

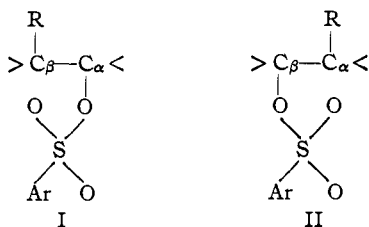
[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Neighboring Carbon and Hydrogen. XIII. The Solvolysis and Internal Rearrangement of 2-Phenyl-1-propyl *p*-Bromobenzenesulfonate^{1,2}

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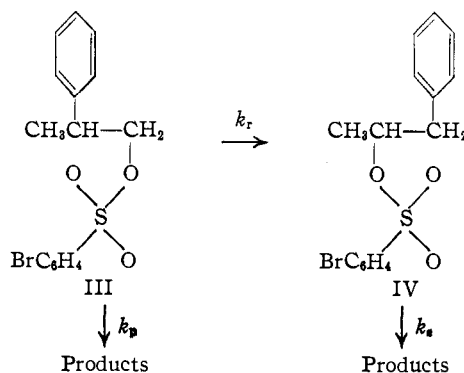
In the case of 2-phenyl-1-propyl *p*-bromobenzenesulfonate, a fast primary arylsulfonate, the accompaniment of solvolysis by internal rearrangement to benzylmethylcarbinyl *p*-bromobenzenesulfonate is detectable through an upward trend in acetolysis rate constant and by isolation of rearranged ester from partially solvolyzed reaction mixture. A thorough kinetic analysis of acetolysis of 2-phenyl-1-propyl *p*-bromobenzenesulfonate and synthetic mixtures of primary and rearranged secondary esters, designed to give constant first-order solvolysis rate constants, shows the rearrangement to be internal and uncomplicated by external *p*-bromobenzenesulfonate ion. Also, this analysis gives first-order rate constants for solvolysis and rearrangement of the primary ester. The importance of the internal phenomenon in acetolysis is comparable in the present case, two other unsymmetrical cases with neighboring aryl, the *exo*-norbornyl, the 3-phenyl-2-butyl and the α,α -dimethylallyl systems. The present data supply more orientation on the magnitude of driving forces due to participation of carbon.

The solvolysis of 2-phenyl-1-propyl *p*-bromobenzenesulfonate is of interest for several reasons. First, it furnishes another calibration point in the development of a picture of the order of magnitude of driving forces³ due to participation of neighboring groups in Wagner-Meerwein type rearrangement. Secondly, it is of interest in connection with internal rearrangements, symbolized by I \rightarrow II, which ac-



company solvolysis. In symmetrical cases such as that represented by *exo*-norbornyl⁴ and 3-phenyl-2-butyl⁵ arylsulfonates, rearrangement of the sulfonate maintains structure and the rearrangement can be followed by comparison of polarimetric with titrimetric rates. In most unsymmetrical cases the rearranged sulfonate would solvolyze at a rate too fast to observe the rearrangement. It could be anticipated that 2-phenyl-1-propyl *p*-bromobenzenesulfonate (III) was a favorable case for the observation of internal rearrangement accompanying solvolysis for 2-phenyl-1-propyl *p*-bromobenzenesulfonate (III) was expected⁶ to be a fast primary sulfonate, while the product of internal rearrangement involving migration of a phenyl group, namely, benzylmethylcarbinyl *p*-bromobenzenesulfonate (IV), was already known⁶ to be a slightly retarded secondary sulfonate. Therefore, the expected gap in solvolysis rate between the secondary and primary isomers was expected to be well below the usual value, possibly low enough to make observable the accumulation of secondary isomer starting with primary bromobenzenesulfonate. The results of our investigation of the kinetics of the solvolysis-rearrangement of 2-phenyl-1-propyl *p*-bromobenzene-

sulfonate (III) and some related matters are reported in the present paper.



