dipole moments of VI and VII, measurements were made of the dielectric constants and refractive indices of several solutions of each compound (0.0–1.1%) in benzene at 30°. The method used for calculating the dipole moments was that of Everard, Hill, and Sutton.[15] For the system, benzene at 30°, eq 5[15] is obtained in

$$\mu = (\text{mol wt})^{1/2}(0.00945\alpha + 0.00024\beta + 0.0287\gamma + 0.0028)^{1/2} \quad (5)$$

which μ is the dipole moment and α, β, and γ are parameters which represent the changes in dielectric constant, density, and refractive index with composition. For compounds having a dipole moment greater than 1.5 D., β can be neglected without introducing appreciable error.[16]

The apparatus used for measurement of the electrical properties of the solutions was a General Radio Corp. Model 1610-A capacitance bridge. From the capacitance of each solution, the dielectric constant was calculated, using the directions of the manufacturer. Typical data for VI are given in Table I, p 117.

Registry No.—I, 13132-28-0; II, 13132-29-1; III, 13132-30-4; IV, 13132-31-5; Va, 13132-32-6; Vb, 13132-33-7; VI, 13132-34-8; VII, 13132-35-9; acenaphthylene, 208-96-8.

(15) K. B. Everard, R. A. W. Hill, and L. E. Sutton, *Trans. Faraday Soc.*, **46**, 417 (1950).

(16) D. D. Tanner and T. S. Gilman, *J. Am. Chem. Soc.*, **85**, 2892 (1963).

Neighboring Hydroxyl Group Effect in Solvolysis Reactions of Common Ring *p*-Toluenesulfonates

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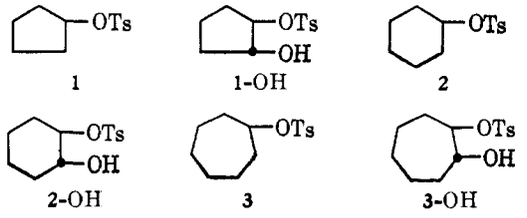
Solvolysis rates of cyclopentyl (**1**), cyclohexyl (**2**), cycloheptyl (**3**), *trans*-2-hydroxycyclopentyl (**1**-OH), *trans*-2-hydroxycyclohexyl (**2**-OH), and *trans*-2-hydroxycycloheptyl (**3**-OH) *p*-toluenesulfonate have been determined in a series of solvents of varying ionizing strength. Analysis of the kinetic data by the mY relationship supports an SN1-type mechanism for the compounds in question. Further analysis of the kinetic data suggests that *I* strain plays a significant role in the competition between the neighboring hydroxyl group assistance and inductive effects while conformational factors have little influence upon the neighboring-group effect. The fact that the enthalpy difference controls the magnitude of the rate ratios k^1/k^2 and $k^{1\text{-OH}}/k^{2\text{-OH}}$ lends additional support to the significant influence of *I* strain upon the neighboring group-effect.

In a recent solvolytic investigation,[1] the slight influence of a neighboring *trans*-hydroxyl group on the reaction rate of cyclooctyl derivatives was rationalized in terms of a balance between opposing neighboring-group assistance and electronic effects upon the free energy of activation. The relative importance of conformational factors in the neighboring-group effect was not specifically described and a more detailed investigation was needed.

In this paper the kinetic investigation of the solvolytic reactions of cycloalkane derivatives was extended to include the five-, six-, and seven-membered ring compounds. The data indicate that the influence of a neighboring hydroxyl group is sensitive to medium and *I* strain effects but insensitive to conformational effects.



The first-order rate constants for solvolysis of **1**–**3** and **1**-OH–**3**-OH in various solvents are summarized in Table I. The solvolysis reaction of **3**-OH in the 1:1 acetic acid–formic acid solvent mixture yielded integrated first-order rate constants that tended to decrease as reaction progressed; consequently, the rate constant was calculated from the initial slope of a plot of log $(a - x)$ *vs.* time. All other reactions were first order in *p*-toluenesulfonate up to at least 80% conversion. The activation parameters were obtained by IBM 1620 computer regression analysis of ln k/T *vs.* $1/T$.

The linear free-energy relationship given by eq 1 is useful for mechanistic classification of solvolysis

$$\log k = \log k^0 + mY \quad (1)$$

reactions.[2a,3a] The plots of the logarithms of selected rate data from Table I *vs.* Y result in the well-known[4,5] dispersion of points into two nonparallel lines (*cf.* Figures 1–3), one for the aqueous alcohol solvent mixtures and one for the carboxylic acid solvent mixtures. This dispersion of points into two correlation lines can be ascribed to at least two factors. First, the nucleophilic character of the solvent is important to the solvolysis rate of the compounds in question because their solvolysis is not limiting.[4] Second, the presence of multiple solvation mechanisms, neglected[3b] by the mY relationship, will produce plots with different slopes for each different two-component solvent system.

Concerning factor 1, the importance of the solvent nucleophilic character in the solvolysis of **1**–**3**, there is abundant support in the literature[6,7-9] for the

(1) D. D. Roberts and J. G. Traynham, *J. Org. Chem.*, **32**, 3177 (1967).

(2) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962: (a) pp 63, 64; (b) p 96.

(3) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963: (a) pp 297–300; (b) pp 288, 289.

(4) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **79**, 1597, 1602, 1608 (1957).

(5) S. Winstein, A. H. Fainberg, and E. Grunwald, *ibid.*, **79**, 4146 (1957).

(6) See Table I, footnote *g*.

