Several attempts to isolate aletheine as the oxalate, following the sodium–liquid ammonia reduction of bis-[N-(N-carbobenzoxy-β-alanyl)-2-aminoethyl] disulfide were unsuccessful.[20]

Kinetic Runs.—The kinetic runs were carried out essentially as described previously,[4] following the rate of the disappearance of the thioester group by measuring the ultraviolet absorption at 233 mμ with a Beckman DU spectrophotometer. It was shown that the thioesters obeyed Beer's law strictly; the $\epsilon \times 10^{-3}$ values at 233 mμ for the three thioesters were as follows: III, 4.51 ± 0.027; IV, 5.19 ± 0.082; V, 4.75 ± 0.032.

Isolation of Products. A. From N,S-Diacetylaletheine (V).—One gram of N,S-diacetylaletheine was hydrolyzed in 1 l. of 0.1 *M* sodium hydroxide at room temperature for 5 days, after which air was bubbled through the solution until no test for the thiol group was given using iodine–potassium iodide. The *p*H was brought to 3, with 1 *N* hydrochloric acid, the solution was reduced to dryness at 40°, with a water-pump, and the residue was extracted with 200 cc. of warm anhydrous methanol. The mixture was filtered, and the filtrate was evaporated to dryness with a water-pump. The white crystalline residue weighed 0.85 g. (m.p. 190–200°) and after two crystallizations from methanol yielded 0.80 g. (98%), m.p. 208–209°, of the expected disulfide, diacetylalethine (the disulfide derived from V, R = H); there was no depression on mixed m.p. with an authentic sample.

B. **From γ-Acetaminopropyl Thioacetate (IV).**—By essentially the above procedure, hydrolysis of 1 g. of IV and 0.1 *M* alkali yielded 97% of the expected disulfide (corresponding to IVb), m.p. and mixed m.p. 88.5–90°.

ROCHESTER, N. Y.

(20) T. E. King, C. J. Stewart and V. H. Cheldelin, THIS JOURNAL, **75**, 1290 (1953).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

The Effect of Ring Size on the Rate of Acetolysis of the Cycloalkyl *p*-Toluene and *p*-Bromobenzenesulfonates[1]

BY HERBERT C. BROWN AND GEORGE HAM[2]

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A number of cycloalkyl tosylates (4-, 5-, 6-, 7-, 8-, 9-, 11-, 12-, 13-, 14-, 15- and 17-ring members) have been synthesized and the rates of acetolysis measured at several temperatures in order to ascertain the effect of ring size on reactivity. The behavior of several brosylates (5-, 6- and 7-) was also examined. In the common rings, the cyclopentyl and cycloheptyl derivatives exhibit an enhanced reactivity attributed to the de-eclipsing of bonds in the ionization stage. On the other hand, the decreased reactivity of the cyclohexyl derivatives is attributed to an increase in bond opposition in the ionization stage. A further increase in reactivity is observed in the medium rings (8- to 12-) followed by a decrease in the large rings (13- to 17-) to rates of reactions similar to those observed in open-chain compounds. The maximum in reactivity in the medium rings is attributed to a relief of strain accompanying the loss of a bond in the ionization stage. For the strained rings (5- to 11-members) a simple relationship exists between the association constants for cyanohydrin formation and the rate constants for acetolysis of the tosylates.

Ring compounds exhibit a remarkable change in chemical reactivity with ring size.[3–6] It has been proposed that the changes in chemical reactivity can be correlated with the changes in internal strain accompanying the formation or breaking of a bond to the ring atom in the rate-determining stage.[5–7]

The available data are too few to permit a rigorous test of the utility of the proposed explanation. In order to obtain data of this kind we are currently examining the effect of ring size on the reactivity of ring derivatives in a few representative reactions. The present paper reports a study of the effect of ring size on the acetolysis of cyclic tosylates[8] and certain selected brosylates.