First order rate constants k for the acetolysis of 2-phenyl-1-propyl *p*-bromobenzenesulfonate (III) calculated from equation 1 where a is the initial concentration

$$\ln \frac{a}{a-x} = kt \quad (1)$$

of the ester and x is the concentration of reacted material at time t , rose rapidly. A representative run is given in Table I. Thus it is seen that in the solvolysis of 0.0306 *M* bromobenzenesulfonate the first order reaction rate constant rose from 2.07 to 7.53×10^{-6} sec.⁻¹. In view of the experience with the symmetrical sulfonates,^{4,5} this behavior suggests that indeed the rearrangement accompanying solvolysis is observable. Starting with the

TABLE I
RATE OF ACETOLYSIS OF 0.03061 *M* 2-PHENYL-1-PROPYL
p-BROMOBENZENESULFONATE AT 75.01°

| 10 ⁻⁴ <i>t</i> , sec. | 0.0431 <i>M</i> NaOAc, ml. | 10 ⁶ <i>k</i> , sec. ⁻¹ |
|-------------------------------------|-------------------------------|--|
| 00 | 0.000 | .. |
| 72 | .051 | 2.07 |
| 144 | .166 | 2.32 |
| 217 | .250 | 3.38 |
| 293 | .420 | 4.30 |
| 373 | .538 | 4.41 |
| 493 | .818 | 5.30 |
| 812 | 1.412 | 6.25 |
| 966 | 1.825 | 6.89 |
| 1107 | 1.979 | 7.36 |
| 1717 | 2.508 | 7.14 |
| 1969 | 2.744 | 7.53 |
| ∞ | 3.551 | .. |

(1) Research supported by Office of Naval Research.

(2) Presented before Organic Division of American Chemical Society, Boston, Mass., April 2-5, 1951, page 52M of Abstracts.

(3) S. Winstein, B. Morse, E. Grunwald, K. Schreiber and J. Corse, *THIS JOURNAL*, **74**, 1113 (1952).

(4) S. Winstein and D. Trifan, *ibid.*, **74**, 1154 (1952).

(5) S. Winstein and K. Schreiber, *ibid.*, **74**, 2165 (1952).

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

secondary isomer IV on the other hand, extremely steady first order rate constants of acetolysis are obtained.⁶ Table II presents the data for a typical run and it is clear that first order rate constants show no trend up to 95% solvolysis. Thus the secondary isomer is not developing primary material in solvolysis.

TABLE II

RATE OF ACETOLYSIS OF 0.0296 *M* BENZYL METHYL CARBINYL *p*-BROMOBENZENESULFONATE AT 75.01°

| <i>t</i> , sec. | 0.0304 <i>M</i> NaOAc, ml. | 10 ³ <i>k</i> , sec. ⁻¹ |
|-----------------|-------------------------------|---|
| 0000 | 0.127 | .. |
| 2700 | 0.585 | 3.77 |
| 6420 | 1.143 | 3.76 |
| 8520 | 1.461 | 3.87 |
| 10260 | 1.692 | 3.83 |
| 13680 | 2.105 | 3.95 |
| 16680 | 2.412 | 3.95 |
| 24360 | 3.048 | 3.94 |
| 44580 | 4.030 | 3.90 |
| 81060 | 4.667 | 3.92 |
| ∞ | 4.861 | .. |

Mean 3.88 ± 0.06

On the basis of a first order rearrangement of 2-phenyl-1-propyl *p*-bromobenzenesulfonate (III) accompanying its solvolysis, with *k_p* representing the first order specific solvolysis rate of III, *k_r* the specific rearrangement rate of III into IV, and *k_s* the specific solvolysis rate constant of IV, it is possible to estimate the values of *k_r* and *k_p*. The treatment is analogous to the one employed recently in the case of simultaneous solvolysis and rearrangement in the acetolysis of α,α-dimethylallyl chloride.⁷

