tilled before use. [i] J. Cason and C. F. Allen, *J. Org. Chem.*, **14**, 1036 (1949). [j] From the carbonation of cyclopentylmagnesium bromide. [k] From the hydrogenation of benzoic acid; m.p. 31.0–31.6°. [l] From the hydrogenation of cyclopentanone oxime. [m] M. J. Schlatter, THIS JOURNAL, **63**, 1733 (1941). [n] J. D. Roberts and C. W. Sauer, *ibid.*, **71**, 3925 (1949). [o] Prepared by alkylation of the corresponding cycloalkylamine by a procedure similar to that employed by Roberts and Sauer[n] for cyclobutyldimethylamine. To ensure removal of all primary and secondary amines, the crude product was treated with benzoyl chloride and sodium hydroxide. [p] Picrate, yellow platelets from ethanol, m.p. 177–178° (dec.). *Anal.* Calcd. for $C_{13}H_{12}O_7H_4$: C, 45.61; H, 5.26. Found: C, 45.91; H, 5.44.

TABLE VI

DIELECTRIC CONSTANTS, DENSITIES AND POLARIZATIONS IN BENZENE AT 25°

f_2	ϵ	d	P_2
	Cyclopropyl bromide		
0.00000	(2.2725)	0.87278	(P_1 = 26.66)
.00510	2.290	.87562	75.1
.00999	2.310	.87837	78.7
.01959	2.348	.88386	79.8
.02908	2.386	.88915	79.8
.03844	2.423	.89437	79.6
.04776	2.462	.89990	79.5
	Cyclobutyl bromide		
0.00469	2.300	0.87550	114.1
.00900	2.326	.87792	115.6
.01753	2.376	.88275	113.8
.02604	2.428	.88752	113.9
.03537	2.483	.89304	112.0
.05033	2.574	.90177	111.0
	Cyclopentyl bromide		
0.00406	2.300	0.87524	128.9
.01374	2.361	.88107	125.1
.02429	2.428	.88746	123.6
.03529	2.498	.89420	122.1
.04848	2.583	.90221	120.9
.06033	2.658	.90941	119.5
	Cyclohexyl bromide		
0.00410	2.303	0.87516	147.5
.01458	2.378	.88170	141.3
.02977	2.485	.89084	138.1
.03725	2.535	.89547	135.9
.04519	2.592	.90022	135.1
.05471	2.656	.90587	133.4

Dipole moments were determined by the method described previously.[15] The data are given in Tables III and VI.

Infrared spectra of the cycloalkyl chlorides and bromides were taken with a Baird Recording Infrared Spectrophotometer. The samples were run successively in an 0.025 mm. rock salt cell without solvent and with a rock salt slab in the comparison cell compartment. The curves so obtained are given in Figs. 2 and 3. For the calculation of extinction coefficients, the curves were corrected for the difference in transmission between cell and salt block and Beer's law was assumed. The extinction coefficients at the absorption peaks are given in Table IV. The integrated extinction coefficients per C–H bond were obtained as described earlier.

(15) J. D. Roberts, R. Armstrong, R. F. Trimble, Jr., and M. Burg, THIS JOURNAL, **71**, 843 (1949).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, AND CONVERSE MEMORIAL LABORATORY, HARVARD UNIVERSITY]

Small-Ring Compounds. VIII. Some Nucleophilic Displacement Reactions of Cyclopropyl, Cyclobutyl, Cyclopentyl and Cyclohexyl *p*-Toluenesulfonates and Halides

BY JOHN D. ROBERTS[1] AND VAUGHAN C. CHAMBERS

A study has been made of the rates and products of some nucleophilic displacement reactions of cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl *p*-toluenesulfonates and halides. The solvolysis reactivity sequence of the *p*-toluenesulfonates in dry acetic acid was found to be cyclopentyl ~ cyclobutyl > cyclohexyl ≫ cyclopropyl. The hydrolysis rate sequence for the corresponding chlorides in 50% ethanol–50% water solution was similar except that the cyclobutyl derivative was more reactive than the cyclopentyl derivative. In acetolysis and hydrolysis, the cyclopropyl and cyclobutyl compounds react with rearrangement but without elimination. The cyclopentyl and cyclohexyl derivatives give no detectable rearrangement products but do yield considerable cyclopentene and cyclohexene, respectively. The reactivity sequence of the bromides toward sodium iodide in acetone was found to be cyclopentyl > cyclobutyl > cyclohexyl ≫ cyclopropyl. The significance of the experimental results lies primarily in the lack of any simple correlation of reactivity with ring size in contrast to expectations based on other properties of small-ring compounds.

Despite the very considerable work on the synthesis and reactions of small-ring compounds in the seventy years following the synthesis of cyclopropane by Freund,[2] very little information is available on the nucleophilic displacement reactions of cyclopropyl and cyclobutyl derivatives. Gustavson[3] early noted that cyclopropyl chloride was comparable in reactivity to 1-chloropropene toward alcoholic potassium hydroxide but made no mention of other nucleophilic reagents. Perkin[4] reported that a chloride obtained from "cyclobutanol" and phosphorus pentachloride reacted abnormally slowly with potassium iodide in acetone. However, the purity of Perkin's chloride is questionable since rearrangement products could be expected, not only in his preparation of cyclobutanol,[5,6] but in the reaction of the latter substance with phosphorus pentachloride.[6] No other work on nucleophilic displacement reactivities or reactions of cyclopropyl or cyclobutyl derivatives appears to have been published except for some research on cyclobutyl chloride[6] which will be referred to later

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(2) A. Freund, *Monatsh.*, **3**, 625 (1882).

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

(4) W. H. Perkin, Jr., *J. Chem. Soc.*, **65**, 950 (1894).

(5) (a) N. J. Demjanow, *Ber.*, **40**, 4961 (1907); (b) R. Skrabal, *Monatsh.*, **70**, 420 (1937).

