. One would certainly expect that the *trans* bromide would also be strained, although the case is not as clear with the *trans* chloride, as study of the barriers in compounds such as 1,2-dichloroethane¹⁰ indicates that there is attraction between eclipsed hydrogen and chlorine atoms.

Several possibilities come to mind for the explanation of the absence of increased reactivity predicted by simple I-strain theory. It is conceivable that the internal steric effect of a 2-methyl group is compensated by an increase in steric hindrance to solvation. This line of reasoning is made unattractive by the fact that the solvolysis rates of 1-methylcyclohexyl and 1,2-dimethylcyclohexyl halides are also very close together. While cyclopentyl and cyclohexyl systems are not exactly analogous, the effects of 2-methyl substituents on solvation energies should be rather similar in the two systems.

There is an interesting possibility for elaboration of the I-strain theory to accommodate the results. Perhaps the puckering motion of the cyclopentane ring¹¹ no longer oscillates about the ring in functional derivatives. The substituted ring member in cyclopentyl halides may be permanently displaced from the average plane of the ring. If this is the case, additional substituents in the 1- and 2-positions would enter in more or less staggered conformations. This might account for the small magnitude of the influence of a 2-methyl group. An interesting corollary of this view would be the prediction that substituents in the 3-position would cause further steric acceleration.

Finally, it is, of course, possible that I-strain is less responsible than has been supposed for the difference in reactivity between cyclopentyl and cyclohexyl compounds. The usual conglomerate of effects, such as special electronic considerations, and both internal and external steric effects, should perhaps be reconsidered.

EXPERIMENTAL

Materials. The preparation of *cis*- and *trans*-1,2-dimethylcyclopentanol and 1,2-dimethylcyclopentene is described elsewhere.³ 1-Methylcyclopentanol was prepared by the addition of cyclopentanone to freshly prepared methylmagnesium chloride, b.p., 45–46° at 15 mm., m.p., 35°. The compound has previously been prepared in unspecified yield¹² by the reaction of cyclopentanone with methyl magnesium iodide. It was our experience that all reactions using methylmagnesium iodide or methyl lithium and the addition of

(6) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2770 (1956).

(7) H. C. Brown, R. S. Fletcher, and R. B. Johannesen, *J. Am. Chem. Soc.*, **73**, 212 (1951).

(8) T. D. Nevitt and G. S. Hammond, *J. Am. Chem. Soc.*, **76**, 4124 (1954).

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(10) J. C. M. Li and K. S. Pitzer, *J. Am. Chem. Soc.*, **78**, 1077 (1956).

(11) J. E. Kilpatrick, K. S. Pitzer, and R. Spitzer, *J. Am. Chem. Soc.*, **69**, 2483 (1947).

(12) N. Zelinsky and S. Namjetkin, *Ber.*, **35**, 2683 (1902); G. Chavanne and L. DeVogel, *Bull. soc. chim. Belg.*, **37**, 141 (1928).

methylmagnesium chloride to cyclopentanone gave very low yields of the alcohol (20% or less). The principal product in these reactions was 2-cyclopentylidene-cyclopentanone, b.p. 103–118° at 13 mm., oxime^{13,14} m.p., 122°, and 2,5-dicyclopentylidene-cyclopentanone,¹³ m.p. 66–68°. Addition of the ketone to methylmagnesium chloride gave the alcohol in 62% average yield.

Halides were prepared by reactions of anhydrous hydrogen halides with the alcohols and 1,2-dimethylcyclopentene as described elsewhere.³ Excess hydrogen halide was removed from the reaction mixtures by extraction with cold water and the pentane solution was dried briefly over anhydrous calcium sulfate. No solution was stored for more than an hour before use.

Procedure. The pentane solutions of halides (approximately 0.02 mole in 20–25 cc. of pentane) were diluted to exactly 25 ml. with pentane. Ten-milliliter aliquots were added to 75 ml. absolute alcohol containing 0.1*N* lithium perchlorate. Solvolysis rates were measured using the rapid intermittent titration method.¹⁵ The titrant was a standard 1*N* solution

(13) O. Wallach, *Ber.*, **29**, 2955 (1896).

(14) M. Godchot and F. Taboury, *Bull. soc. chim. France*, [4], **13**, 12 (1913); H. Meerwein, *Ann. Chem.*, **405**, 129 (1914).

(15) J. K. Kochi and G. S. Hammond, *J. Am. Chem. Soc.*, **75**, 3445 (1953).

of triethylamine in absolute ethanol. Bromophenol blue was employed as the visual indicator. Solvolysis of the bromides was followed for about 100 min. and the reactions of the chlorides were followed for about 5000 min. As neither initial concentrations nor infinity titers were known with high precision, the rate constants were determined by the method of Guggenheim.¹⁶ Plots of milliequivalents of base added versus time were used to obtain pairs of concentration values at fixed time intervals (25 min. for the bromides and 1000 min. for the chlorides). The values of $\log(C_2 - C_1)$ were plotted against t and the rate constants were calculated by multiplication of the slopes of the resulting straight lines by 2.303. While rates sometimes decreased slightly toward the end of a run, the data could never be resolved to give two clearly distinct rates. The values reported in Tables I and II represent maximum rates, as earlier points were used in runs in which the decrease in rate was noticeable.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE STATE UNIVERSITY]

Conformational Analysis. IX. The *Gem*-Dimethyl Effect^{1,2}

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The *gem*-dimethyl effect is quantitatively interpreted for a group of ring closure reactions which lead to substituted cyclohexane systems. The pronounced effect of alkyl substituents in shifting the equilibrium toward the cyclic compound is due in part to an enthalpy effect and in part to an entropy effect. The effect of alkyl groups on the enthalpy of ring closure is interpreted in terms of the change in the number of *gauche* interactions in going from the reactant to the product. The entropy effect, after allowing for the different symmetries of the compounds, is interpreted as being due mainly to the increased height of the barriers to internal rotations in the acyclic compounds upon chain branching.

While the fact that alkyl substitution tends to promote the rate of formation of a cyclic system from its noncyclic analog as well as to increase the concentration of the cyclic material at equilibrium has been recognized for nearly half a century,³ no convincing explanation of the effect has been forthcoming.⁴ Various attempts to explain the phenomenon have been made, and some of these such as the "Thorpe-Ingold effect"⁵ and steric hindrance to rotation⁴ are probably of importance in certain cases. It is the purpose of this paper to show that certain aspects of the phenomenon have a straightforward thermodynamic basis

and are completely general. This general effect, which for historical⁴ reasons has been simply called the *gem*-dimethyl effect in this paper, must always be taken into account before the importance of any "special" effects such as the Thorpe-Ingold effect can be ascertained.

The present paper will be limited in scope as far as quantitative aspects are concerned to equilibria, and the treatment will be applied quantitatively to six-membered ring systems since these are particularly amenable to study and the necessary data are available.⁶ The same considerations will apply, in principle, to compounds of other classes equally well.

Consider the reaction of *n*-hexane to give cyclohexane and hydrogen in the gas phase at 25°. This reaction can be taken as the reference point,

(1) This work was supported by a grant from the Sloan Foundation.

(2) Paper VIII, *J. Am. Chem. Soc.*, in press.

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