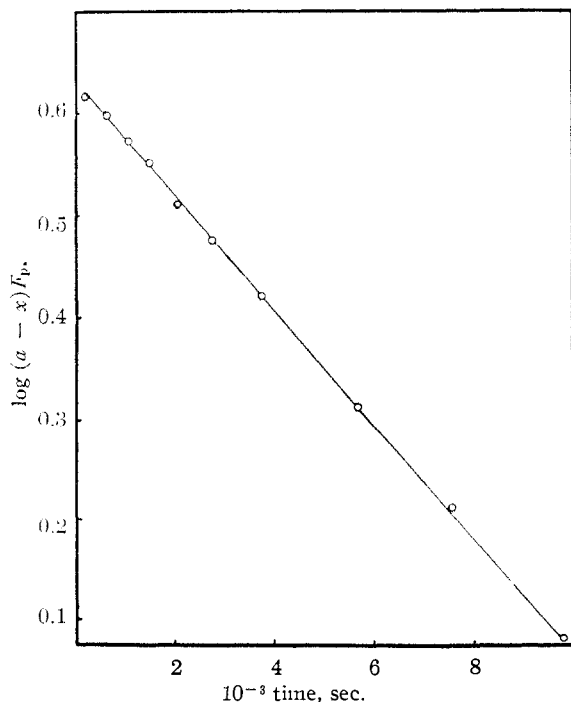


Fig. 1.—Plot of $(a - x)F_p$ vs. time for 2-phenyl-1-propyl *p*-bromobenzenesulfonate.

(7) W. Young, S. Winstein and H. Goering, *THIS JOURNAL*, **73**, 1958 (1951).

From large scale plots of $(a - x)$ vs. t values of the instantaneous rate constant, k , or $(dx/dt)/(a - x)$ were obtained with the aid of a tangent meter. These then furnish what amounts to an analysis of the remaining *p*-bromobenzenesulfonate at any time, t , with the aid of equation 2, where F_p denotes the mole fraction of III

$$k = \frac{(dx/dt)}{(a - x)} = k_p F_p + k_s (1 - F_p) \quad (2)$$

in the residual ester at any time, t . The necessary specific rate constants of benzylmethylcarbinyl *p*-bromobenzenesulfonate, k_s , whose determination is illustrated in Table II, are summarized in Table III. The necessary specific solvolysis rate constants for 2-phenyl-1-propyl *p*-bromobenzenesulfonate, k_p , are the values of the instantaneous rate constant extrapolated to zero time. Because of the rapidly rising instantaneous rate constants, this is a difficult extrapolation and the values of k_p obtained in this way tend to be high.

TABLE III

SOLVOLYSIS DATA FOR BENZYL METHYL CARBINYL *p*-BROMOBENZENESULFONATE

| Temp., °C. | ROBs 10 ² <i>M</i> | Added salt | <i>k_s</i> (sec. ⁻¹) |
|---------------|----------------------------------|---------------------------------------|--|
| 75.01 | 2.96 | | $(3.90 \pm 0.09) \times 10^{-5}$ |
| 75.01 | 2.66 | | $(3.91 \pm 0.07) \times 10^{-5}$ |
| 74.84 | 3.16 | | $(3.78 \pm 0.05) \times 10^{-5}$ |
| 74.99 | 2.49 | 0.0294 <i>M</i> NaOAc | $(4.18 \pm 0.08) \times 10^{-5}$ |
| 74.99 | 2.94 | .0411 <i>M</i> NaOAc | $(4.18 \pm 0.05) \times 10^{-5}$ |
| 74.84 | 3.19 | .0370 <i>M</i> NaOAc | $(4.16 \pm 0.11) \times 10^{-5}$ |
| 74.89 | 3.46 | .0287 <i>M</i> DPGHOBs ^a | $(4.10 \pm 0.10) \times 10^{-5}$ |
| 74.84 | 3.14 | .0224 <i>M</i> DPGHOBs ^a | $(4.16 \pm 0.08) \times 10^{-5}$ |
| 74.95 | 2.63 | .0268 <i>M</i> LiClO ₄ | $(5.98 \pm 0.17) \times 10^{-5}$ |
| 74.94 | 2.84 | .30 <i>M</i> H ₂ O (0.55%) | $(5.31 \pm 0.06) \times 10^{-5}$ |
| 99.67 | 2.61 | | $(4.52 \pm 0.17) \times 10^{-4}$ |
| 99.79 | 2.83 | | $(4.74 \pm 0.09) \times 10^{-4}$ |
| 99.65 | 2.73 | .0411 <i>M</i> NaOAc | $(5.32 \pm 0.16) \times 10^{-4}$ |
| 99.65 | 2.85 | .0411 <i>M</i> NaOAc | $(5.92 \pm 0.27) \times 10^{-4}$ |
| 99.71 | 3.41 | .0411 <i>M</i> NaOAc | $(5.63 \pm 0.05) \times 10^{-4}$ |
| 99.76 | 3.13 | .0411 <i>M</i> NaOAc | $(5.64 \pm 0.07) \times 10^{-4}$ |

^a Diphenylguanidinium *p*-bromobenzenesulfonate.