Results

The *p*-toluenesulfonates of cyclobutanol, cyclopentanol, cyclohexanol, cycloheptanol, cyclooctanol, cyclononanol, cycloundecanol, cyclododecanol, cyclotridecanol, cyclotetradecanol, cyclopentadecanol, cycloheptadecanol and the *p*-bromobenzenesulfonates of cyclopentanol, cyclohexanol and cycloheptanol were prepared by treating the alcohol with *p*-toluenesulfonyl or *p*-bromobenzenesulfonyl chloride in dry pyridine, essentially according to the method described by Tipson.[9]

The *p*-toluenesulfonates of cycloheptanol, cycloöctanol, cyclononanol and cycloundecanol were relatively unstable, the cycloheptyl compound undergoing decomposition after several days at room temperature and the others undergoing decomposition after several days at 0–10°. The product obtained by treatment of cyclodecanol with *p*-toluenesulfonyl chloride in dry pyridine decomposed rapidly at room temperature upon removal of the ether with which it had been extracted. Before the preparation could be repeated, it was learned that the compound had been synthesized in another laboratory and its rate of acetolysis measured.[8] Accordingly no attempt was made to repeat this preparation.

The properties of the cyclanols and the aryl-

(1) Chemical Effects of Steric Strains. XII.

(2) Research assistant on a contract supported by the Office of Naval Research and a grant provided by the National Science Foundation.

(3) V. Prelog, *J. Chem. Soc.*, 420 (1950).

(4) J. D. Roberts and V. C. Chambers, THIS JOURNAL, **73**, 5034 (1951).

(5) H. C. Brown, R. S. Fletcher and R. B. Johannesen, *ibid.*, **73**, 212 (1951).

(6) H. C. Brown and M. Borkowski, *ibid.*, **74**, 1894 (1952).

(7) P. D Bartlett, *Bull. soc. chim.*, C100 (1951).

(8) In the course of discussions with Professor V. Prelog during the Fourteenth International Congress of Pure and Applied Chemistry in Zurich, July 21–27, 1955, it was learned that Professor Prelog and Dr. R. Heck had carried out a similar study of the acetolysis of the cycloalkyl tosylates (6-, 7-, 8-, 9-, 10-, 11-, 12- and 20-ring members). These results have since been published: R. Heck and V. Prelog, *Helv. Chim. Acta*, **38**, 1541 (1955). The present study includes data on certain tosylates (4-, 5-, 13-, 14-, 15- and 17-ring members) and brosylates (5-, 6- and 7-) not included in the investigation by Heck and Prelog. Moreover, it should be of interest to compare the agreement realized in a closely similar study in two different laboratories. Consequently, we are reporting all of our results even where these duplicate those obtained by Heck and Prelog.

(9) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

TABLE I

PHYSICAL PROPERTIES OF CYCLANOLS AND CYCLOALKYL ARYLSULFONATES

n	Observed B.p., °C. (mm.)	Observed M.p., °C.	Observed $n^{20}D$	Literature B.p., °C. (mm.)	Literature M.p., °C.	Literature $n^{20}D$	Ref.
Cyclanols, $(CH_2)_{n-1}CHOH$							
4	123.0–124.0			125.0			*g*
5	138.2 (754)		1.4529	139		1.4530	*h*
6	160.5–161.0		1.4647	158–159		1.4642	*i*
7	86.0 (20)		1.4770	95 (24)		1.4772^{25}	*f*
8			1.4835			1.4848^{25}	*f*
9	115.0–116.0 (16)		1.4901	115 (17)			*d*
11	118.0–119.0 (7)			128–131 (20)			*d*
12		75.0–76.0			80		*d*
13		59.5–60.3			60–60.5		*d*
14		79.0–80.0			79.0–80.0		*d*
15		80.5–81.2			81		*d*
17		80.0–81.0			81		*d*
Cycloalkyl tosylates, $(CH_2)_{n-1}CHOTs$							
4		24.0–25.0			24–25		*e*
5		28.5–29.0			27.0–28.0		*e*
6		44.5–45.0			43.5–44.0		*c*
7		19.0–19.6	1.5263		Liq.		*k*
8			1.5276		Liq.		*k*
9		43.7–44.5			Liq.		*k*
11		44.2–45.4			43–44		*k*
12		87.0–87.6			88–89.5		*k*
13		36.3–37.2					*a*
14		77.5–78.8					*a*
15		47.2–48.0					*a*
17			1.5092^{25}				*a*
Cycloalkyl brosylates, $(CH_2)_{n-1}CHOBs$							
5		45.8–46.6			45.5–46.0		*j*
6		48.5–49.0			48.1–48.6		*b*
7		32.0–32.5					*a*

