mole) of sulfur trioxide in 175 ml. of ethylene chloride. Aliquots withdrawn at various intervals were hydrolyzed, and the aqueous layer and washings from the ethylene chloride layer were digested with excess barium carbonate. After removal of the barium sulfate and barium carbonate, the filtrate was analyzed for barium ion as barium sulfate.

The solution was kept at 0° for 19.5 hours. After 0.5, 1.5 and 19.5 hours the percentages of sulfur trioxide reacting to form soluble barium salts were 9.3, 9.5 and 12.7, respectively. The solution was then allowed to warm to 25°. After a total of 25.5 hr. the percentage of sulfur trioxide-forming soluble barium salts was still 12.7; after a total of 116.5 hr. the amount had risen to 13.8%. Chloride ion from ethylene chloride reaction amounted to less than 2% of the soluble barium salts produced.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF WISCONSIN]

The Solvolysis of 6-Ketocyclodecyl *p*-Toluenesulfonate and *p*-Bromobenzenesulfonate

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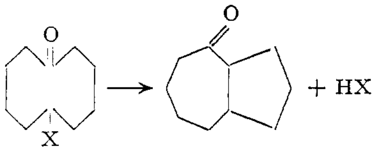
RECEIVED MAY 28, 1956

The solvolysis of 6-ketocyclodecyl *p*-toluenesulfonate (Ia) in ethanol results in the formation of a mixture of *cis*- and *trans*-[5.3.0]bicyclodecan-2-one (II). The composition of this mixture (60-80% *trans* isomer) is indistinguishable from that resulting from treatment of the *p*-toluenesulfonate with base. Ethanolysis of Ia is autocatalytic—the solvolysis is acid catalyzed. The dependence of the rate on various concentrations indicates that solvolysis involves an acid-catalyzed (second-order) reversible enolization followed by conversion of the enol III to product II. The enol III is solvolyzed much faster than cyclodecyl *p*-toluenesulfonate. The high reactivity of the enol and its conversion to the bicyclic ketone II are evidently manifestations of a transannular interaction between the carbon–carbon double bond and C_1.

In the course of an investigation of cyclodecyl and cyclodecenyl arylsulfonates in which transannular interactions might be expected, we have studied the ethanolysis of 6-ketocyclodecyl *p*-toluenesulfonate (Ia) and *p*-bromobenzenesulfonate (Ib). This reaction shows two unusual features. (i) Instead of the expected product from an E_1 or S_N1 reaction, [5.3.0]bicyclodecan-2-one (II) appears to be the exclusive product—an 88% yield of pure II was isolated. (ii) Contrary to the usual behavior of alkyl arylsulfonates in hydroxylic solvents, the ethanolysis of I is catalyzed by acid and thus is autocatalytic. The uncatalyzed solvolysis is so slow compared to the acid-catalyzed reaction that essentially all of the product is formed by the acid-catalyzed process.



Ia, X = $—OSO_2C_6H_4CH_3$-*p* II
Ib, X = $—OSO_2C_6H_4Br$-*p*

The [5.3.0]bicyclodecan-2-one (II) resulting from the ethanolysis of I, *i.e.*, the product of the acid-catalyzed process, was compared with that which results from the treatment of Ia with *t*-butoxide in *t*-butyl alcohol.[2] The products obtained by the two methods had indistinguishable infrared spectra and gave similar mixtures of 2,4-dinitrophenylhydrazones and oximes. Thus it appears that the *cis–trans* compositions of the two products are very similar. Evidently the thermodynamically controlled product is obtained in each case. Isomeric 2,4-dinitrophenylhydrazones were formed in a ratio of 3–4:1. From this observation, together with the fact that the previously known[3] *trans*-[5.3.0]bicyclodecan-2-one oxime was formed in larger amounts than the *cis* isomer, we infer that the ketone mixture, II, consists of 60–80% of the *trans* isomer.

The rates of ethanolysis of 6-ketocyclodecyl *p*-toluenesulfonate (Ia) and *p*-bromobenzenesulfonate (Ib) were measured at 20 and 30°. The progress of the reaction was followed by titration of the acid produced by the solvolysis. Plots of acid concentration *vs.* time for the ethanolysis of Ia and Ib are shown in Fig. 1. These data clearly show that the reaction is autocatalytic and suggest that the process is nearly first order in keto-*p*-toluenesulfonate and in one of the solvolysis products. If the process were cleanly first order in both reactant and product, the sigmoidal curves in Fig. 1 would be symmetrical with the steepest slope (greatest rate) at 50% completion.