(6) J. D. Roberts and R. H. Mazur, THIS JOURNAL, **73**, 2509 (1951).

TABLE I

RATES, ENTHALPIES AND ENTROPIES OF ACTIVATION, AND PRODUCTS OF SOLVOLYSIS OF CYCLOALKYL *p*-TOLUENESULFONATES (RX) IN ACETIC ACID CONTAINING 1% OF ACETIC ANHYDRIDE

R	RX, *M*	KOAc, *M*	Temp., ±0.2°C.	k_1, hr.$^{-1}$	k_1', hr.$^{-1}$[a]	$\Delta H^{\ddagger}$, kcal.[b]	$\Delta S^{\ddagger}$, e.u.[c]	Relative rate, 60°[d]	Reaction products[e]
Cyclopropyl	0.097	0.115	170.0	0.167	...				
	.095	.102	171.0	.182	.182				
	.095	.102	175.0	.254	.256	33.8	−2.9	2×10^{-5}[f]	100% allyl acetate
	.095	.102	180.0	.385	.36				
	.469	.509	175.0	.330	...				
Cyclobutyl	.099	.107	50.0	.121[g]	...				
	.089	.103	55.1	.274	.04	(30)	(20?)[h]	14	65% cyclopropylcarbinol acetate
	.089	.107	60.1	.497	.08				22% cyclobutyl acetate
	.496	.500	50.0	.191[i]	.020				13% allylcarbinyl *p*-toluenesulfonate
Cyclopentyl	.099	.113	50.0	.154	.065				
	.098	.103	55.1	.291	.125	27.6	+6.7	16	61% cyclopentyl acetate
	.096	.103	60.1	.568	.222				39% cyclopentene
	.491	.515	50.0	.259	.101				
Cyclohexyl	.098	.102	75.0	.217	.183				
	.099	.102	80.0	.385	.327	27.4	+0.6	1.00	15% cyclohexyl acetate
	.099	.104	85.0	.671	.557				85% cyclohexene
	.491	.511	75.0	.394	.335				
Phenyl	.099	.106	190.0	.00	...				

[a] First-order rate constant for formation of unsaturated material as determined by bromide–bromate titrations. [b] For solvolysis reaction, probable error ± 1.0 kcal. except for cyclobutyl derivative where probable error is ±3 kcal. [c] For solvolysis reaction, probable error ±2 e.u. [d] Rate relative to cyclohexyl *p*-toluenesulfonate, taken as 1.00, with 0.1 *M* KOAc at 60°. [e] With 0.5 *M* KOAc, at temperature given for 0.5 *M* KOAc kinetic experiment. [f] Extrapolated from rate at 170°. [g] Under similar conditions (0.1 *M* KOAc, 50°) allylcarbinyl *p*-toluenesulfonate was 3% solvolyzed in 72 hr. [h] The uncertainty in the value of $\Delta H^{\ddagger}$ for the cyclobutyl compound prevented accurate calculation of $\Delta S^{\ddagger}$. [i] Under these conditions (0.5 *M* KOAc, 50°) allylcarbinyl *p*-toluenesulfonate was 14% solvolyzed in 72 hr.

and a preliminary announcement[7] that the unimolecular hydrolysis of 1-methyl-1-chlorocyclobutane is exceedingly slow compared to that of *t*-butyl chloride. In the present investigation, a study has been made of the behavior of a series of cycloalkyl derivatives in typical nucleophilic displacement reactions of the stepwise ionization (S_N1) and one-stage (S_N2) varieties.

The solvolysis of *s*-alkyl *p*-toluenesulfonates in dry acetic acid appears to proceed by a mechanism involving a slow ionization step, the rate of which is determined more by the ionizing than by the nucleophilic properties of the solvent.[8] This fact, along with the evidence presented[9] for the occurrence of the same sort of mechanism in the acetolysis of cyclohexyl *p*-toluenesulfonate indicates the suitability of the solvolysis of these esters in acetic acid as model ionization (S_N1) reactions for cycloalkyl derivatives. Data obtained on the rates and products of the acetolysis of cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl *p*-toluenesulfonates are summarized in Table I. The solvolysis of the cyclobutyl derivative is accompanied by a first-order (apparently intramolecular) rearrangement reaction which yields allylcarbinyl *p*-toluenesulfonate at a rate about one-tenth that of solvolysis. A similar although somewhat faster rearrangement was noted previously in the acetolysis of cyclobutyl chloride.[6]

The solvolysis of cyclopropyl *p*-toluenesulfonate proceeds with rearrangement and yields allyl acetate. This behavior parallels that observed in the cyclopropylamine–nitrous acid reaction which yields allyl alcohol and no cyclopropanol.[10] While it is not certain that the cyclopropyl cation is actually an intermediate in these reactions, the very low reactivity of cyclopropyl *p*-toluenesulfonate makes it unlikely that the relatively stable allyl cation is formed directly in the rate-determining step. Acetolysis of cyclobutyl *p*-toluenesulfonate at 50° yields 25% cyclobutyl acetate and 75% cyclopropylcarbinyl acetate. The product ratio is quite analogous to those obtained in other carbonium ion reactions of cyclobutyl derivatives.[6] Cyclopentyl and cyclohexyl *p*-toluenesulfonates solvolyze without rearrangement but yield 39% cyclopentene and 85% cyclohexene, respectively.

The solvolysis kinetics of all of the *p*-toluenesulfonates studied in the present work were followed to better than 80% reaction and proved to be strictly first-order (*cf.* Fig. 1). Positive salt effects were found, as would be expected for rate-determining ionizations.[11] The salt effects increased fairly smoothly with ring size and the changes in rate constant ranged from 30% for cyclopropyl *p*-toluenesulfonate to 82% for the corresponding cyclohexyl derivative in the transition from $\mu = 0.1$ to $\mu = 0.5$. The rate and activation energy data (Table I) indicate the ease of ionization of the cycloalkyl *p*-toluenesulfonates to be cyclopentyl ~ cyclobutyl > cyclohexyl ≫ cyclopropyl. This order is quite unexpected on the basis of the customary gradations of physical and other chemical properties of cycloalkyl derivatives

(7) (a) H. C. Brown and M. Gerstein, THIS JOURNAL, **72**, 2926 (1950); (b) H. C. Brown, R. S. Fletcher and R. B. Johannesen, *ibid.*, **73**, 212 (1951).