[a] New compound. [b] S. Winstein, E. Grunwald and L. Ingraham, THIS JOURNAL, **70**, 821 (1948). [c] S. Winstein, E. Grunwald, R. E. Buckles and C. Hanson, *ibid*, **70**, 816 (1948). [d] M. Kobelt, P. Barman, V. Prelog and L. Ruzicka, *Helv. Chim. Acta*, **32**, 256 (1949). [e] Ref. 4. [f] H. H. Zeiss and M. Tsutsui, THIS JOURNAL, **75**, 897 (1953). [g] J. D. Roberts and C. W. Sauer, *ibid.*, **71**, 3925 (1949). [h] C. R. Noller and R. Adams, *ibid.*, **48**, 1080 (1926). [i] H. E. Ungnade and D. Nightingale, *ibid.*, **66**, 1219 (1944). [j] R. B. Loftfield, *ibid.*, **73**, 4707 (1951). [k] Ref. 8.

TABLE II

RATE CONSTANTS AND DERIVED DATA FOR THE ACETOLYSIS OF THE CYCLOALKYL TOSYLATES $(CH_2)_{n-1}CHOTs$

n	Temp., °C.	Rate constant k_1, sec.$^{-1}$	Rel. rate at 70°	$\Delta H^{\pm}$, kcal./mole	$\Delta S^{\pm}$, e.u.
4	70.0	2.67×10^{-4}[a]	11.3		
	80.0	7.38×10^{-4}			
	90.0	1.65×10^{-3}			
5	30.0	3.23×10^{-6}	14.0	24.1	−4.2
	50.0	3.82×10^{-5}			
	70.0	3.32×10^{-4}			
6	50.0	1.82×10^{-6}	1.00	27.3	−0.5
	70.0	2.37×10^{-5}			
	90.0	2.22×10^{-4}			
7	50.0	6.45×10^{-5}	25.3	23.3	−5 7
	70.0	6.00×10^{-4}		(23.5)[b]	(−5.4)[b]
	90.0	3.95×10^{-3}			
8	25.0	2.82×10^{-5}	191	22.3	−4.5
	50.0	5.68×10^{-4}		(22.5)[b]	(−4.1)[b]
	70.0	4.52×10^{-3}			
9	25.0	2.43×10^{-5}	172	22.5	−4.2
	35.0	8.72×10^{-5}		(23.9)[b]	(+0.1)[b]
	70.0	4.08×10^{-3}			
10	25.0	(4.69×10^{-5})[b]	380[c]	(23.0)[b]	(−1.1)[b]
	50.0	(1.03×10^{-3})[b]			
11	35.0	2.02×10^{-5}	48.9	23.7	−3.2
	50.0	1.29×10^{-4}		(24.7)[b]	(−0.2)[b]
	70.0	1.16×10^{-3}			
12	50.0	5.97×10^{-6}	3.25	27.6	2.8
	70.0	7.70×10^{-5}		(27.9)[c]	(3.8)[b]
	90.0	7.63×10^{-4}			
13	50.0	7.27×10^{-6}	3.50	26.2	−1.3
	70.0	8.30×10^{-5}			
	90.0	7.25×10^{-4}			
14	50.0	2.47×10^{-6}	1.32	27.8	1.7
	70.0	3.12×10^{-5}			
	90.0	3.28×10^{-4}			
15	50.0	4.30×10^{-6}	2.19	26.5	−1.3
	70.0	5.18×10^{-5}			
	90.0	4.53×10^{-4}			
17	50.0	4.38×10^{-6}	2.17	26.5	−1.4
	70.0	5.15×10^{-5}			
	90.0	4.60×10^{-4}			
20	50.0	(3.57×10^{-6})[b]	1.80[c]	(26.6)[b]	(−1.3)[b]
	75.0	(7.52×10^{-5})[b]			
$(n\text{-}C_3H_7)_2$-CHOTs	70.0	3.15×10^{-5}	1.33		

[a] Initial rate constant, uncorrected for rearrangement. [b] Ref. 8. [c] Calcd. from extrapolated value of rate constant.

sulfonates used in this investigation are summarized in Table I.