(7) S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Am. Chem. Soc.*, **70**, 821 (1948).

(8) J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5034 (1951).

(9) A. Streitwieser, Jr., *ibid.*, **78**, 4935 (1956).

TABLE I

FIRST-ORDER SOLVOLYSIS RATES

Tosylate[a]	Solvent, vol. %[b]	Temp, °C	k^1, sec^{-1} [c]	ΔH^*, kcal/mole	ΔS^*, eu
Cyclopentyl	EtOH	30[d]	5.01×10^{-6}	21.8	−11
	EtOH	40	17.8×10^{-6}		
	EtOH	50[d]	50.0×10^{-6}		
	80% aq EtOH	30	4.90×10^{-5}	18.8	−16
	80% aq EtOH	45	24.0×10^{-5}		
	80% aq EtOH	60	90.0×10^{-5}		
	60% aq EtOH	30	1.74×10^{-4}	17.2	−17
	60% aq EtOH	45	7.80×10^{-4}		
	60% aq EtOH	60	25.0×10^{-4}		
	AcOH	30	3.10×10^{-6}	24.0	−5
	AcOH	40	12.0×10^{-6}		
	AcOH	45[e]	22.2×10^{-6}		
	AcOH	50[f]	42.1×10^{-6}		
	50% HCOOH	30	1.60×10^{-4}	16.9	−19
	50% HCOOH	45	7.30×10^{-4}		
	50% HCOOH	60	22.0×10^{-4}		
	HCOOH	20	0.43×10^{-3}	17.0	−15
	HCOOH	30	1.20×10^{-3}		
	HCOOH	45	4.70×10^{-3}		
trans-2-Hydroxy-cyclopentyl	EtOH	30	1.20×10^{-6}	22.3	−10
	EtOH	45	7.80×10^{-6}		
	EtOH	60	39.0×10^{-6}		
	80% aq EtOH	30	0.70×10^{-5}	21.2	−12
	80% aq EtOH	45	4.40×10^{-5}		
	80% aq EtOH	60	18.5×10^{-5}		
	60% aq EtOH	30	1.40×10^{-5}	21.2	−11
	60% aq EtOH	45	8.00×10^{-5}		
	60% aq EtOH	60	37.0×10^{-5}		
	AcOH	30	3.10×10^{-6}	17.6	−24
	AcOH	45	12.0×10^{-6}		
	AcOH	60	47.0×10^{-6}		
	50% HCOOH	30	9.80×10^{-6}	22.1	−6
	50% HCOOH	45	61.0×10^{-6}		
	50% HCOOH	60	290×10^{-6}		
	HCOOH	30	2.70×10^{-5}	19.4	−15
	HCOOH	45	12.8×10^{-5}		
	HCOOH	60	53.0×10^{-5}		
Cyclohexyl	EtOH	50[g]	1.41×10^{-6}	25.5[g]	−6[g]
	EtOH	75[g]	2.63×10^{-5}		
	80% aq EtOH	30	1.65×10^{-6}	22.8	−10
	80% aq EtOH	40	5.70×10^{-6}		
	80% aq EtOH	60	55.0×10^{-6}		
	60% aq EtOH	30	7.20×10^{-6}	22.9	−8
	60% aq EtOH	40	23.6×10^{-6}		
	60% aq EtOH	60	230×10^{-6}		
	50% aq EtOH	40	5.30×10^{-5}		
	AcOH	50[h]	1.40×10^{-6}	27.2[h]	−0.8[h]
	AcOH	75[h]	3.60×10^{-5}		
	AcOH	100[h]	5.90×10^{-4}		
Cyclohexyl	50% HCOOH	30	0.84×10^{-5}	22.8	−4
	50% HCOOH	45	5.60×10^{-5}		
	50% HCOOH	60	28.0×10^{-5}		
	75% HCOOH	45	1.76×10^{-4}		
	HCOOH	25[g]	3.87×10^{-5}	22.4[i]	−2[i]
	HCOOH	50[g]	93.0×10^{-5}		
trans-2-Hydroxy-cyclohexyl	EtOH	40	1.10×10^{-5}	25.0	−4
	EtOH	50	3.70×10^{-5}		
	EtOH	60	13.0×10^{-5}		
	80% aq EtOH	30	1.70×10^{-6}	21.5	−14
	80% aq EtOH	40	6.50×10^{-6}		
	80% aq EtOH	60	44.0×10^{-6}		
	60% aq EtOH	30	2.20×10^{-5}	23.4	−7
	60% aq EtOH	40	7.60×10^{-5}		
	60% aq EtOH	60	80.0×10^{-5}		
	50% aq EtOH	40	2.00×10^{-5}		
	AcOH	30	3.40×10^{-6}	26.6	−3
	AcOH	40	14.9×10^{-6}		
	AcOH	50	56.0×10^{-6}		
	50% HCOOH	30	0.54×10^{-7}	24.9	−7
	50% HCOOH	45	4.40×10^{-7}		
	50% HCOOH	60	24.2×10^{-7}		
	75% HCOOH	45	5.50×10^{-7}		
	HCOOH	30	0.80×10^{-7}	26.0	−5
	HCOOH	40	3.90×10^{-7}		
	HCOOH	60	43.0×10^{-7}		
Cycloheptyl	EtOH	30[j]	6.40×10^{-6}	21.0	−13
	EtOH	40[j]	19.1×10^{-6}		
	EtOH	50	58.5×10^{-6}		
	80% aq EtOH	45	2.80×10^{-4}		
	60% aq EtOH	45	1.00×10^{-3}		
	AcOH	30	5.00×10^{-6}	24.4	−2
	AcOH	40	20.2×10^{-6}		
	AcOH	50[k]	64.5×10^{-6}		
	HCOOH	15[l]	49.7×10^{-6}	19.3	−5
	HCOOH	25[l]	162×10^{-6}		
	HCOOH	35[l]	480×10^{-6}		
trans-2-Hydroxy-cycloheptyl	EtOH	30	1.80×10^{-5}	23.7	−5
	EtOH	45	11.0×10^{-6}		
	EtOH	60	68.0×10^{-6}		
	80% aq EtOH	45	5.80×10^{-5}		
	60% aq EtOH	45	1.30×10^{-4}		
	AcOH	30[m]	1.20×10^{-6}	23.2	−9
	AcOH	45[m]	8.00×10^{-6}		
	AcOH	60[m]	42.0×10^{-6}		
	50% HCOOH	45	1.00×10^{-4}		
	HCOOH	30[n]	1.00×10^{-4}	16.1	−24
	HCOOH	45[n]	3.60×10^{-4}		
	HCOOH	60[n]	12.0×10^{-4}		