(8) E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948).

(9) S. Winstein, E. Grunwald and L. L. Ingraham, *ibid.*, **70**, 821 (1948).

(10) P. Lipp, J. Buchkremer and H. Seeles, *Ann.*, **499**, 1 (1932); N. Kishner, *J. Russ. Phys. Chem. Soc.*, **37**, 304 (1905).

(11) E. D. Hughes, *Trans. Faraday Soc.*, **37**, 603 (1941).

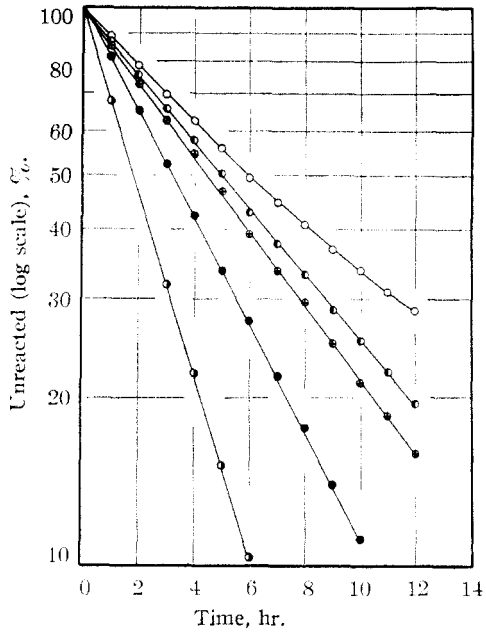

Fig. 1.—Solvolysis rate curves for cycloalkyl *p*-toluenesulfonates in acetic acid containing 1% acetic anhydride and 0.1 *N* potassium acetate: ◑, cyclopropyl *p*-toluenesulfonate, 180°; ○, cyclobutyl *p*-toluenesulfonate, 50°, not corrected for unimolecular rearrangement to allylcarbinyl *p*-toluenesulfonate; ◐, cyclobutyl *p*-toluenesulfonate, 50°, corrected for unimolecular rearrangement; ⊕, cyclopentyl *p*-toluenesulfonate, 50°; ●, cyclohexyl *p*-toluenesulfonate, 75°.

and is not well in accord with anticipations based on postulated steric effects.[7] The extremely low reactivity of cyclopropyl *p*-toluenesulfonate and chloride[3] is probably best ascribed to the same factors which cause the inertia of vinyl and phenyl derivatives. In this regard might be mentioned: (1) the greater electronegativity of vinyl carbons as compared to saturated carbons[12] which would be expected to decrease the ionic character of the C–X bonds undergoing ionization; (2) delocalization of unshared electron pairs on X[13] which should increase the C–X bond strengths; and (3) greater steric strain in the ionization transition states than in the normal molecules.[7,14] The relative importance of (1), (2) and (3) cannot yet be evaluated. We find the argument[7a] for the superiority of steric over electrical factors in reactions of other small-ring compounds unconvincing for cycloalkyl derivatives in view of our work on the electrical effects of cycloalkyl groups.[13a]

The high reactivities of cyclobutyl and cyclopentyl *p*-toluenesulfonates relative to the cyclohexyl derivatives are not explicable on the basis of any combination of factors (1), (2) or (3) mentioned above. The abnormal reactivity of the cyclobutyl compound may mean that the cyclobutyl cation is indeed more stable than otherwise might have been expected or that the cyclopropylcarbinyl cation (or some other particularly stable carbonium ion)[6,15] is formed directly in the rate-determining step. In the latter event, ionization would be facilitated by stabilization of the transition state through contributions of resonance forms resembling the product. An alternative possibility would be a rate-determining isomerization of cyclobutyl *p*-toluenesulfonate to a more reactive[6] cyclopropylcarbinyl ester, such ionization competing with the observed formation of unreactive allylcarbinyl *p*-toluenesulfonate. This interpretation is rendered somewhat unlikely by the fact that in aqueous ethanol, where isomerization proceeds much more slowly relative to solvolysis,[6] cyclobutyl chloride is actually *more* reactive than cyclopentyl chloride (*vide infra*). In any discussion of the reaction rates of cyclopentyl and cyclohexyl derivatives, it is helpful to have a comparison with the rates of typical secondary alkyl compounds. Cyclohexyl *p*-bromobenzenesulfonate[9] solvolyzes in acetic acid at 70° at about the same rate as the isopropyl derivative[8] and somewhat more slowly than the α-methylneopentyl ester.[8] On this basis, we might consider the difficulty of ionization of cyclohexyl derivatives to be reasonably typical of saturated secondary compounds and regard cyclopentyl derivatives as being more than normally reactive. Inspection of the thermodynamic data of Table I reveals that the difference in rate between cyclohexyl and cyclopentyl *p*-toluenesulfonates in acetic acid is possibly largely due to differences in the entropies of activation $\Delta S^{\ddagger}$. The significant factor may well be hydrogen–hydrogen repulsions which should be particularly important for cyclopentyl *p*-toluenesulfonate because, on ionization, the carbinyl hydrogen of this substance changes from an opposed to a staggered position relative to its neighbors. For a planar cyclopentane ring, this would allow recovery of some 2 kcal. of energy not available from the ionization of the cyclohexyl derivative. Although it might be expected that this energy change should principally influence $\Delta H^{\ddagger}$, Prof. Paul D. Bartlett suggests that the cyclopentane ring, which is bent and stiffened by hydrogen–hydrogen repulsions, may be relaxed correspondingly on ionization and, therefore, the effect might show also in $\Delta S^{\ddagger}$. The argument can be applied in reverse to account for the entropies of semicarbazone formation with cyclopentanone and cyclohexanone.[16]

The mechanisms of the solvolysis of secondary aliphatic halides in solvents like aqueous ethanol have not yet been definitely established. The demonstrations,[8,11] that the nucleophilic as well as the ionizing power of such solvents are important in determining the reaction rates, seem to indicate the operation of mechanisms near the borderline between the ionization (S_N1) and one-stage (S_N2)

(12) A. D. Walsh, *Discussions Faraday Soc.*, **2**, 18 (1947); *Trans. Faraday Soc.*, **45**, 179 (1949).