On the above basis, $(a - x)F_p$ represents the concentration of III and this should show a first order decrease with time with the apparent rate constant of $(k_r + k_p)$, according to equation 3

$$(k_r + k_p)t = \ln \frac{a}{(a - x)F_p} \quad (3)$$

Applying the above treatment to the experimental data, there is indeed obtained a linear relationship between $\log(a - x)F_p$ and t . A sample plot, shown in Fig. 1, illustrates the good linearity obtained.

The results of this treatment of the acetolysis-rearrangement of III are summarized in Table IV. Thus, for example, in acetolysis without addition of materials such as sodium acetate, k_p at 75° is estimated at 2.3×10^{-6} sec.⁻¹, while at the same temperature $(k_p + k_r)$ has the value 9.7×10^{-6} sec.⁻¹ and thus k_r is 7.4×10^{-6} sec.⁻¹, some three times as large as k_p . Similarly at 100°, k_p is 4.6×10^{-5} sec.⁻¹, while $(k_p + k_r)$ is 12.7×10^{-5} sec.⁻¹ and thus k_r is 8.1×10^{-5} sec.⁻¹, again higher than k_p .

Confirming the indications from the kinetic behavior of 2-phenyl-1-propyl *p*-bromobenzenesulfonate (III) in acetolysis, the rearranged isomer

IV may actually be isolated from partially acetylyzed III. For example, as described in the experimental part, partial acetylysis of 24 g. of III yielded 13.4 g. of recovered *p*-bromobenzenesulfonate in three fractions. This quantity represents a 94% recovery since the amounts of III and IV expected to survive, calculated from the necessary rate constants and equations 10 and 11 in the Appendix, are 11.6 and 2.6 g., respectively. The third fraction, containing most of the IV, was shown to contain 70% IV both by infrared and kinetic analyses.

TABLE IV
DATA FOR ACETOLYSIS OF 2-PHENYL-1-PROPYL *p*-BROMOBENZENESULFONATE

| Temp., °C. | (ROBS) $10^4 M$ | Added salt | $10^5 (k_r + k_p)$ (sec. ⁻¹) | $10^6 k_p$ (sec. ⁻¹) | $10^6 k_r$ (sec. ⁻¹) |
|------------|-----------------|--------------------------------|--|----------------------------------|----------------------------------|
| 75.02 | 3.213 | | 9.7 | 2.3 | 7.4 |
| 74.90 | 4.091 | | 9.7 | 2.1 | 7.6 |
| 74.90 | 3.061 | | 9.8 | 1.9 | 7.9 |
| 74.84 | 3.274 | | 9.7 | 1.9 | 7.8 |
| 74.84 | 3.181 | | 9.7 | 2.5 | 7.2 |
| 75.02 | 3.929 | 0.0411 M NaOAc | 10.1 | 2.8 | 7.3 |
| 75.02 | 3.385 | .0411 M NaOAc | 10.1 | 3.0 | 7.1 |
| 74.84 | 3.194 | .0370 M NaOAc | 10.2 | 2.9 | 7.3 |
| 74.84 | 3.177 | .0370 M NaOAc | 10.3 | 2.8 | 7.5 |
| 74.92 | 2.897 | .0290 M DPGHOBs ^a | 11.1 | 2.8 | 8.3 |
| 74.84 | 3.176 | .0227 M DPGHOBs | 10.9 | 2.6 | 8.3 |
| 74.84 | 3.186 | .0242 M DPGHOBs | 11.3 | 2.6 | 8.7 |
| 74.92 | 2.981 | .0273 M LiClO ₄ | 12.1 | 3.1 | 9.0 |
| 74.92 | 2.971 | .30 M H ₂ O (0.55%) | 13.0 | 3.6 | 9.4 |
| 99.97 | 2.505 | | 114 | 47 | 67 |
| 99.96 | 2.651 | | 124 | 48 | 76 |
| 99.98 | 3.385 | | 130 | 45 | 85 |
| 99.96 | 2.945 | .0411 M NaOAc | 122 | 54 | 68 |
| 99.96 | 3.283 | .0411 M NaOAc | 130 | 52 | 78 |

^a Diphenylguanidinium *p*-bromobenzenesulfonate.