[a] Initial concentrations: 0.040–0.050 *M*. [b] *x* vol. % aqueous alcohol solvent means *x* volumes of EtOH plus 100*x* volumes of water, both at 25° before mixing; *x* vol. % formic acid solvent means *x* volumes of HCOOH plus 100*x* volumes of acetic acid, both at 25° before mixing. [c] The standard deviation of these rate constants ranged from ±0.4 to ±1.8%. [d] W. Huckel and H. D. Sauerland, *Ann.*, **592**, 190 (1955). [e] Taken from the data of I. Lillien and K. Khaleeluddin, *Chim. Ind.* (Paris), **88**, 1028 (1964). [f] Taken from ref 2b. [g] S. Winstein and N. J. Holmes, *J. Am. Chem. Soc.*, **77**, 5562 (1955). [h] Taken from data of S. Winstein, E. Grunwald, R. E. Buckles, and C. Hanson, *ibid.*, **70**, 817 (1948). [i] Average of values reported in footnote *g* and H. C. Brown and G. Ham, *ibid.*, **78**, 2735 (1956). [j] Taken from data of W. Huckel and J. Wachter, *Ann.*, **672**, 62 (1964). [k] Taken from data of W. Huckel and O. Honecker, *ibid.*, **678**, 10 (1964). [l] R. Huisgen, E. Rouenbusch, G. Seidl, and I. Wimmer, *ibid.*, **671**, 39, 41 (1964). [m] Contained 0.050 *M* NaOAc. [n] Contained 0.050 *M* HCO_2Li.

SN1 mechanism in all solvents[10-12] with the possible exception of absolute ethanol. In addition, the variation in the solvent rate sequences, EtOH:AcOH:HCOOH for the tosylates **1**–**4** (Table II) reflects a greater dependency upon solvent ionizing strength than nucleophilic character. Supplementing this analysis are the rate ratios listed in Table II which estimate the effect of solvent nucleophilicity on the solvolysis rates. The rate ratios are all of the correct order of magnitude for a substrate only slightly dependent on solvent nucleophilicity.[2a]

Table III compares the neighboring hydroxyl substituent effect in the four cycloalkyl tosylates in a spectrum of solvents varying in ionizing strength from ethanol to formic acid. The response of the cyclopentyl and cycloheptyl tosylates parallels that previously observed[1] for cyclooctyl tosylate. Based upon electrostatic considerations, a 10^{-2} rate retarding influence upon SN1 type reactions was calculated for the neighboring *trans*-hydroxy group[13] in tertiary chlorides and was found to be in good agreement with the experimental value of 6.5×10^{-3}. The application[9] of Taft's equation to polar effects in the acetolysis of secondary carbinyl sulfonates yields a similar value for the neighboring hydroxyl group inductive effect. It is readily apparent from the data presented in Table III

(10) Product distribution data[8,11,12] indicate, however, a considerable difference among the three compounds in the partitioning of the carbonium-like intermediate into products.

(11) See Table I, footnote *d*.

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

(13) S. Winstein and E. Grunwald, *J. Am. Chem. Soc.*, **70**, 828 (1948).

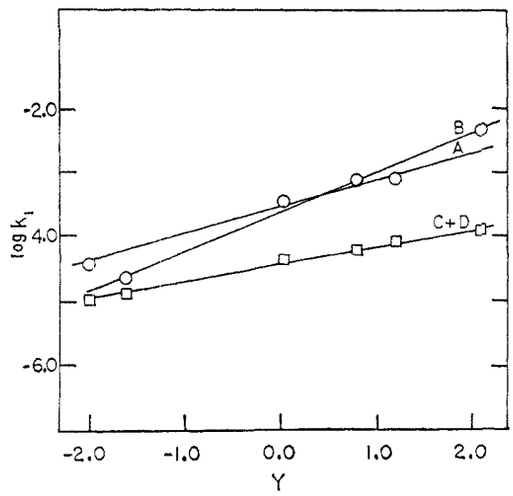


Figure 1.—The linear dependence of log k_1 on Y at 45°: A, cyclopentyl tosylate in aqueous alcohol solvents; B, cyclopentyl tosylate in carboxylic acid solvents; C, *trans*-2-hydroxycyclopentyl tosylate in aqueous alcohol solvents; D, *trans*-2-hydroxycyclopentyl tosylate in carboxylic acid solvents. Data taken from Table I and ref 3.