(13) (a) J. D. Roberts and V. C. Chambers, THIS JOURNAL, **73**, 5030 (1951); (b) M. T. Rogers and J. D. Roberts, *ibid.*, **68**, 843 (1946); (c) M. T. Rogers, *ibid.*, **69**, 2544 (1947); (d) C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, [7] **40**, 1 (1949).

(14) It is also possible that solvation of the incipient cation in the transition state may be inhibited by steric repulsions or the like for vinyl, phenyl and cyclopropyl compounds. However, the importance of this sort of influence is likely to be small since it is generally recognized that steric hindrance (in the customary sense) is not particularly significant in the ionization reactions of alkyl halides.

(15) J. D. Roberts and R. H. Mazur, THIS JOURNAL, **73**, 3542 (1951).

(16) F. P. Price, Jr., and L. P. Hammett, *ibid.*, **63**, 2387 (1941).

types.[17] Solvolysis data on the cycloalkyl halides in 50% ethanol–50% water solution are summarized in Table II. The pattern of the results is generally

TABLE II

SOLVOLYSIS RATE CONSTANTS OF CYCLOALKYL CHLORIDES (RCl) IN 50% ETHANOL–50% WATER (BY VOLUME)

R	Temp., ±0.2°C.	k_1, hr.$^{-1}$	Olefin,[a] %	Relative rate, 95°
Cyclopropyl	95	<0.0005	..	0
	200	.05		
Cyclobutyl	95	1.36	..	41
Cyclopentyl	95	.48	36	15
Cyclohexyl	95	.033	57	100

[a] Determined by the hydrogenation procedure of Roberts.[34]

similar to that observed with cycloalkyl *p*-toluenesulfonates in acetic acid except that the reactivity sequence is slightly different with cyclobutyl > cyclopentyl > cyclohexyl ≫ cyclopropyl. We conclude that in aqueous ethanol, the cycloalkyl chlorides most probably react by the ionization mechanism.

The reaction of iodide ion with alkyl halides in acetone has been definitely shown to be a one-stage process involving the Walden inversion[18] and was chosen for the determination of the reactivities of cycloalkyl derivatives in reactions having this type of mechanism. Rate data for the reaction of iodide ion with cycloalkyl bromides in acetone are given in Table III. The reactivity

TABLE III

BIMOLECULAR RATE CONSTANTS FOR THE REACTION OF CYCLOALKYL BROMIDES (RBr) WITH 0.034 *M* POTASSIUM IODIDE IN ACETONE

R	Temp., ±0.2°C.	RBr, *M*	k_2, l. mole^{-1} min.$^{-1}$
Cyclopropyl	100.0	0.178	No reaction[a]
Cyclobutyl	90.0	.119	0.0110[b]
Cyclopentyl	60.5	.119	.0437
Cyclohexyl	90.0	.118	.0077

[a] Cyclopropyl chloride (0.02 *M*) was found to give no measurable reaction with 0.01 *M* potassium iodide in acetone in 8 hours at 200°. [b] Rate constant corrected for rapid initial reaction which was complete in 30 minutes and corresponded to 4% impurity in the cyclobutyl bromide sample.

sequence is cyclopentyl > cyclobutyl > cyclohexyl ≫ cyclopropyl. The reactivities of the three, four and five-membered ring compounds fit a simple graded sequence while the cyclohexyl derivative is distinctly anomalous. The behavior of cyclohexyl bromide is not surprising since this reaction is quite sensitive to steric hindrance[19,20] and it should be expected that a compound with a puckered ring would not necessarily fit into a reactivity sequence of formally similar substances but having nearly flat rigid rings.[21] The order, cyclopentyl > cyclobutyl ≫ cyclopropyl, may be due to the operation of any or all of the factors mentioned earlier with regard to the low ionizing reactivity of cyclopropyl derivatives. It is also possible that steric hindrance to the back-side approach of a nucleophilic agent may increase with decreasing ring valence angle by virtue of an increase in the effective van der Waals interference radii of the ring atoms through delocalization of the bonding electrons.

Acknowledgment.—One of us (V.C.C.) is indebted to the Swarthmore Chapter of the Society of Sigma Xi for a fellowship.

Experimental

Materials

***p*-Toluenesulfonates.**—Cyclopropyl, cyclopentyl and cyclohexyl *p*-toluenesulfonates were prepared from the corresponding alcohols and *p*-toluenesulfonyl chloride by the procedure used by Sekera and Marvel[22] for low-molecular weight alcohols. The purification of the cyclopropyl derivative was described earlier.[23] The crude cyclopentyl ester started to decompose on distillation and was purified by crystallization from ether–hexane at Dry Ice temperatures. The material discolored on long standing at room temperature but kept well in a refrigerator. The bulk of the product had m.p. 27.0–27.8°. A small sample recrystallized for analysis showed m.p. 28.0–28.2°.

Anal. Calcd. for $C_{12}H_{16}O_3S$: C, 59.98; H, 6.71; S, 13.34; sapn. equiv., 240. Found: C, 59.95; H, 6.47; S, 13.31; sapn. equiv., 237.

The cyclohexyl ester was similarly purified, m.p. 44.4–44.8° (lit., 43.5–44.0°,[24] 44–45°[25]).