The rates of acetolysis of the cyclic arysulfonates were measured in acetic acid containing 0.046 mole per liter of acetic anhydride essentially according to the procedure described by Winstein and co-workers.[10] In order to have the value for a typical open-chain compound for comparison, 4-heptyl tosylate was synthesized and its rate of acetolysis determined. The results are summarized in Tables II and III.

TABLE III

RATE CONSTANTS AND DERIVED DATA FOR THE ACETOLYSIS OF THE CYCLOALKYL BROSYLATES ($CH_2)_{n-1}$CHOBs

n	Temp., °C.	Rate constant k_1, sec.$^{-1}$	$\Delta H^{\pm}$, kcal./mole	$\Delta S^{\pm}$, e.u.
5	25.0	6.28×10^{-6}	22.7	−6.3
	50.0	1.29×10^{-4}		
	70.0	1.10×10^{-3}		
6	50.0	6.60×10^{-6}	26.8	0.4
	70.0	8.02×10^{-5}		
	90.0	7.28×10^{-4}		
7	25.0	1.04×10^{-5}	23.0	−4.2
	50.0	2.23×10^{-4}		
	60.0	6.70×10^{-4}		
	70.0	1.98×10^{-3}		

The enthalpies and entropies of activation for the acetolysis of cyclopentyl and cyclohexyl *p*-toluenesulfonates have been reported previously both by Roberts and Chambers[4] and by Winstein and his co-workers.[11] Unfortunately, their results are not in agreement. Therefore we undertook to measure the rate constants for these two compounds in order to compare our values with those previously reported. The available data are summarized in Table IV.

TABLE IV

ENTHALPIES AND ENTROPIES OF ACTIVATION FOR THE ACETOLYSIS OF CYCLOPENTYL AND CYCLOHEXYL TOSYLATES

Tosylate	$\Delta H^{\pm}$, kcal./mole	$\Delta S^{\pm}$, e.u.	Ref.
Cyclopentyl	27.6	6.7	Roberts[4]
	23.7	−6.4	Winstein[11]
	24.1	−4.2	Present study
Cyclohexyl	27.4	0.6	Roberts[4]
	27.0	−1.1	Winstein[11]
	27.3	−0.5	Present study

Roberts and Chambers found no significant difference in the enthalpies of activation for the cyclopentyl and cyclohexyl tosylates and therefore attributed the difference in reactivity to a large entropy factor. On the other hand, Winstein and his co-workers attributed the difference in reactivity of the two compounds primarily to the difference of 3.3 kcal./mole in the enthalpy of activation. Our present results indicate a difference in the enthalpy of activation of 3.2 kcal./mole and therefore support the conclusion reached by Winstein.

The change in the rate constants with temperature observed in the three studies is shown in Fig. 1.

The solvolysis of the brosylates proceeds at a considerably greater rate than that of the tosylates. However, the effect of ring size on the solvolysis rate is essentially identical in the two systems.

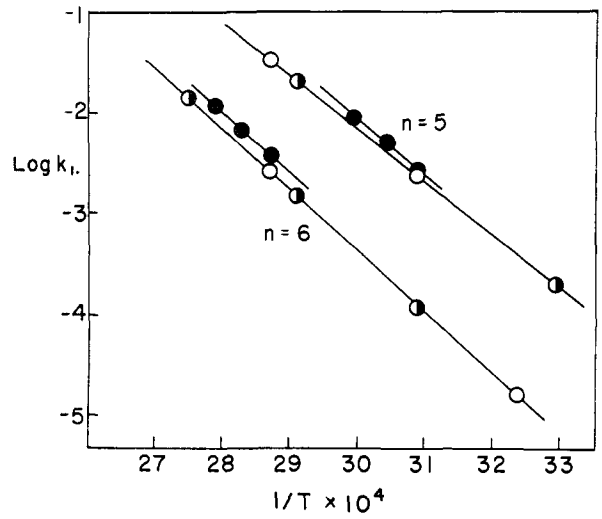


Fig. 1.—Activation energies for the acetolysis of cyclohexyl and cyclopentyl *p*-toluenesulfonates: O, data reported by Winstein and co-workers[11]; ●, data reported by Roberts and co-workers[4]; ◑, data obtained in this study.