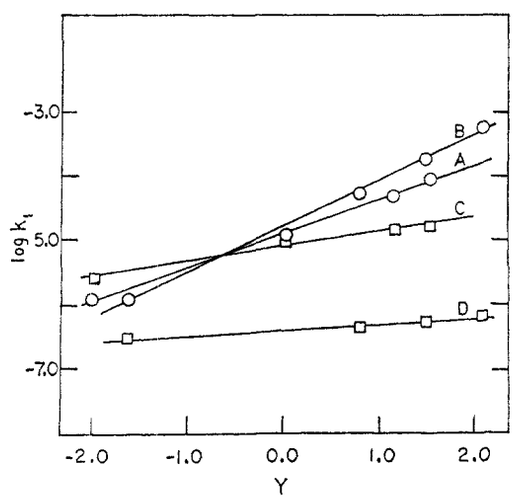


Figure 2.—The linear dependence of log k_1 on Y at 45°: A, cyclohexyl tosylate in aqueous alcohol solvents; B, cyclohexyl tosylate in carboxylic acid solvents; C, *trans*-2-hydroxycyclohexyl tosylate in aqueous alcohol solvents; D, *trans*-2-hydroxycyclohexyl tosylate in carboxylic acid solvents. Data taken from Table I and ref 3.

TABLE II
EFFECT OF SOLVENT NUCLEOPHILICITY ON SOLVOLYSIS RATES

	$k_{rel}^{45°}$			(k^{ROH}/k^{RCOOH}) Y[a]	
Tosylate	EtOH	AcOH	HCOOH	AcOH	HCOOH
Cyclopentyl **1**	1.00	0.65	1.38×10^2	2.5	0.50
Cyclohexyl **2**	1.00	1.04	5.47×10^2	1.1	0.32
Cycloheptyl **3**	1.00	0.95	2.43×10^2	1.4	0.25
Cyclooctyl **4**	1.00[b]	6.85	4.35×10^3	0.31	0.07
p-Methoxyneophyl	1.00[c]	3.00	4.64×10^2		

[a] A measure of substrate response to solvent nucleophilic character where k^{RCOOH} = specific rate in acetic or formic acid and k^{ROH} = specific rate in ethanol–water mixture of equal ionizing power; *cf.* ref 2. [b] Data taken from ref 1. [c] Representative of a tosylate that follows a limiting SN1 mechanism in a variety of solvents: S. G. Smith, A. H. Fainberg, and S. Winstein, *J. Am. Chem. Soc.*, **83**, 618 (1961).

that the order of magnitude of the expected[14,15] rate retardation is approached only in carboxylic acid solvents of high ionizing strength and is equaled and exceeded only by the cyclohexyl ring compound.

TABLE III
COMPARISON OF REACTION RATES OF *trans*-2-HYDROXYCYCLOALKYL AND CYCLOALKYL TOSYLATE IN VARIOUS SOLVENTS AT 45°

	(k^{OH}/k^{H})					
Tosylate	EtOH	80% EtOH	60% EtOH	AcOH	50% HCOOH	HCOOH
Cyclopentyl	0.23	0.18	0.10	0.54	0.084	0.027
Cyclohexyl	1.84	1.00	0.35	0.23	0.0083	0.0011
Cycloheptyl	0.31	0.21	0.13	0.24	0.080	0.042
Cyclooctyl[a]	0.78	0.51	0.42	0.38		0.025

[a] Data taken from ref 1.

There is ample stereochemical evidence[16,17] for *trans* neighboring-group assistance in solvolysis reactions of cyclohexyl sulfonates. The presence of a similar neighboring-group effect in the five and seven-membered ring compounds is established by the retention of configuration in base-catalyzed hydrolysis reactions of **1**-OH and **3**-OH.[18] Mousseron[19] has shown, in the hydrolysis of *trans*-2-hydroxycyclopentyl and -cyclohexyl chlorides, the nearly exclusive formation of *trans*-glycols. Similarly, in the ethanolysis reactions of **1**-OH and **2**-OH, the exclusive formation of *trans*-2-ethoxycycloalkanols (*cf.* Experimental Section) supports participation by the neighboring hydroxyl group.

Steric assistance due to relief of unfavorable conformational factors is ruled out as a satisfactory explanation for the neighboring hydroxyl group effect by a number of considerations. First, the introduction of a methyl group in the 2 position, *trans* to the departing group, of both the cyclopentane and cyclohexane rings has little effect on the solvolytic reactivity of 1-methylcyclopentyl[20] and 1-methylcyclohexyl[12] chloride or cyclopentyl and cyclohexyl tosylate.[21] Even the introduction of the bulkier isopropyl group in the same ring position does not enhance the solvolytic reactivity of the tosylate.[21] If the introduction of the hydroxyl group in the 2 position, *trans* to the departing group, of either the cyclopentane or cyclohexane ring were accompanied by some unfavorable conformational factor, then introduction of the bulkier alkyl groups should intensify this conformational effect. The absence of marked effects of this kind for the alkyl-substituted cycloalkyl compounds, suggests that steric acceleration due to relief of unfavorable conformational effects introduced by the hydroxyl group is not a major factor in the solvolysis reactions of **1**-OH and **2**-OH.