Cyclobutyl *p*-toluenesulfonate was prepared as follows. Cyclobutanol[26] (10 g., 0.14 mole) was added dropwise to a stirred suspension of 3.5 g. (0.145 mole) of sodium hydride in 100 ml. of anhydrous ether contained in a nitrogen-filled flask. The resulting mixture was stirred and heated under reflux for an hour and then a solution of 27.7 g. (0.145 mole) of *p*-toluenesulfonyl chloride in 125 ml. of ether was added. After an additional hour under reflux, the mixture was allowed to stand overnight. The excess sodium hydride was decomposed with water and the aqueous layer was separated and extracted with ether. The ether extracts were combined, dried over magnesium sulfate and the ether distilled. The residual crude ester was contaminated with a halogen-containing substance which could not be removed by distillation. The impure material was dissolved in an equal weight of pyridine, allowed to stand for 5 min. and then poured into water. The aqueous mixture was extracted with ether and the resulting ether extract washed with 5% hydrochloric acid, 5% sodium carbonate solution and water. The ether solution was treated with carbon, filtered, dried over magnesium sulfate and the ether distilled. The residual halogen-free cyclobutyl *p*-toluenesulfonate was distilled in a molecular still at 0.3–0.4 mm. with a bath temperature of 107°. The yield of material $n^{25}D$ 1.5206–1.5221 was 23 g. (73%). For the rate runs, the ester was recrystallized from absolute ethanol and had m.p. 24–25° ($n^{25}D$ 1.5228).

Anal. Calcd. for $C_{11}H_{14}O_3S$: C, 58.37; H, 6.24; S, 14.17; sapn. equiv., 226. Found: C, 58.02, 58.32; H, 6.21, 6.33; S, 14.11; sapn. equiv., 229.

(17) We here retain the Hughes–Ingold[11] idea of two distinct mechanisms for nucleophilic substitution at a saturated carbon atom with experimental distinction depending on whether or not the existence of a cationic *intermediate* can be definitely demonstrated. This approach, primarily based on *product criteria*, leads to an operational classification of nucleophilic substitutions as *stepwise* (S_N1) or *nonstepwise* (S_N2).

(18) E. D. Hughes, F. Juliusburger, S. Masterman, B. Topley and J. Weiss, *J. Chem. Soc.*, 1525 (1935).

(19) P. D. Bartlett and L. J. Rosen, THIS JOURNAL, **64**, 543 (1942).

(20) I. Dostrovsky, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 173 (1946).

(21) An alternative explanation has been offered[7b] on the ground that steric hindrance does not seem to be similarly important in determining the relative reactivities of cyclohexanone and cyclopentanone toward carbonyl reagents. The argument is weakened by the fact that there is no reason to believe that steric hindrance will necessarily be of comparable importance for reactions at saturated and unsaturated carbon atoms.

(22) V. C. Sekera and C. S. Marvel, THIS JOURNAL, **55**, 345 (1933).

(23) J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 3176 (1951).

(24) S. Winstein, E. Grunwald, R. E. Buckles and C. Hanson, *ibid.*, **70**, 816 (1948).

(25) W. Hückel, O. Neunhoeffer, A. Gercke and E. Frank, *Ann.*, **477**, 99 (1929).

(26) J. D. Roberts and C. W. Sauer, THIS JOURNAL, **71**, 3925 (1949).