Discussion

At the present time, three sources of steric strains are recognized: (1) the compression of van der Waals radii, (2) the distortion of bond angles, and (3) bond opposition forces. In the case of small rings, the distortion of bond angles appears to be the major source of strain.[5,6] In cyclopentane and cycloheptane it is the bond opposition forces which are primarily responsible for the strains revealed in combustion studies,[12] while the available evidence suggests that both bond oppositions and compressions of van der Waals radii are probably responsible for the strains exhibited by the medium rings.[3]

It was suggested that reactions involving an increase in these internal strains will be hindered, whereas those proceeding with a decrease in internal strains will be assisted.[5] Ideally one should discuss the effect of making or breaking a bond to one of the ring atoms in terms of each of these possible strain factors. Unfortunately, this cannot be done at the present time. These different strains are not mutually independent nor can they be estimated individually with any precision at the present time.

The net change in internal strain accompanying the formation or the breaking of a bond to a ring atom can be estimated with considerable precision from rate, equilibrium and thermochemical data. In view of this circumstance it appears more desirable at the present time to discuss the reactions

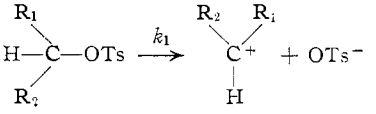
(10) S. Winstein, C. Hanson and E. Grunwald, THIS JOURNAL, **70**, 812 (1948).

(11) S. Winstein, E. Grunwald and L. Ingraham, *ibid.*, **70**, 821 (1948); S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan and H. Marshall, *ibid.*, **74**, 1127 (1952).

(12) K. S. Pitzer, *Science*, **101**, 672 (1945); J. E. Kilpatrick, K. S. Pitzer and R. Spitzer, THIS JOURNAL, **69**, 2483 (1947).

of ring compounds in terms of the net change in internal strain accompanying the reaction (I-strain). It should be recognized that I-strain will be made up of individual contributions from angle deformations, bond oppositions and atomic compressions, the relative magnitudes of which will vary from system to system.

The solvolysis of secondary alkyl *p*-toluenesulfonates in dry acetic acid is considered to proceed by a mechanism involving a slow rate-determining ionization of the *p*-toluenesulfonate group.[13]



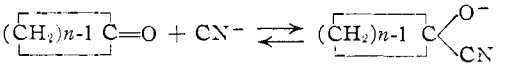
The I-strain theory predicts that such ionization reactions should proceed relatively slowly in the 3- and 4-membered rings primarily because of an increase in angle strain accompanying ionization.[5] Such a slow reaction has been observed in the cyclopropyl tosylate and in 1-chloro-1-methylcyclobutane.[6] However, the rate of solvolysis of cyclobutyl tosylate is relatively fast.[4] The fast rate of this derivative is confirmed in the present study (Table II). Roberts and Chambers noted that the solvolysis of cyclobutyl tosylate is accompanied by extensive rearrangement.[4] It may be that the ionization does not proceed to the strained cyclobutyl carbonium ion, but instead proceeds directly to a more stable rearranged structure. In that event, the I-strain theory would not be applicable.

According to the I-strain interpretation, an ionization reaction should be strongly favored in the strained 5- and 7-ring systems, but not in the stable, unstrained cyclohexyl derivatives. Indeed, in the cyclohexyl carbonium ion there will be introduced two partial oppositions,[14] so that this molecule should tend to resist the ionization reaction in comparison to an open-chain derivative.

Prelog has presented convincing evidence that the medium rings are strongly strained.[3] The strain is presumably the effect of bond opposition forces, with some contribution possible from atom compression. Here also the internal strain should be partially relieved by a decrease in the number of bonds. Finally, the large rings should be essentially strain free and the reactivities should approach those of the open-chain compounds.

The experimental results (Fig. 2) are in complete accord with the predictions of the I-strain interpretation.

According to the I-strain hypothesis the opposite effects should be observed in rate or equilibrium data involving a reaction in which there is an increase in the number of bonds attached to a ring atom. The similarity in the effects of ring size on the rates of acetolysis of the cycloalkyl tosylates (Fig. 2) and on the equilibrium constants for the formation of the cyclic cyanohydrins[15] is noteworthy.