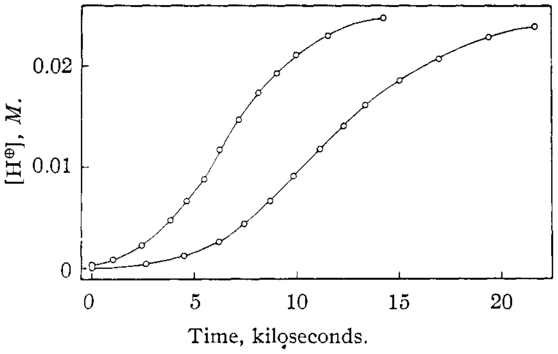


Fig. 1.—The solvolyses of 6-ketocyclodecyl esters in absolute ethanol at 30.05°: upper curve, *p*-bromobenzenesulfonate (expt. 2a); lower curve, *p*-toluenesulfonate (expt. 1a).

It was demonstrated readily that the autocatalytic behavior is due to catalysis by the acid formed in the solvolysis. The rate during the induction period is so slow that it is clear that essentially all of the material reacts by the acid-catalyzed process. It was not possible to determine the rate of the uncatalyzed reaction by solvolyzing the keto-*p*-toluenesulfonate in the presence of base because under these conditions I is rapidly converted to II

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(1) (a) Minnesota Mining and Mfg. Fellow, 1952–1953; (b) Carbide and Carbon Fellow, 1955–1956.

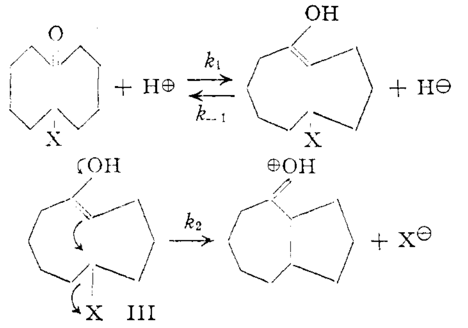
(2) A. C. Cope and G. Holzman, THIS JOURNAL, **72**, 3062 (1950).

(3) W. Hückel and L. Schnitzspahn, *Ann.*, **505**, 274 (1933).

by an intramolecular base-catalyzed alkylation reaction.[2]

The acid catalysis suggested that solvolysis might involve the two-step process illustrated in Chart I. According to this scheme the ketone is converted to enol by a reversible second-order (acid-catalyzed)[4] process. The enol, because of a transannular interaction between the double bond and C_1 as illustrated by III is much more reactive than the ketone and is converted to the conjugate acid of II by a first-order process. Thus k_1 and k_{-1} are second-order rate constants and k_2 is a first-order constant.

CHART I



According to this scheme the relationship between the rate ($d[H^{\oplus}]/dt$) and the various rate constants and concentrations is given by equation 1 in which $\alpha = k_{-1}/k_2$. Equation 1 can be rearranged to equation 2 from which it is clear that the scheme in Chart I requires a linear relationship between $[I]/(d[H^{\oplus}]/dt)$ and $1/[H^{\oplus}]$.

$$d[H^{\oplus}]/dt = [I][H^{\oplus}]k_1/(1 + \alpha[H^{\oplus}]) \quad (1)$$

$$[I]/(d[H^{\oplus}]/dt) = 1/k_1[H^{\oplus}] + \alpha/k_1 \quad (2)$$

The instantaneous rates, $d[H^{\oplus}]/dt$, were evaluated by measuring the slopes of large scale plots of $[H^{\oplus}]$ *vs.* time (Fig. 1) with the aid of a tangent meter. From these values, together with the corresponding values of $[H^{\oplus}]$ and [I], plots of $[I]/(d[H^{\oplus}]/dt)$ *vs.* $1/[H^{\oplus}]$ were prepared. As illustrated in Fig. 2 these plots were indeed found to be linear. The slope ($1/k_1$) and intercept (α/k_1) were determined by the method of least squares and both α and k_1 were determined from these parameters. Values of k_1 and α for the solvolysis of Ia and Ib in ethanol and 99% ethanol (by weight) are shown in Table I. For the solvolysis without added acid the acid concentration changes by a factor of about 10 over the part of the reaction that was carefully followed. Under these conditions the extrapolation of equation 2 to the intercept is short compared to the measured portion of the curve and the standard deviation for α was about ±10%. In runs with added acid the changes in acid concentration during the time the reactions were examined (10 to 90% completion) were two- or threefold. Under these conditions the extrapolation is as long as the measured portion of the curve and consequently the uncertainty is large for the intercept even though it is satisfactory for the slope. For these cases values of α are not given because of the large probable errors which were often as large as α itself.