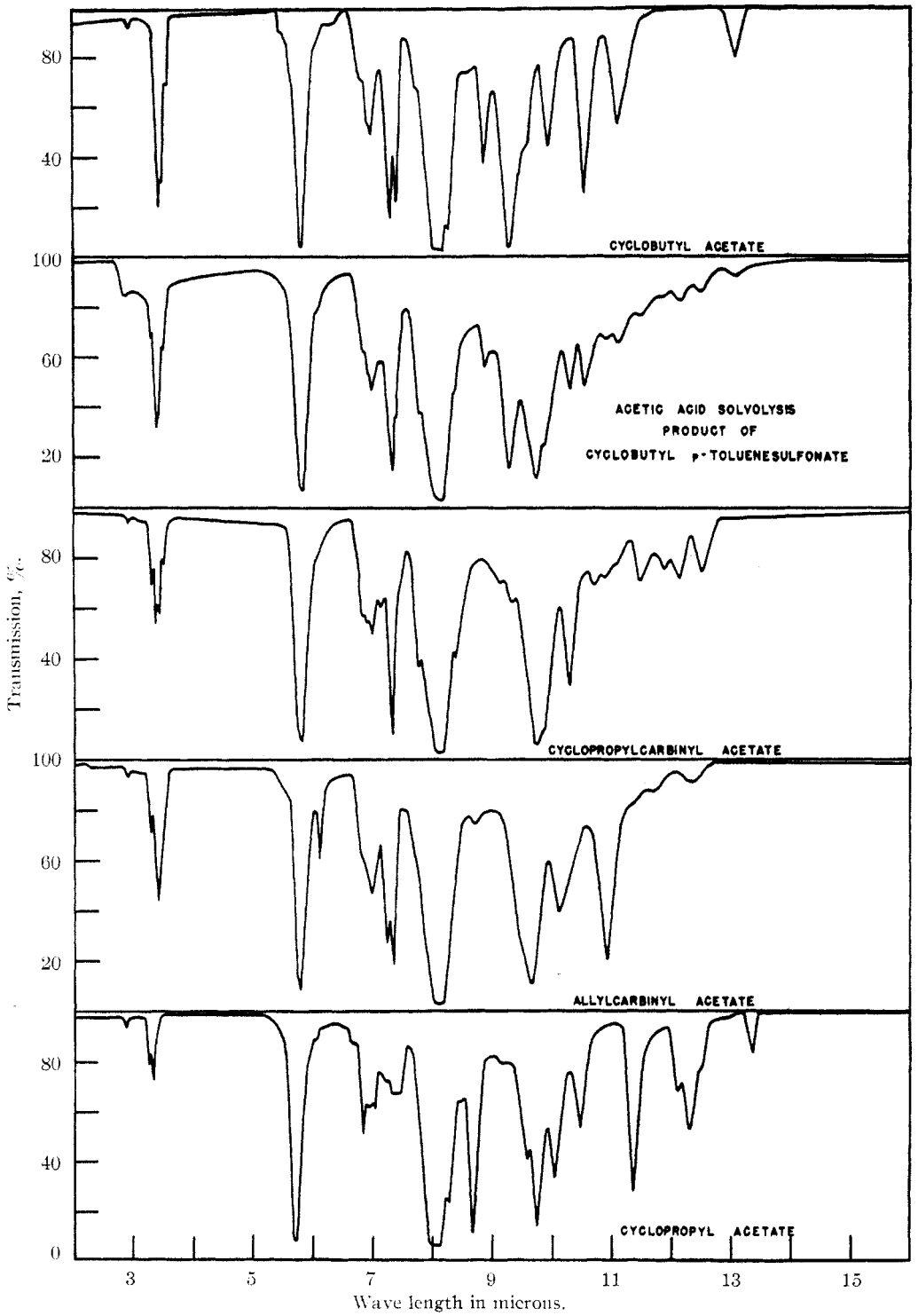

Fig. 2.—Infrared spectra: Baird spectrograph with NaCl prism, solutions of 50 mg. of compounds in 0.50 ml. of carbon disulfide except in the regions 4.2–5.0μ and 6.2–7.4μ where carbon tetrachloride was used as solvent.

Allylcarbinyl *p*-toluenesulfonate was prepared by a similar procedure and distilled with a bath temperature of 108–115° at 0.25 mm. The yield was 78% of material having $n^{25}D$ 1.5134–1.5137.

Anal. Calcd. for $C_{11}H_{14}O_3S$: C, 58.38; H, 6.24. Found: C, 58.52; H, 6.13.

Phenyl *p*-toluenesulfonate was prepared by the method used by Tipson and co-workers[27] for the synthesis of the corresponding thymyl derivative. The yield was 96%; m.p. 94.8–95.6°.

Cycloalkyl bromides and chlorides were the same samples used previously.[13a]

Cycloalkyl Acetates.—The preparation of cyclopropyl acetate has been described.[23] The infrared spectrum is given in Fig. 2. Cyclobutyl acetate was synthesized as follows. Cyclobutanol (2.5 g., 0.035 mole) was added to a stirred suspension of 1 g. (0.04 mole) of sodium hydride in 100 ml. of ether contained in a nitrogen-filled flask. The mixture was refluxed for 4 hr. and 3.6 g. (0.046 mole) of

(27) R. S. Tipson, M. A. Clapp and L. H. Cretcher, *J. Org. Chem.*, **12**, 133 (1947).

acetyl chloride added dropwise. The whole was allowed to stand overnight, water was added and the ether layer separated. The ethereal solution was washed with 5% sodium bicarbonate solution and water and then dried over magnesium sulfate. The aqueous layer from the reaction mixture was continuously extracted with ether for 4 days. The ether extract was dried, combined with the ether solution from the reaction mixture and distilled. The yield of cyclobutyl acetate, b.p. 130–132° and $n^{25}D$ 1.4150–1.4163, was 2.7 g. (68%). For the infrared spectrum (Fig. 2) the material was fractionated through an efficient center-tube column[28]; b.p. 131–131.3°, $n^{25}D$ 1.4162.

Anal. Calcd. for $C_6H_{10}O_2$: C, 63.12; H, 8.83. Found: C, 62.89; H, 8.70.

Allylcarbinyl acetate was prepared from allylcarbinol[6] by a procedure similar to that used for cyclobutyl acetate. The yield of material, b.p. 68–69° (108 mm.), was 76%. The material was fractionated through a center-tube column[28]; b.p. 127°, $n^{25}D$ 1.4066–1.4070 (lit.,[29] b.p. 126°, $n^{20}D$ 1.4105). The infrared spectrum is given in Fig. 2.

Cyclopropylcarbinyl acetate was similarly prepared from cyclopropylcarbinol.[6] The yield of crude ester was 73%; b.p. 134–136.8°, $n^{25}D$ 1.4159–1.4170. The material from two such preparations was combined and washed with sodium bicarbonate solution to remove some acidic impurity. Fractionation of the product through a center-tube column[28] gave the pure ester; b.p. 136–136.5°, $n^{25}D$ 1.4160–1.4162. The infrared spectrum is shown in Fig. 2.

Anal. Calcd. for $C_6H_{10}O_2$: C, 63.12; H, 8.83. Found: C, 63.40; H, 8.88.

Cyclopentyl acetate was prepared from cyclopentanol and acetic anhydride in 91% yield; b.p. 50° (12 mm.), $n^{25}D$ 1.4288 (lit.,[30] b.p. 152.5–153°, $n^{25}D$ 1.4318).

Kinetic Runs

Acetolysis of *p*-Toluenesulfonates.—The solvolysis rates of the *p*-toluenesulfonate esters in acetic acid containing 1% of acetic anhydride and 0.1–0.5 *M* potassium acetate were measured by procedures similar to those employed by Winstein and co-workers[24] except that weight burets were used for the standard solutions of perchloric acid in acetic acid to avoid corrections for thermal volume changes. The extent of formation of unsaturated materials in the reactions was determined by the bromide–bromate method.[31] The use of a bromination catalyst was found to be unnecessary for acetic acid solutions. All saturated starting materials and products were found to give negligible blanks in the unsaturation analysis. Data for typical runs on each of the cycloalkyl *p*-toluenesulfonates are plotted in Fig. 1. The solvolysis of cyclobutyl *p*-toluenesulfonate did not follow the first-order law in the later stages of the reaction (Fig. 1) and the rate became negligible at 90% of the theoretical amount of reaction. It was thought at first that 10% of an unreactive isomeric impurity was present in the original material but highly purified ester gave similar results. The anomaly was shown to be due to a first-order rearrangement reaction yielding allylcarbinyl *p*-toluenesulfonate by measurement of the rate of formation of unsaturated material (data for a typical run are given in Table IV) and isolation of allylcarbinyl *p*-toluenesulfonate from the reaction mixture (see below).