Second, the rate of acetolysis of *cis*- and *trans*-2-chlorocyclohexyl brosylate, in which participation does not occur, are both about 10^{-4} slower than that for cyclohexyl brosylate.[22] The lack of any significant difference between the rate retarding neighboring-

(14) See ref 9.
(15) See Table II, footnote *c*.
(16) See ref 7.
(17) S. Winstein, E. Grunwald, and H. W. Jones, *J. Am. Chem. Soc.*, **73**, 2700 (1951).
(18) (a) L. N. Owen and P. N. Smith, *J. Chem. Soc.*, 4026 (1952); (b) L. N. Owen and G. S. Sahara, *ibid.*, 2582 (1953).
(19) H. Bordat, J. Gullien, and M. Mousseron, *Bull. Soc. Chim. France*, 1101, 1110 (1958).
(20) H. C. Brown and F. J. Chloupek, *J. Am. Chem. Soc.*, **85**, 2322 (1963).
(21) W. Huckel, R. Bross, O. Fechtig, H. Feltkamp, S. Geiger, M. Hanock, M. Heinzel, A. Hubele, J. Kurz, M. Maier, O. Mauchen, G. Naher, R. Neidlein, and R. Rashingkar, *Ann.*, **624**, 142 (1959).
(22) E. Grunwald, *J. Am. Chem. Soc.*, **73**, 5458 (1951).

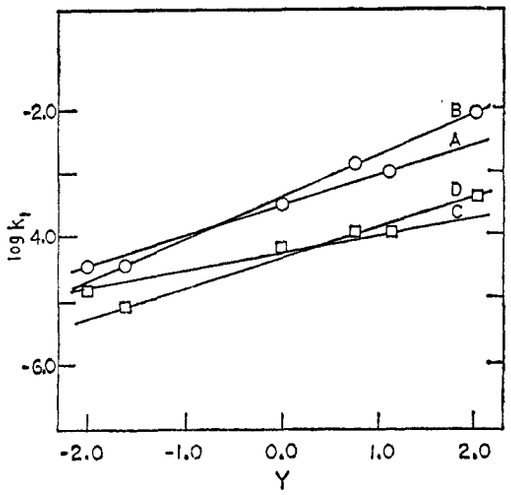


Figure 3.—The linear dependence of log k_1 on Y at 45°: A, cycloheptyl tosylate in aqueous alcohol solvents; B, cycloheptyl tosylate in carboxylic acid solvents; C, *trans*-2-hydroxycycloheptyl tosylate in aqueous alcohol solvents; D, *trans*-2-hydroxycycloheptyl tosylate in carboxylic acid solvents. Data taken from Table I and ref 3.

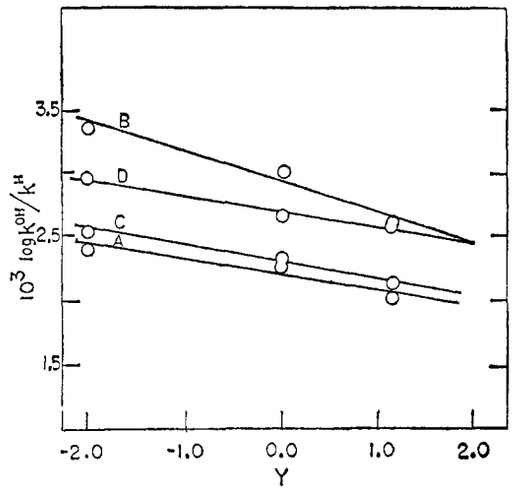


Figure 4.—The linear dependence of log k^{OH}/k^H on Y in aqueous alcohol solvents at 45°: A, cyclopentyl tosylate; B, cyclohexyl tosylate; C, cycloheptyl tosylate; D, cyclooctyl tosylate. Data taken from Table III and ref. 1 and 3.

group effect of the *cis* and *trans*-chloro group upon the acetolysis rate supports the absence of a significant conformational influence upon the corresponding inductive effect of the neighboring hydroxyl group.

Finally, the magnitude and response of the (k^{OH}/k^H) value to variable solvent ionizing strength is very similar in the five-, seven-, and eight-membered ring compounds. Since the variation in geometry and conformational factors among these three ring systems is significant,[23a] the insensitivity of the (k^{OH}/k^H) value to ring size further suggests that conformational effects do not have a significant influence upon the hydroxyl neighboring group effect.

The use of the mY relationship to learn something about the nature of the neighboring-group effect in the compounds in question is quite instructive. Plots of log (k^{OH}/k^H) *vs.* Y for the nucleophilic solvents (Figure 4) emphasize the significant vertical displacement of the 6-correlation line above that for the five- and seven-membered ring systems. These rate effects associated with change in ring size clearly support the greater sensitivity of 2-OH to neighboring-group participation in nucleophilic solvolyses. The plots of log (k^{OH}/k^H) *vs.* Y for the ionizing solvents (Figure 5) reveal the significantly greater slope value for the 6-correlation line. These rate effects also associated with change in ring size clearly support the much greater sensitivity of 2-OH to the hydroxyl group inductive effect with increasing charge development in the transition state.