Hammett has demonstrated the existence of linear free energy relationships in *meta* and *para* aromatic systems.[16] In general, aliphatic derivatives do not obey such relationships.[17] However, in the case of the rigid 4-substituted bicyclo[2:2:2]-octane-1-carboxylic acids Roberts and Moreland have demonstrated the existence of similar linear free energy relationships.[18] Presumably, the existence of such free energy relationships in both the benzene and bicycloöctane systems is due to the rigidity of the structures and the fact that the structural changes are far removed from the reaction center.

It was of interest to examine the possible existence of a similar quantitative relationship between the rate constants for the acetolysis of the cycloalkyl tosylates and the equilibrium constants for the formation of the cyclic cyanohydrins (Fig. 3). The rings from 5- to 11-members do appear to obey a simple linear relationship, with the larger rings and the simple open-chain derivatives possibly defining a second line.

It will be important to determine whether this linear relationship is obeyed by other reactions of the cyclic systems. If so, it may be a consequence of the fact that the rings from 5- to 11-members do not possess the free mobility of the larger rings or of the open-chain derivatives.

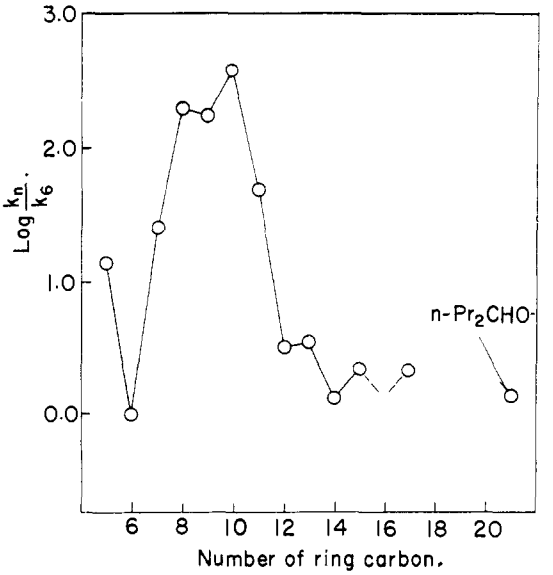


Fig. 2.—The effect of ring size on the rate of acetolysis of the cycloalkyl *p*-toluenesulfonates at 70°. (The value for cyclodecyl tosylate was provided by Professor V. Prelog, ref. 8.)

Experimental Part

Kinetic Measurements.—The solvent was prepared by treating 8.0 l. of reagent grade acetic acid (Baker and

(13) E. Grunwald and S. Winstein, THIS JOURNAL, **70**, 846 (1948).

(14) H. C. Brown, J. H. Brewster and H. Shechter, *ibid.*, **76**, 467 (1954).

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

(16) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

(17) In recent years R. Taft has succeeded in developing such linear relationships in a few selected aliphatic systems by introducing a correction term for the steric effect. See R. Taft, THIS JOURNAL, **74**, 2729, 3120 (1952); **75**, 4231, 4534, 4538 (1953).

(18) J. D. Roberts and W. T. Moreland, Jr., *ibid.*, **75**, 2167 (1953).

Adamson) with a slight excess of acetic anhydride. The product was fractionated. From a cooling curve on the distillate, the acid was found to be 0.042 M in an impurity assumed to be acetic anhydride. Analysis indicated the solvent to be 0.046 M in acetic anhydride. This product was used for all of the kinetic measurements.

The procedure for determining the rate constants was essentially that of Winstein and co-workers.[10]

Rate measurements were made at three different temperatures for each compound, usually over a range of 40°. The temperatures were controlled to ±0.02°. The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were obtained by plotting log k_1/T *versus* $1/T$ and determining $\Delta H^{\ddagger}$ from the slope and $\Delta S^{\ddagger}$ from the intercept of the best straight line through the three points as calculated by the methods of least squares.

Materials.—The cyclanones are all known compounds which were synthesized by methods previously described in the literature.