The acetolysis rate constants are given in Table I along with enthalpies and entropies of activation calculated by the usual equations.[32]

Hydrolysis of Chlorides.—The procedures employed for the determination of the solvolysis rates[33] and extents of olefin formation[34] of the cycloalkyl chlorides in 50% ethanol–50% water (by volume) have been described earlier. The results are summarized in Table II.

TABLE IV

SOLVOLYSIS AND ISOMERIZATION OF CYCLOBUTYL *p*-TOLUENESULFONATE IN ACETIC ACID CONTAINING 1% ACETIC ANHYDRIDE AND 0.500 *M* POTASSIUM ACETATE AT 50.0°

Time, hr.	$HClO_4$, g.[a]	% of theor. solvolysis	Br–BrO_3, ml.[b]	$Na_2S_2O_3$, ml.[c]	% of theor. olefin	% Olefin / % solvolysis
0	9.988	0	7.98	7.34	0	..
1	8.250	17.5	8.05	7.12	1.5	0.09
2	6.883	31.2	..	..	..	..
3	5.771	42.5	8.01	6.60	4.2	.10
4	4.891	51.4	..	..	..	..
5	4.220	58.3	..	..	..	..
6	3.647	63.9	8.99	7.01	6.9	.11
7	3.210	68.4	..	..	..	..
8	2.866	71.8	..	..	..	..
9	2.519	75.4	8.97	6.80	7.9	.10
10	2.305	77.4	..	..	..	..
11	2.143	79.0	..	..	..	..
12	1.965	80.9	7.84	5.50	9.3	.11
13	1.855	82.0	..	..	..	..
14	1.770	82.9	..	..	..	..
00	1.296	87.6	8.02	5.52	10.4	.08

[a] Wt. of solution of perchloric acid in acetic acid (0.1000 eq./kg.) used to titrate 2.00-ml. sample of rate run solution containing initially 0.500 *M* potassium acetate and 0.496 *M* cyclobutyl *p*-toluenesulfonate. [b] 0.1000 *N*. [c] 0.1088 *N*.

Reaction of Bromides with Potassium Iodide in Acetone.—The procedure was similar to that used by Conant and Kirner.[35] The acetone (reagent grade) was refluxed over soda-lime and potassium permanganate and then fractionated (b.p. 56.7–56.9°) before use. The potassium iodide (reagent grade) was dried for 2 hr. at 110° and stored in a desiccator. All of the solutions were made up at 25.0°. Typical rate data are plotted in Fig. 3 and the bimolecular rate constants k_2 are summarized in Table III. Some iodine formation was noted with cyclohexyl bromide after about 10 hr. The cyclobutyl bromide contained about 4% of a reactive bromide (possibly cyclopropylcarbinyl bromide) and the rate data in Fig. 3 are corrected for the initial rapid reaction which was complete in less than 30 min. at 90°

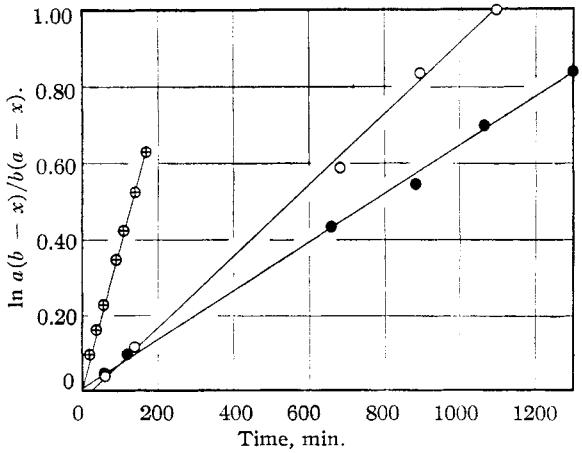

Fig. 3.—Rate curves for reaction of cycloalkyl bromides with potassium iodide in acetone: O, cyclobutyl bromide, 90°, corrected for 4% reactive impurity; ⊕, cyclopentyl bromide, 60.5°; ●, cyclohexyl bromide, 90°.

Isolation of Acetolysis Products

Cyclopropyl *p*-Toluenesulfonate.—An acetic acid solution (45 ml.) containing 0.47 *M* cyclopropyl *p*-toluenesulfonate

(28) The fractionating section of this column was similar to that described by E. A. Naragon and C. E. Lewis, *Ind. Eng. Chem., Anal. Ed.*, **18**, 448 (1946).

(29) J. Verhulst, *Bull. soc. chim. Belg.*, **40**, 85 (1931).

(30) A. I. Vogel, *J. Chem. Soc.*, 1809 (1948).

(31) S. Siggia, "Quantitative Organic Analysis via Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 33.

(32) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw–Hill Book Co., Inc., New York, N. Y., 1941, p. 14.

(33) J. D. Roberts, L. Urbanek and R. Armstrong, THIS JOURNAL, **71**, 3049 (1949).

(34) J. D. Roberts, *ibid.*, **71**, 1880 (1949).