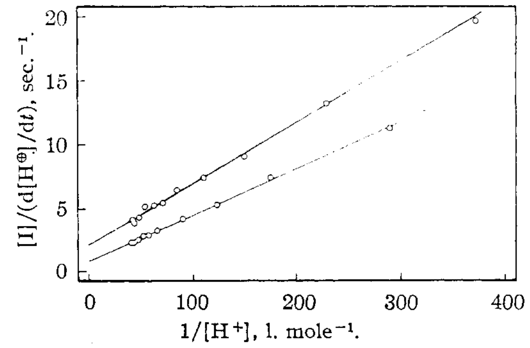


Fig. 2.—Plots for evaluation of k_1 and α for solvolysis of 6-ketocyclodecyl esters in absolute ethanol at 30.05°: upper curve, *p*-toluenesulfonate (expt. 1a); lower curve, *p*-bromobenzenesulfonate (expt. 2a).

TABLE I

THE SOLVOLYSIS OF 0.025 *N* 6-KETOCYCLODECYL *p*-TOLUENESULFONATE AND *p*-BROMOBENZENESULFONATE

Expt.	Cmpd.	Solvent[a]	Temp., °C.	[TsOH] 10^2M	10^3k_1,[b] l. mole^{-1} sec.$^{-1}$	α,[b,c] l. mole^{-1}
1	Ia	EtOH	30.05	..	24.2 ± 0.7	42 ± 3
1a	Ia	EtOH	30.05	..	20.0 ± .6	42 ± 3
2	Ib	EtOH	30.05	..	25.5 ± .6	25 ± 5
2a	Ib	EtOH	30.05	..	27.3 ± .3	22 ± 1
3	Ia	99% EtOH[d]	30.05	..	3.5 ± .1	
4	Ia	99% EtOH	30.05	..	2.3 ± .1	
5	Ia	99% EtOH	30.05	1.28	2.3 ± .2	
6	Ia	99% EtOH	30.05	2.54	1.8 ± .2	
7	Ib	99% EtOH	30.05	1.25	2.2 ± .1	
8	Ib	99% EtOH	30.05	2.52	2.5 ± .1	
9	Ia	EtOH	19.86	..	9.6 ± .5	60 ± 6
10	Ia	EtOH[e]	19.86	1.25	5.1 ± .4	
11	Ia	EtOH[f]	19.86	2.49	3.0 ± .5	
12	Ia	99% EtOH	20.07	2.53	0.7 ± .05	

[a] EtOH designates absolute ethanol; 99% EtOH (by weight) corresponds to 0.43 *M* water. In experiments 5–8 and 10–12 the toluenesulfonic acid was added as the monohydrate. Thus the solvent in experiments 10 and 11 contains as much water as toluenesulfonic acid. For solvolysis in 99% ethanol the water added with the acid is negligible. [b] The indicated errors are the standard deviations from the least square fit (Fig. 2). [c] Equal to k_{-1}/k_2 in Chart I. [d] The solvent contained 0.095 *M* $LiClO_4$. [e] The solvent contained 0.0125 *M* water (see footnote *a*). [f] The solvent contained 0.025 *M* water (see footnote *a*).

The standard deviations for k_1 and α included in Table I indicate that the data are fit quite well by equation 2. Moreover the constants (k_1 and α) are reproducible to within 20%, *cf.* expts. 1 with 1a and 2 with 2a, and k_1 is independent of acid concentration, *cf.* expts. 4, 5 and 6. Thus it appears that the kinetic data are consistent with the scheme shown in Chart I. It appears that the reproducibility of the constants is satisfactory, considering the limitations of the graphical method. In this connection it should also be pointed out that some deviations of the data from equation 2 might result from the simplifying assumption in Chart I (and in the corresponding equations) that the rates of uncatalyzed enolization and ketonization are negligible compared to the acid-catalyzed rates even at very low acid concentrations.