As shown in Fig. 2, the isomeric esters III and IV differ substantially in their infrared spectra in the general region of 10–11.5 μ , and this region was employed for analysis of mixtures. As shown in Fig. 3, comparison of the spectrum of the isolated

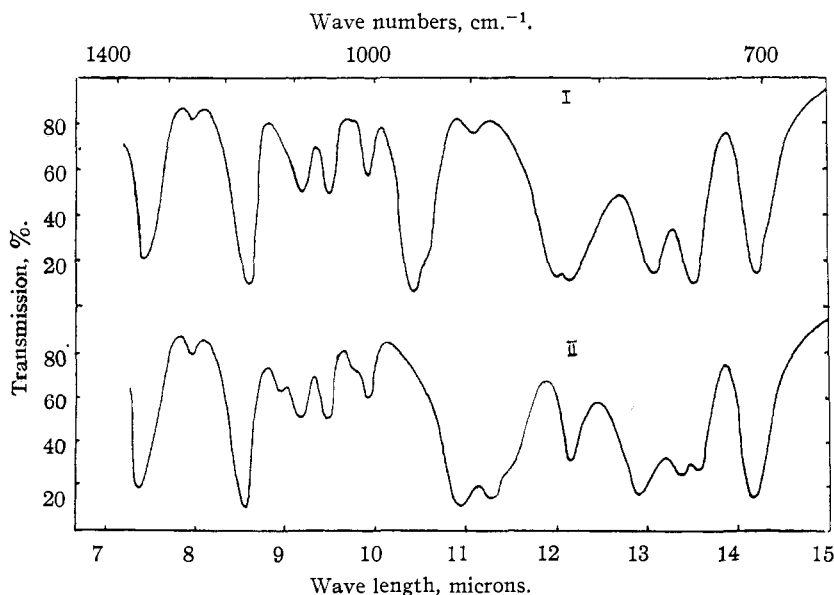


Fig. 2.—Infrared absorption spectra: I, 2-phenyl-1-propyl *p*-bromobenzenesulfonate; II, benzylmethylcarbonyl *p*-bromobenzenesulfonate.

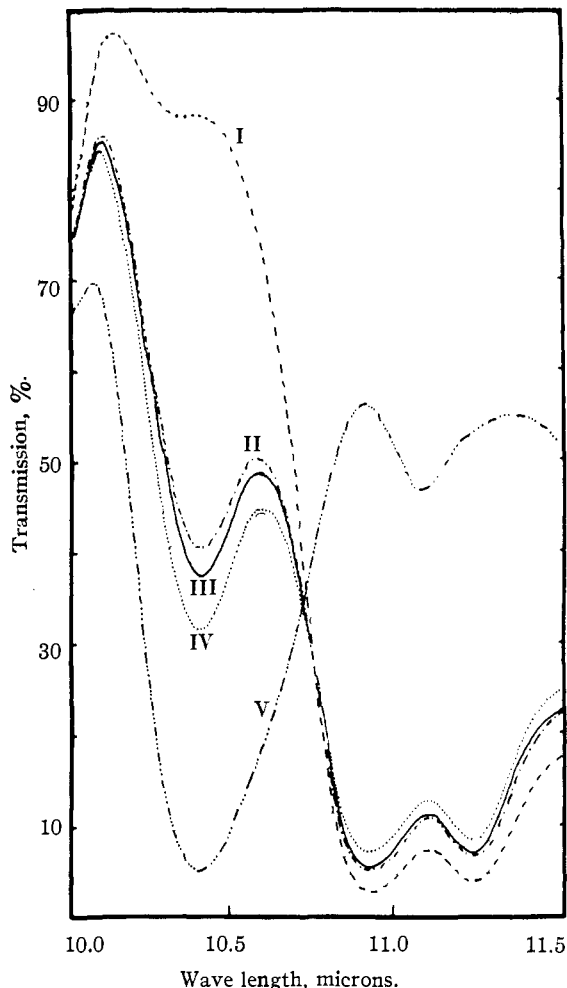
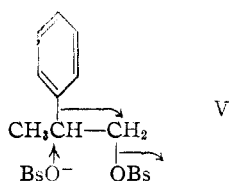