TABLE V

ANALYTICAL DATA ON THE CYCLANYL ARYLSULFONATES

Compound	Sapon. equiv. Calcd.	Found	Analyses, % Calcd. C	H	Found C	H
Cycloheptyl tosylate			62.66	7.51	62.78	8.00
Cyclooctyl tosylate	282	287				
Cyclononyl tosylate	296	296				
Cycloundecyl tosylate	324	324				
Cyclododecyl tosylate	339	339	67.41	8.93	67.26	9.05
Cyclotridecyl tosylate	324	324	68.14	9.15	68.37	9.46
Cyclotetradecyl tosylate	367	370	68.81	9.35	69.08	9.33
Cyclopentadecyl tosylate	382	383	69.25	9.51	69.35	9.77
Cycloheptadecyltosylate	409	418	70.54	9.87	70.96	10.34
Cycloheptyl brosylate			46.85	5.12	47.01	5.26

The pure ketones were reduced on a small scale (2.0–3.0 g.) by lithium aluminum hydride in ethyl ether. The yields were from 80 to 95% of the theoretical. The properties of the cyclanols are summarized in Table I.

We were uncertain of the purity of the cycloheptanol and therefore undertook to purify it by the preparation and recrystallization of cycloheptyl 3,5-dinitrobenzoate, followed by hydrolysis of the ester to recover the cycloheptanol. Cycloheptyl 3,5-dinitrobenzoate, recrystallized twice from ethanol and twice from aqueous acetone, melted at 81.0–82.0°. *Anal.* Calcd. for $C_{14}H_{16}N_2O_6$: C, 54.55; H, 5.23. Found: C, 54.84; H, 5.16.

Because of the small amount of materials available, considerable time was devoted to a study of the preparation of the cycloalkyl *p*-toluenesulfonates and *p*-bromobenzenesulfonates in good yield on a small scale. The following procedure gave the esters in yields of 70 to 90%.

The alcohol (1.0–2.0 g.) was mixed with cooling with twice the theoretical quantity of the arylsulfonyl chloride and sufficient dry pyridine to make the solution approximately 1.0 molar in alcohol. After 12 to 24 hours at 0°, a small quantity of water was carefully added with cooling to the mixture to hydrolyze the excess sulfonyl chloride. Additional water was then added, until the solution had been diluted to 2 to 5 times its original volume. The aqueous pyridine mixture was extracted with ether. The ether extract was washed with cold dilute hydrochloric acid solution, sodium bicarbonate solution, water and then dried over anhydrous sodium sulfate. The ether was then removed under reduced pressure. The product was usually recrystallized from petroleum ether.

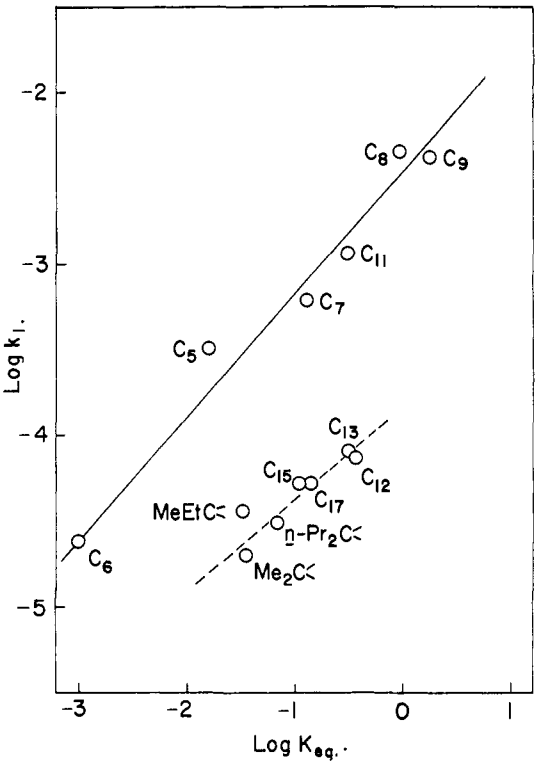


Fig. 3.—Relationship between the effect of ring size on the rate of acetolysis of the cycloalkyl tosylates (70°) and the equilibrium constants (22°) for the formation of the cyclic cyanohydrins. (The equilibrium constants for the aliphatic cyanohydrins at 22° were calculated from the data at 35° of D. D. Evans and J. R. Young, *J. Chem. Soc.*, 1310 (1954).)

Analytical data on the new cyclanyl arylsulfonates are summarized in Table V.

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LAFAYETTE, IND.