It is of interest to compare the rates of reaction of Ia and Ib. Ordinarily in solvolytic reactions

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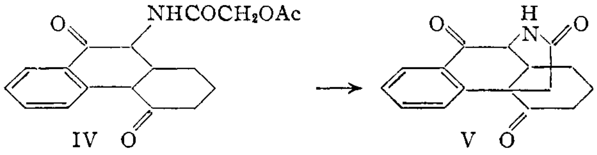
(4) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, 1st ed., Chapt. 8.

p-bromobenzenesulfonates react 2.5[5] to 5[6] times faster than the corresponding *p*-toluenesulfonates. In the present case Ib reacts only slightly faster than Ia (under identical conditions the time elapsed between 10 and 50% reaction is about 14% less for Ib than for Ia). According to the above scheme we would expect k_1 (and k_{-1}) to be similar for Ia and Ib and α to be about $^1/_2$ to $^1/_5$ as large for Ib as for Ia (k_2 would be expected to be 2–5 times greater for Ib than for Ia). As shown in Table I the values for k_1 are indeed similar for Ia and Ib. Moreover the difference in α is in the expected direction and about of the expected magnitude.

The catalytic second-order rate constant for enolization, k_1, defined in Chart I should remain constant as acid concentration is varied. In order to test this the initial acid concentration was varied from zero to 0.025 N[7] by the addition of *p*-toluenesulfonic acid monohydrate. For some of the early experiments using absolute ethanol as the solvent the addition of acid increased the rate of reaction; however, the rate constants (k_1) were markedly lower; *cf.* expts. 9–11. Evidently the decrease in k_1 is due to the presence of the small amount of water added with the *p*-toluenesulfonic acid. Evidence for this is seen in the lower rate constants in 99% ethanol (by weight) than in absolute ethanol; *cf.* expt. 1 with 4 and 11 with 12. When 99% ethanol is the solvent, the initial water content (0.43 M) is changed only slightly percentagewise by the addition of up to 0.025 M *p*-toluenesulfonic acid monohydrate. For this reason this solvent was chosen for the experiments in which the initial acid concentrations were varied and, as shown by expts. 4–8, k_1 is constant over the range of acid concentrations investigated.

In connection with the effect of small amounts of water on k_1 it is interesting to note that Tubandt[8] has observed that the rate of mutarotation of menthone, by acid-catalyzed enolization, is retarded by small amounts of water. For example, the specific rate constant for mutarotation (which presumably is directly proportional to the rate constant for acid-catalyzed enolization) in ethanol containing 0.01 N hydrogen chloride is decreased about 60% by the addition of 0.05% (by volume; 0.027 M) water to the solvent. This decrease is similar in magnitude to that resulting from the addition of 0.025 M water in the present work; *cf.* k_1 for expts. 9 and 11. The rate of the acid-catalyzed mutarotation of menthone in dry ethanol is seven times greater than in 99.8% ethanol (0.11 M H_2O) and one thousand times greater than in 90% ethanol (5.7 M H_2O). The similarity of the effects of water on k_1 and the rate of mutarotation of menthone is additional evidence that k_1 is in fact a specific second-order rate constant for acid-catalyzed enolization.

The above observations suggest that I solvolyzes by the process depicted in Chart I, a process that amounts to an intramolecular acid-catalyzed alkylation of a ketone. There do not appear to be any known examples of the intermolecular counterpart of this reaction. Although several examples of intermolecular acid-catalyzed alkylations of carbonyl compounds have been reported,[9] the function of the acid in many cases is not clear and all examples appear to be limited to compounds in which the methylene group is doubly activated, *e.g.*, by two carbonyl groups or by carbonyl and cyano groups. Evidently the acid-promoted conversion of the diketoamide IV to the diketolactam V reported by Ginsburg and Pappo[10] is a reaction similar to the conversion of I to II observed in the present work.



The rate of ethanolysis of Ia can be compared with that of cyclodecyl *p*-toluenesulfonate by comparing apparent instantaneous rate constants $k' = (d[H^{\oplus}]/dt)/[Ia]$ at specified acid concentrations with the first-order constants for cyclodecyl *p*-toluenesulfonate. The rates of acetolysis and ethanolysis of cyclodecyl *p*-toluenesulfonate and *p*-bromobenzenesulfonate were determined in connection with another phase of this research, and are presented in Table II. In all of these experiments the reactions were cleanly first order and no trends were observed in the rate constants.