Fig. 3.—Infrared spectra: I, benzylmethylcarbonyl *p*-bromobenzenesulfonate (BMC); II, 3(BMC):1(2P1P); III, fraction 3 of recovered bromobenzenesulfonate; IV, 2(BMC):1(2P1P); V, 2-phenyl-1-propyl *p*-bromobenzenesulfonate (2P1P).

fraction with mixtures of III and IV, 67 and 75% IV, respectively, indicates a composition of 70% IV. Determination of the acetylysis rate of the fraction gave an initial rate constant of 2.8×10^{-5} sec.⁻¹ at 74.90°, which, from equation 2, corresponds to a composition of 70.4% IV. This analysis corresponds to 1.7 g. of IV, or 65% of the theoretically calculated quantity of IV, in the one fraction alone.

Further scrutiny of the kinetics, especially of the effect of added acetate ion, *p*-bromobenzenesulfonate ion and water supplies further evidence, as in the symmetrical cases,^{4,5} that the rearrangement of III into IV is an internal process. The possibility that the rearrangement of III into IV is an S_N2' process,³

formula V, involving attack by external *p*-bromobenzenesulfonate ion (OBs^-), may be disposed of



easily. If the rearrangement of III into IV were first order in OBs^- , then in a run without added OBs^- , rearrangement would start at a zero rate constant and climb as OBs^- develops. Thus $(k_r + k_p)$ would start at the value of k_p for the conditions prevailing and rise. It is clear that this is not the observed behavior. Furthermore, added OBs^- initially would give a much increased value of $(k_r + k_p)$. In actual fact, as summarized in Table IV, the inclusion of diphenylguanidinium *p*-bromobenzenesulfonate at a concentration approximately equal to that of 2-phenyl-1-propyl *p*-bromobenzenesulfonate, makes no changes in the relative values of $(k_r + k_p)$, k_r and k_p beyond small effects ascribable to salt effects. If inclusion of external OBs^- in a run did increase the initial rate of rearrangement of III into IV, this would greatly increase the early climb of over-all solvolysis rate which is observed in a run because of the more rapid formation of IV. This would be true unless external OBs^- also decreased the solvolysis rates of the bromobenzenesulfonate (e.g., by a mass law effect⁸). It is clear that external OBs^- does not so decrease solvolysis rates from the observed rate of solvolysis of IV (Table III) and the extrapolated value of k_p for III (Table IV) in the presence of originally added OBs^- . What is observed is a slight increase in these values, ascribable to a medium effect. Therefore, a comparison of the early course of solvolysis of III with and without originally added OBs^- is valid in ruling out the SN_2' process. Such a comparison is summarized in Table V, where it is clear that addition of 0.0234 *M* diphenylguanidinium *p*-bromobenzenesulfonate does not change appreciably the development of acid in the solvolysis of III.

TABLE V
ACETOLYSIS OF 0.0318 *M* 2-PHENYL-1-PROPYL *p*-BROMO-
BENZENESULFONATE AT 74.84°

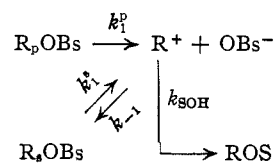
| 10 ⁻⁴ , sec. | Reaction, % | | |
|----------------------------|------------------|----------------------------|---------------------------|
| | No salt added | 0.0234 <i>M</i> DPGHOBs | 0.03704 <i>M</i> NaOAc |
| 6.3 | 1.46 | 1.54 | 1.26 |
| 9.9 | 3.09 | 3.13 | 2.41 |
| 15.3 | 5.58 | 5.73 | 4.34 |
| 17.1 | 6.09 | 6.02 | 5.30 |
| 24.0 | 9.77 | 10.4 | 8.17 |
| 28.2 | 12.6 | 13.3 | |
| 36.0 | 17.2 | 18.1 | 15.4 |
| 39.0 | 18.5 | | 16.6 |
| 50.4 | 24.9 | 26.6 | 23.6 |

It also is clear that the rearrangement of III into IV is not due to external return.^{8,9} An ex-

(8) L. Bateman, M. Church, E. Hughes, C. Ingold and N. Taher, *J. Chem. Soc.*, 979 (1940).