(35) J. B. Conant and W. R. Kirner, *ibid.*, **46**, 245 (1924).

and 0.51 *M* potassium acetate was heated in a thermostat at 175° for 10 hr. The reaction mixture was transferred to a flask equipped with stirrer, dropping funnel and thermometer and carefully neutralized with 10 *N* sodium hydroxide solution keeping the temperature below 15° with an ice-bath. The slightly alkaline solution was extracted continuously with ether for several days and the ether extract dried over magnesium sulfate. Distillation of the ether extract gave 0.2 g. of colorless liquid, b.p. 88–98°, which reacted readily with bromine and potassium permanganate solution. The infrared spectrum of the product indicated it to be a mixture of 40% allyl alcohol, 40% allyl acetate and 20% ethanol (from the ethyl ether used in the extraction). A synthetic mixture of this composition had the same refractive index (n^{25}D 1.3912) and infrared spectrum. The allyl alcohol is presumed to arise from the saponification of allyl acetate in the neutralization process. No cyclopropyl acetate was detected or would be expected on the basis of the correspondence of solvolysis and unsaturation rate data.

Cyclobutyl *p*-Toluenesulfonate.—An acetic acid solution (80 ml.) containing 0.46 *M* cyclobutyl *p*-toluenesulfonate, 0.46 *M* potassium acetate and 1% of acetic anhydride was heated in a thermostat at 50° for 18 hours in a flask carrying a reflux condenser which was connected to a Dry Ice-cooled trap. The flask was then equipped with a stirrer and dropping funnel and the acetic acid neutralized with saturated sodium hydroxide solution. During the neutralization, the reaction mixture was stirred and cooled with an ice-bath. The slightly alkaline solution was extracted with ether for a week and the extract dried over magnesium sulfate. No volatile material collected in the Dry Ice trap during the solvolysis or neutralization processes.

The ether extract was fractionated through a center-tube column[28] and yielded 1.44 g. of an inseparable mixture of esters and alcohols having b.p. 128–133.5° and n^{25}D 1.4173–1.4152, as well as 1.30 g. of an ester mixture, b.p. 133.5–135.5°, n^{25}D 1.4159, whose infrared spectrum is shown in Fig. 2. The material of b.p. 128–133.5° gave only a very slight test for unsaturation and consequently contained no significant amount of unsaturated material such as allylcarbinyl acetate. The infrared spectrum of a fraction, b.p 128.4–129.4°, was quite similar to that of the ester mixture shown in Fig. 2 except for a prominent OH band at 2.9 μ. The alcoholic components of these fractions are presumably cyclopropylcarbinol and cyclobutanol formed by hydrolysis of the ester products in the isolation procedures. The infrared spectra of the various fractions indicated that cyclopropylcarbinyl and cyclobutyl acetates were formed in a ratio of 3:1.

Formation of allylcarbinyl *p*-toluenesulfonate in the solvolysis mixtures was demonstrated in the following way. A mixture of 7.9 g. (0.035 mole) of cyclobutyl *p*-toluenesulfonate, 5.0 g. (0.05 mole) of potassium acetate, 75 ml. of acetic acid and 1 ml. of acetic anhydride was heated in a thermostat at 50° for three days. All of the low-boiling material was removed under reduced pressure at 50–60°. The residue was taken up in 20 ml. of water and extracted with ether. The ether extract was washed with water and 5% sodium bicarbonate, dried over potassium carbonate and the ether removed under reduced pressure. The residual crude allylcarbinyl *p*-toluenesulfonate (0.6 g.) showed infrared absorption bands characteristic of carboxylic esters. Distillation at 0.4 mm. yielded material which had an infrared spectrum practically identical with that of authentic allylcarbinyl *p*-toluenesulfonate and contained less than 3% of carboxylic ester.

Cyclopentyl *p*-Toluenesulfonate.—The procedure was similar to that employed for the cyclobutyl derivative. The acetic acid solvent (100 ml.) contained 11.9 g. (0.050 mole) of cyclopentyl *p*-toluenesulfonate, 5.18 g. (0.053 mole) of potassium acetate and 1% of acetic anhydride. The reaction time was 84 hr. at 50°. After the neutralization was complete, the pressure was reduced over the reaction mixture to transfer any low-boiling material to a Dry Ice cooled trap. The contents of the trap were vaporized and passed through Drierite and Ascarite tubes. Condensation of the effluent gas yielded 0.20 g. of liquid (n^{25}D 1.4196) whose infrared spectrum was the same as that of an authentic sample of cyclopentene (b.p. 43.7–44.0°, n^{25}D 1.4191) prepared by the procedure of Harries and Tank.[36]

The ether extract of the neutralized reaction mixture was fractionated and yielded 2.1 g. of distillate; b.p. 48° (12 mm.), n^{25}D 1.4339–1.4331. All of the absorption bands in the infrared spectrum of this material could be identified with those of authentic cyclopentanol and cyclopentyl acetate. The infrared spectrum indicated the presence of 15% cyclopentanol and 85% cyclopentyl acetate. The cyclopentanol is considered to have been formed by hydrolysis of the cyclopentyl acetate in the isolation procedures.

Cyclohexyl *p*-Toluenesulfonate.—The procedure for the isolation of the ester product was similar to those used for the cyclobutyl and cyclopentyl derivatives and a mixture (heated at 75° for 72 hr.) of 32 g. (0.125 mole) of cyclohexyl *p*-toluenesulfonate, 12.5 g. (0.13 mole) of potassium acetate and 250 ml. of acetic acid containing 1% of acetic anhydride yielded 1.84 g. of material; b.p. 74–75° (25 mm.), n^{25}D 1.4482–1.4500. The product was shown by its infrared spectrum to be a mixture containing 70% of cyclohexyl acetate and 30% of cyclohexanol.

Distillation (before neutralization) of a similar reaction mixture, prepared from 18 g. (0.07 mole) of cyclohexyl *p*-toluenesulfonate, 8 g. (0.08 mole) of potassium acetate and 150 ml. of acetic acid containing 1% of acetic anhydride and heated at 75° overnight, yielded 6 g. of crude cyclohexene. The distillate was taken up in ether, washed twice with 5% sodium bicarbonate solution, dried over potassium carbonate and distilled. The yield of cyclohexene, b.p. 79–82°, n^{25}D 1.4428, was 3.2 g. The infrared spectrum was identical with that of authentic material.

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