TABLE II

RATES OF SOLVOLYSIS OF CYCLODECYL *p*-TOLUENESULFONATE AND *p*-BROMOBENZENESULFONATE AT 20.11°

Cmpd.[a]	Solvent	10^5k, sec.$^{-1}$
Tos	AcOH	2.42 ± 0.06[b]
Bros	AcOH	8.79 ± .08
Tos	EtOH	0.42 ± .02
Bros	EtOH	2.11 ± .04[c]

[a] Tos designates *p*-toluenesulfonate; Bros designates *p*-bromobenzenesulfonate. [b] Since these data were obtained, Heck and Prelog (ref. 13) have published rate constants for other temperatures which give 2.41×10^{-5} sec.$^{-1}$ when extrapolated to 20.11°. [c] At 30.11° the rate constant is $(8.45 \pm 0.08) \times 10^{-5}$ sec.$^{-1}$.

When Ia is solvolyzed in dry ethanol at 20° the apparent instantaneous rate constant k' is 1.7×10^{-2} sec.$^{-1}$ at an acid concentration of 0.0019 M (this corresponds to 7.7% reaction in the present experiment). Thus under these conditions Ia is *ca.* 10^3 times as reactive as cyclodecyl *p*-toluenesulfonate. Since the steady state concentration of III is probably less than one-hundredth that of I, k_2 is likely > 100 times larger than k'. Thus it appears that the enol (III) is well over 10^5 times more reactive than the cyclodecyl ester.

Experimental

Materials.—6-Ketocyclodecyl *p*-toluenesulfonate (Ia), m.p. 76.4–77.0° (ether-pentane), was prepared as de-

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(5) S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan and H. Marshall, THIS JOURNAL, **74**, 1127 (1952).

(6) S. Winstein, M. Brown, K. C. Schreiber and A. H. Schlesinger, *ibid.*, **74**, 1140 (1952).

(7) Because the reaction was followed by measuring the change in acid concentration and because of the rapid rate at high acid concentration it was not feasible to start with acid concentrations higher than the initial concentration of I.

(8) C. Tubandt, *Ann.*, **354**, 259 (1907).

(9) C. R. Hauser, *et al.*, THIS JOURNAL, **62**, 2385, 2389, 2611 (1940); **65**, 552 (1943); **67**, 2050 (1945); C. Raha, *ibid.*, **75**, 4098 (1953); **76**, 622 (1954).

(10) D. Ginsburg and R. Pappo, *J. Chem. Soc.*, 1524 (1953).

scribed by Cope and Holzman[2] (lit.[2] m.p. 71–72°). Because of the difference between the observed and reported melting points, the compound was analyzed.

Anal. Calcd. for $C_{17}H_{24}O_4S$: C, 62.93; H, 7.46; solv. equiv., 324.4. Found: C, 63.05; H, 7.44; solv. equiv., 322.

6-Ketocyclodecyl *p*-bromobenzenesulfonate (Ib) was prepared by an analogous method in 70% yield (crude), m.p. 81.8–82.3° (ether–pentane).

Anal. Calcd. for $C_{16}H_{21}BrO_4S$: C, 49.36; H, 5.44; solv. equiv., 389.3. Found: C, 49.67; H, 5.17; solv. equiv., 381, 382.

The above compounds are stable for at least several weeks at 5°.

[5.3.0]Bicyclodecan-2-one (II). **Method A.**—Twenty-four grams of 6-ketocyclodecyl *p*-toluenesulfonate, treated with potassium *t*-butoxide as described by Cope and Holzman,[2] yielded 7.2 g. of a mixture of *cis*- and *trans*-[5.3.0]-bicyclodecan-2-one, b.p. 126° (21 mm.), $n^{25}D$ 1.4872 (lit.[2] b.p. 104–105° (10 mm.), $n^{25}D$ 1.4862). The product gave a mixture of 2,4-dinitrophenylhydrazones which was separated[2] into isomers of m.p. 220° and 160–163° in 3–4:1 ratio (lit.[2] 219–220° and 162–163°).

Method B.—A solution of 16.2 g. (0.05 mole) of 6-ketocyclodecyl *p*-toluenesulfonate in 500 ml. of absolute ethanol was refluxed for one hour. The cooled reaction mixture was diluted with 500 ml. of water, and extracted with three 150-ml. portions of petroleum ether (30–35°). The combined extracts were washed with water, 10% sodium hydroxide and saturated aqueous sodium chloride, and dried over magnesium sulfate. After removal of solvent, the residue was fractionated through a wire spiral column. Three indistinguishable fractions of bicyclic ketone, b.p. 105–106° (9 mm.), $n^{25}D$ 1.4870–1.4872, weighed 6.70 g. (0.044 mole, 88%).