(9) S. Winstein, E. Grunwald and H. Jones, *THIS JOURNAL*, **73**, 2700 (1951).

ample of a scheme involving external return is



In this scheme k_r is given by equation 4

$$k_r = k_1^p \frac{k_{-1}(\text{OBs}^-)}{k_{s\text{OH}} + k_{-1}(\text{OBs}^-)} \quad (4)$$

and the rate of solvolysis at any time, dx/dt , by equation 5

$$dx/dt = (k_1^p P + k_1^s S) \left[\frac{1}{1 + (k_{-1}/k_{s\text{OH}})(\text{OBs}^-)} \right] \quad (5)$$

Again, the concentration of *p*-bromobenzenesulfonate ion would play a serious role in controlling solvolysis and rearrangement rate and this is contrary to the facts. More complex schemes involving external return are conceivable but these too are inconsistent with the facts.

Acetolysis of Mixtures of III and IV.—Further support for the above formulation of the kinetic behavior of III in solvolysis and further assistance in selecting better values for k_p and k_r are derived from the solvolysis of synthetic mixtures of III and IV. As is clear from the derivations in the Appendix, the situation where III simultaneously gives solvolysis products and IV in a first order fashion, the latter giving solvolysis products also, leads to the following behavior of *S*, the concentration of IV, *S/P*, the ratio of concentrations of IV to III and the instantaneous solvolysis rate constant, k .

In solvolysis of initially pure primary *p*-bromobenzenesulfonate, *S* will begin at zero and will go through a maximum value. For a case such as the present one, with $k_s > (k_r + k_p)$, the ratio *S/P* will begin at zero and will climb until it approaches a value *R* equal to $k_r/(k_s - k_r - k_p)$ at infinite time.¹⁰ The instantaneous rate constant begins at the value of the primary ester, k_p and climbs until it approaches the value $(k_r + k_p)$ at infinite time. In solvolysis of a mixture of III and IV with the original value of *S/P* less than *R*, *S/P* will tend to climb to *R* and the instantaneous rate constant will climb to the same final value of $(k_r + k_p)$. When *S/P* is initially greater than *R*, *S/P* decreases in a run and approaches *R* while the instantaneous rate constant will start appropriately high and decrease, approaching the same limiting value, $(k_r + k_p)$ as before. For a mixture with *S/P* initially equal to *R*, *S/P* is predicted to remain perfectly constant, and the instantaneous rate constant to remain constant at the value $(k_r + k_p)$, which is reached in the limit in the other cases. When synthetic mixtures of III and IV were solvolyzed, this prediction was verified. This is illustrated in Table VI, where the first order constants, calculated from equation 1, in acetolysis of a 1:0.253 mixture of III and IV are seen to be very steady.

(10) For the case where $(k_r + k_p) > k_s$ the composition of residual *p*-bromobenzenesulfonate approaches pure *S* and the instantaneous solvolysis rate constant approaches k_s .

TABLE VI
RATE OF ACETOLYSIS OF A 1:0.253 MIXTURE OF 2-PHENYL-1-PROPYL AND BENZYL METHYLCARBINYL *p*-BROMOBENZENESULFONATES AT 99.96°

| 10 ⁻⁴ , sec. | 0.0411 M NaOAc, ml. | 10 ⁴ k, (sec. ⁻¹) |
|----------------------------|------------------------|---|
| 000 | 0.311 | .. |
| 003 | .475 | 1.31 |
| 006 | .623 | 1.31 |
| 012 | .905 | 1.29 |
| 018 | 1.152 | 1.27 |
| 024 | 1.396 | 1.28 |
| 030 | 1.615 | 1.27 |
| 036 | 1.840 | 1.29 |
| 046 | 2.113 | 1.26 |
| 060 | 2.500 | 1.26 |
| 081 | 2.976 | 1.28 |
| 105 | 3.298 | 1.24 |
| 157 | 3.881 | 1.28 |
| ∞ | 4.430 | .. |
| Mean | | 1.28 ± 0.02 |

In Table VII are summarized the data on the solvolysis of synthetic mixtures of III and IV.