The unusual behavior of the six-membered ring compounds in the two binary solvent systems can be interpreted in terms of the I strain concept,[12] *i.e.*, the variation in internal energy of the cycloalkanes with change in coordination number of a ring atom. For this purpose, it is informative to examine the effect of ring size on reaction rate with changing reaction medium. The relative rates of the cycloalkyl tosylates presented in Table IV decrease with increasing solvent ionizing strength. This finding is in accord with Streitwieser's[2b] observations and reflects the variable nature of I strain with varying reaction medium. For example, in SN1-type reactions, cyclopentyl and cycloheptyl compounds react appreciably faster than open-chain compounds (Table IV) owing to bond opposition strain in the ground state,[24] while the reactivity of cyclohexyl compounds is nearly normal. In SN2 reactions, however, the cyclopentyl and cycloheptyl compounds react normally[24] while the reactivity of the cyclohexyl compounds due to bond-opposition strain in the transition state is appreciably slower than open-chain compounds. The over-all effect as suggested by the data in Table IV is a *decrease in the relative rate* (k/k_6) *with decreasing nucleophilic contribution to the transition state.*

TABLE IV
COMPARISON OF RATE CONSTANTS IN VARIOUS SOLVENTS AT 45°

	(k/k_6)					
Tosylate	EtOH	80% EtOH	60% EtOH	AcOH	50% HCOOH	HCOOH
Cyclopentyl	27	24	17	17	13	8.4
Cyclohexyl	1.00	1.00	1.00	1.00	1.00	1.00
Cycloheptyl	28	28	22	28	22	15
Isopropyl	5[a]	3[b]	1.3[b]	0.6[c]	0.6[d]	0.4[a]
	$(k/k_6)^{OH}$					
trans-2-Hydroxycyclopentyl	3.4	4.4	5.5	40	137	203
trans-2-Hydroxycyclohexyl	1.00	1.00	1.00	1.00	1.00	1.00
trans-2-Hydroxycycloheptyl	4.8	5.8	9.0	27	225	570

[a] W. Huckel and K. Tomopulos, *Ann.*, **610**, 78 (1957). [b] Estimated from data in footnote *a* by use of the mY relationship. [c] W. Pritzkow and K. H. Schoppler, *Ber.*, **95**, 834 (1962). [d] Estimated by use of the mT relationship.

The relative rates of the *trans*-2-hydroxycycloalkyl tosylates, $(k/k_6)^{OH}$, presented in Table IV clearly exhibit a different response to changing reaction medium. In the aqueous alcohol solvents, (k/k_6) is decreased by the neighboring hydroxyl group and, in the carboxylic acid solvents, (k/k_6) is significantly increased by the

(23) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1966: (a) Chapter 4; (b) p 205.

(24) E. L. Eliel, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p 121 ff.

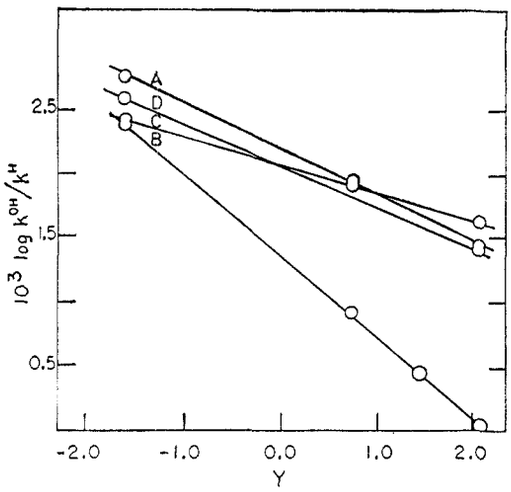


Figure 5.—The linear dependence of $\log k^{OH}/k^H$ on Y in carboxylic acid solvents at 45°: A, cyclopentyl tosylate; B, cyclohexyl tosylate; C, cycloheptyl tosylate; C, cyclooctyl tosylate. Data taken from Table III and ref 1 and 3.

neighboring hydroxyl group. The over-all effect is an *increase in the relative rate* $(k/k_s)^{OH}$ *with decreasing nucleophilic contribution to the transition state.*

An explanation for this contrasting behavior is associated with the variable *I* strain influence upon the competing neighboring-group assistance and rate retarding inductive effects. In nucleophilic solvents where the sensitivity of the subtrate to nucleophilic assistance is enhanced, the role of supplying a close range backside attack on carbon by the neighboring hydroxyl group is supported by the nearly exclusive formation of the previously mentioned *trans* reaction products. Furthermore, in the SN2 reaction, as explained earlier, only the cyclohexyl compounds demonstrate a reduced rate which is attributed[2b,23b] at least in part to the development of bond-opposition strains between some of the ring hydrogen atoms and the entering group. Because nucleophilic participation by the neighboring hydroxyl group would mitigate the crowding introduced by an external nucleophile, the solvolysis rate of the six-membered ring compound would be expected to be more sensitive to neighboring group assistance. Supporting this interpretation is the increasingly positive vertical gap between the correlation line for the cycloalkyl ring data in Figure 4 and the correlation lines for the cyclopentyl and cycloheptyl ring data as the reaction becomes more dependent upon nucleophilic assistance.

On the other hand, in carboxylic acid solvents where a more limiting type solvolysis mechanism is involved, steric acceleration (relief of *I* strain) plays an important role in the solvolysis reactions of the five- and seven-membered ring compounds. Additionally, the markedly greater stability of cyclopentene oxide relative to cyclohexene oxide[23b] (also *cf.* Experimental Section) suggests that neighboring-group participation in the SN1 reaction of 1-OH and 3-OH would be accompanied by relief of some *I* strain, a factor which would tend to increase the sensitivity of the five- and seven-membered ring tosylates to hydroxyl neighboring group assistance. In the case of the six-membered ring compounds, however, *I* strain plays a minor role in limiting type solvolyses, and consequently, the neighboring-group inductive effect in the reaction of 2-OH in carboxylic acid solvents would be similar to that observed[9,13] for the open-chain compounds. Consistent with this explanation is the greatly enhanced sensitivity of the six-membered ring compound to the neighboring group inductive effect with increasing solvent ionizing strength as illustrated in Figure 5.