2,4-Dinitrophenylhydrazones were prepared and separated[2] giving isomers of m.p. 219.1–220.2° and 160.5–162.8° in *ca.* 4:1 ratio. Melting points of mixtures of each isomer with its counterpart from method A were not depressed. One gram of ketone mixture was converted[11] to 1.05 g. (95%) of a mixture of oximes, m.p. 121–135.5°. Five-tenths gram of this material gave 0.15 g. of *trans*-[5.3.0] bicyclodecan-2-one oxime, m.p. 137.5–140.5° (lit.[3] 140°), after five recrystallizations from 95% ethanol. Concentration of mother liquors from the first recrystallization gave a few mg. of oxime, m.p. 107–108°, which presumably is primarily the oxime of *cis*-[5.3.0]bicyclodecan-2-one (lit.[3] m.p. 119°).

Cyclodecyl *p*-Toluenesulfonate.—Cyclodecanol[12] was converted to the *p*-toluenesulfonate in 56% yield by the above method,[2] using a 3-hour reaction time at 0°. After recrystallization from ether–petroleum ether at −80°, the product had m.p. 53.0–54.2° (lit.[13] 60°), unchanged after further recrystallization. Attempted carbon–hydrogen analyses gave low results because of sample decomposition during drying for only 15 minutes at 23° (0.1 mm.). Samples not dried under reduced pressure were stable for several days in the cold. Calcd.: solv. equiv., 310.5. Found: solv. equiv., 312.

Cyclodecyl *p*-bromobenzenesulfonate was prepared in 69% yield by an analogous method, allowing a 7-hour reaction time at 0°. After the usual work-up, the dry ether solution of product was diluted with petroleum ether and cooled to −78°. The m.p. of the product thus obtained, 44–47°, was not changed by further recrystallization. Attempts to prepare an analytical sample were unsuccessful. Calcd.: solv. equiv., 375.3. Found: solv. equiv., 378.

Kinetic Measurements.—Absolute ethanol was used to prepare the 99% ethanol (by weight). Acetic acid (99.5%) was refluxed 8 hours with the calculated amount of acetic anhydride before distillation. Lithium perchlorate (G. F. Smith Chemical Co.) was dried for 24 hours at 120° under 1 mm. pressure.

Reaction mixtures were prepared by dissolving weighed samples of *p*-toluenesulfonate Ia or *p*-bromobenzenesulfonate Ib in measured volumes of thermostated solvent. Measured volumes of stock solutions of standard *p*-toluenesulfonic acid were also added in those experiments with acid initially present. All experiments involving a given solvent (absolute or 99% ethanol) used material from a single batch of that solvent. At intervals, 4.95-ml. aliquots of reaction mixture were delivered into nearly enough ice-cold standard 0.05 *M* sodium methoxide (from a 5-ml. micro-buret) to neutralize the acid present. The titrations were then rapidly completed to the brom thymol blue end-point.

An aliquot of solvolysis mixture of 6-ketocyclodecyl *p*-toluenesulfonate in absolute ethanol, treated near zero time (before appreciable reaction) with one-half of an equivalent of 0.05 *M* sodium methoxide at room temperature (*ca.* 30°), became acid to brom thymol blue in *ca.* 6 minutes. The change took 55 minutes at 0°. This shows that delivery of aliquots into *excess* base (followed by back titration) would have replaced the acid-catalyzed reaction by an even faster base-catalyzed reaction, giving erroneous results.

Solvolyses of cyclodecyl compounds were followed by previously described methods.[14] The integrated equation for a first-order reaction was used for calculation of rate constants.

MADISON, WISCONSIN

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[11] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, New York, N. Y., 1948, p. 170.

[12] V. Prelog, K. Schenker and H. H. Günthard, *Helv. Chim. Acta*, **35**, 1598 (1952).

[13] R. Heck and V. Prelog, *ibid.*, **38**, 1541 (1955).

[14] S. Winstein, E. Grunwald and L. L. Ingraham, THIS JOURNAL, **70**, 821 (1948); H. L Goering and R. L. Reeves, *ibid.*, **78**, 4931 (1956).