In terms of activation parameters, the reduced acetolysis reactivity of cyclohexyl tosylate compared to that for cyclopentyl tosylate (I strain) has been attributed[25-27] to increased enthalpy of activation. The data reported in Table V confirm this interpretation for a range of solvents. The presence of a *trans*-2-hydroxy group does not alter the enthalpy control of the rate difference between the six- and five-membered ring tosylates. The fact that all six substrates, **1–3** and 1-OH–3-OH, failed to be correlated by an isokinetic relationship emphasizes the irregular partitioning of the activation parameters and prevents a detailed enthalpy–entropy analysis.

TABLE V

PARTITIONING OF ACTIVATION PARAMETERS

Solvent	$\Delta Y_2^* - \Delta Y_1^*$ $\Delta\Delta F^*$	$\Delta\Delta H^*$	$T\,\Delta\Delta S^*$[a]	$\Delta Y_{2\text{-OH}}^* - \Delta Y_{1\text{-OH}}^*$ $\Delta\Delta F^*$	$\Delta\Delta H^*$	$T\,\Delta\Delta S^*$[a]
EtOH	2.1	3.7	1600	0.8	2.7	1900
80% EtOH	2.0	4.0	2000	0.9	0.3	−600
60% EtOH	1.8	4.7	2900	1.0	2.2	1200
AcOH	1.8	3.2	1400	2.3	9.0	6700
50% HCOOH	1.6	6.0	4400	3.1	2.8	−300
HCOOH	1.3	5.4	4100	3.4	6.6	3200

[a] T = 318° K.

Experimental Section

Melting and boiling points were not corrected for stem exposure. The former were taken on a Mel-Temp apparatus. Spectra were determined on a Perkin-Elmer Model 21 spectrophotometer. An F &M Model 700 gas chromatograph equipped with a hydrogen-flame detector and a 6-ft column of 20% SE 30 on Celite was used for analytical vpc work.

Cyclopentyl *p*-Toluenesulfonate (1).—To a cold solution of recrystallized *p*-toluenesulfonyl chloride (8.58 g, 45 mmoles) in 30 ml of dry pyridine was added all at once 2.58 g (30 mmoles) of cyclopentanol. The mixture was stored overnight in the refrigerator and then hydrolyzed by the addition of cold, dilute hydrochloric acid. The precipitated oil was taken up in 40 ml of methylene chloride, washed once with cold, dilute hydrochloric acid, once with cold water, dried over anhydrous sodium sulfate, and concentrated by rotary evaporation to yield 5.0 g of an oil. Recrystallization from petroleum ether (bp 39–55°) gave 4.0 g (55% yield) of white crystals, mp 29.0–29.5° (lit.[11] mp 29.1°).

Cyclohexyl *p*-toluenesulfonate (2) was prepared in 75% yield by the method described for **1**, mp 44.0–44.8° (lit.[8] mp 44.4–44.8°).

Cycloheptyl *p*-toluenesulfonate (3) was prepared in 83% yield by the method of Heck and Prelog.[28] The crude ester was washed with cold petroleum ether (bp 39–55°) to yield an oil[28] of 99% purity by infinity titer.

Cyclopentene Oxide.—To a solution of 20.4 g (0.17 mole) of cyclopentene (Aldrich Chemical Co.) in 100 ml of chloroform maintained at 10–15° by means of an ice water bath was added 48 g of 40% peracetic acid (containing 4 g of sodium acetate) over a 60-min period. After stirring an additional 2 hr at 10–15°, the mixture was neutralized at the same temperature by the slow addition of 20% aqueous sodium hydroxide. The chloroform layer was separated, washed twice with 150 ml portions of

(25) See H. C. Brown and G. Ham, footnote *i*, Table I.
(26) See ref 1.
(27) S. Winstein, B. Morse, E. Grunwald, H. W. Jones, and J. Corse, *J. Am. Chem. Soc.*, **74**, 1127 (1952).
(28) R. Heck and V. Prelog, *Helv. Chim. Acta*, **38**, 1541 (1955).

cold water, and dried over anhydrous sodium sulfate. Distillation through a 12-cm glass, helix-packed column yielded 17.0 g (60%) of the oxide: bp 98–100°; n^{25}D 1.4377 (lit.[29] bp 99–100°).

Cycloheptene oxide was prepared in 53% yield by the method described for cyclopentene oxide: bp 66–68° (25 mm), n^{22}D 1.4623; lit.[18b] bp 65–67° (25 mm), n^{22}D 1.4620.

***trans*-2-Hydroxycyclopentyl *p*-Toluenesulfonate (1-OH).**—To a solution of 6.1 g (72 mmoles) of cyclopentene oxide in 50 ml of dry ether maintained at 5–10° by means of an ice water bath was added 12.4 g (72 mmoles) of *p*-toluenesulfonic acid over a 15-min period. After stirring the mixture for 2 hr at room temperature, the ether was removed by rotary evaporation and the oily residue dissolved in 50 ml of methylene chloride. The methylene chloride solution was washed twice with 50-ml of portions of cold, saturated sodium bicarbonate solution, dried over anhydrous sodium sulfate and the solvent removed *via* rotary evaporation to yield 9.0 g of an oil. The crude ester was dissolved in hot petroleum ether (bp 39–55°) and cooled to −78°. The solvent was removed from the precipitated ester by decantation and rotary evaporation to yield 7.0 g (38%) of an oil, 99% purity by an infinity titer. Treatment of a portion of the oil with *p*-toluenesulfonyl chloride in pyridine yielded the *trans*-ditosylate derivative, mp 108–109° (lit.[18a] mp 109°).

***trans*-2-Hydroxycyclohexyl *p*-Toluenesulfonate (2-OH).**—*p*-Toluenesulfonic acid (12.4 g, 72 mmoles) was added over a 15-min period to a solution of cyclohexene oxide (Aldrich Chemical Co., 7.0 g, 72 mmoles) in 25 ml of dry ether maintained at 5–10° by means of an ice water bath. After standing at room temperature for 14 hr, the ether was removed by rotary evaporation to yield 14.0 g (72% yield) of a white solid; the melting point, after two recrystallizations from hot petroleum ether (bp 39–55°)–ethyl acetate, was 95–96° (lit.[30] 96°).

***trans*-2-Hydroxycycloheptyl *p*-toluenesulfonate (3-OH)** was prepared in 50% yield by the method described for **1**-OH. The oil was 95% pure by infinity titer. Treatment of a portion of the oil with *p*-toluenesulfonyl chloride in pyridine yielded the *trans*-ditosylate derivative, mp 111–112° (lit.[18b] mp 112°).

***trans*-2-Ethoxycyclopentanol (5).**—Sodium metal (1.84 g, 80 mmoles) was dissolved in 100 ml of absolute ethanol and to the resultant solution of sodium ethoxide in ethanol was added all at once 6.7 g (80 mmoles) of cyclopentene oxide. After stirring at room temperature for 24 hr, most of the alcohol was removed by rotary evaporization. The residue was dissolved in a mixture of methylene chloride–water (40 and 40 ml). The organic layer was separated, washed twice with 40-ml portions of cold water, dried over anhydrous sodium sulfate, and distilled to yield 7.0 g (67% yield) of product, bp 60° (2 mm), n^{25}D 1.4510 (lit.[31] bp 182°, n^{25}D 1.4512).

***trans*-2-Ethoxycyclohexanol (6)** was prepared in 65% yield by the method described for *trans*-2-ethoxycyclopentanol, bp 60° (2 mm), n^{20}D 1.4560 (lit.[32] bp 65–67° (2 mm), n^{20}D 1.4562).

Reaction of Oxides with Aqueous Sodium Hydroxide.—Cyclohexene oxide (7.8 g, 80 mmoles) was stirred in 100 ml of 10% sodium hydroxide solution for 72 hr at room temperature. The mixture was then extracted twice with 40-ml portions of methylene chloride. The combined extracts were washed once with 20 ml of cold water, dried over anhydrous sodium sulfate and the solvent removed by rotary evaporation to yield 1.0 g of diol, mp 102–103° (lit.[33] mp 101.5–103°). Similar basic treatment of cyclopentene oxide failed to yield any detectable quantity of diol.

Solvents.—Solvents were prepared as previously reported.[1]

Rate Measurements.—The rates of solvolysis were followed titrimetrically. At appropriate times, 2-ml aliquots were analyzed for liberated *p*-toluenesulfonic acid. In ethanol and aqueous ethanol solvents, aliquots were analyzed for developed acid by titrating with aqueous sodium hydroxide to a brom thymol blue end point. In acetic acid, aliquots were analyzed for developed acid by titrating with standard sodium acetate in acetic acid to the yellow end point of bromphenol blue. In the acetolysis reactions of **3**-OH, the aliquot was added to an excess of standardized perchloric acid dissolved in acetic acid before back titrating with sodium acetate. The rate of the reaction in formic acid was followed by quenching the aliquots in 10 ml of purified dioxane and titrating to the yellow end point of bromcresol green. In the formolysis reactions of **3**-OH, the aliquots were quenched in 10 ml of dioxane containing an excess of standardized perchloric acid in acetic acid and then back-titrated with sodium acetate in acetic acid.

Product Studies.—Solvolyses of **1**-OH (3.0 g, 11.7 mmoles) and **2**-OH (2.5 g, 9.2 mmoles) were carried out in 100 ml of absolute ethanol at 60° for 12 half-lives. In each reaction, most of the solvent was removed by rotary evaporization and residue dissolved in 40 ml of methylene chloride. After washing twice with 30-ml portions of cold sodium bicarbonate solution and drying over anhydrous sodium sulfate, the solvent was removed by rotary evaporization to yield 1.5 (97%) and 1.3 g (99%) of product, respectively. By comparison with authentic samples (gc and infrared spectra), the identity of the **1**-OH ethanolysis product with **5** and the **2**-OH ethanolysis product with **6** was established.

Registry No.—**1**, 3558-06-3; **1**-OH, 15051-88-4; **2**, 953-91-3; **2**-OH, 15051-90-8; **3**, 957-29-9; **3**-OH, 15051-92-0; **4**, 6597-09-7; **5**, 15051-94-2; **6**, 15051-95-3; cyclopentene oxide, 285-67-6; cycloheptene oxide, 286-45-3.

(29) A. J. Durbetaki, *J. Org. Chem.*, **26**, 1017 (1961).
(30) R. Criegee and H. Stranger, *Ber.*, **69**, 2753 (1936).
(31) M. Mousseron, R. Granger, and A. Merle, *Bull. Soc. Chim. France*, 459 (1947).
(32) G. B. Payne and C. W. Smith, *J. Org. Chem.*, **22**, 1680 (1957).
(33) A. Roebuck and H. Adkins, *Org. Syn.*, **3**, 217 (1955).