TABLE VII

SUMMARY OF SOLVOLYSES OF MIXTURES OF 2-PHENYL-1-PROPYL AND BENZYL METHYLCARBINYL *p*-BROMOBENZENESULFONATES

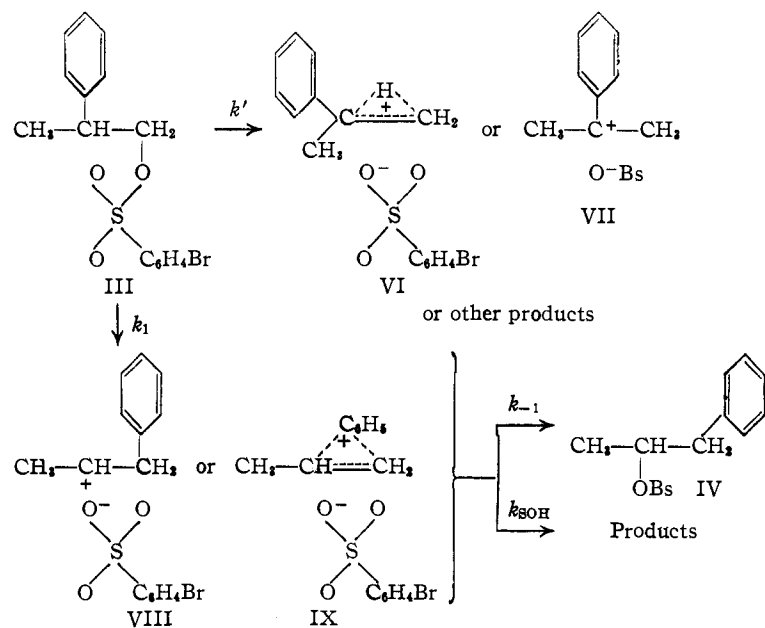
| Temp., °C. | Exptl. S/P | Added salt | 10 ⁴ k _{obsd.} , sec. ⁻¹ | 10 ⁴ k _p Calcd., sec. ⁻¹ | 10 ⁵ (k _r + k _p) sec. ⁻¹ | 10 ⁴ k _r sec. ⁻¹ | S/P Calcd. |
|---------------|---------------|-----------------------------|--|--|--|--|---------------|
| 75.01 | 0.236 | ... | 0.88 ± 0.02 | 1.7 | 0.97 | 8.0 | 0.273 |
| 74.92 | .287 | ... | 0.98 ± 0.02 | 1.5 | 0.97 | 8.2 | .280 |
| 74.90 | .243 | 0.041 M NaOAc | 1.09 ± 0.03 | 3.4 | 1.01 | 6.7 | .211 |
| 74.90 | .193 | .037 M NaOAc | 0.94 ± 0.03 | 3.1 | 1.01 | 7.0 | .221 |
| 74.90 | .243 | .042 M DPGHOBs ^a | 1.00 ± 0.03 | 2.4 | 1.11 | 8.7 | .291 |
| 99.96 | .253 | ... | 12.8 ± 0.2 | 42 | 12.7 | 85 | .251 |
| 99.86 | .252 | .041 M NaOAc | 14.8 ± 0.3 | 43 | 12.7 | 84 | .202 |
| 99.78 | .189 | .037 M NaOAc | 12.7 ± 0.5 | 45 | 12.7 | 82 | .188 |

^a Diphenylguanidinium *p*-bromobenzenesulfonate.

The column "S/P expl." lists the ratios used in the experiments and the column "10⁴k obsd." gives the observed first-order rate constants which were steady and showed no definite trend. From the

composition of the mixture and the observed rate constant, k_p can be calculated using equation 2. The values of k_p , thus derived, are shown as "10⁴ k_p calcd." These values are a little lower and more reliable than those in Table IV since the latter, obtained by extrapolation, tend to be high. Retreatment of the data of solvolysis of pure III (Table IV) using the new values of k_p leaves ($k_r + k_p$) virtually unchanged, since these are quite insensitive to the choice of k_p . The values of ($k_r + k_p$) are given in Table VII, and by subtraction of k_p from them, new values of k_r , given in Table VII, are obtained. The theoretical value of S/P for a mixture with a constant rate constant, calculated as $k_r/(k_s - k_r - k_p)$, is given in Table VII in the column headed "S/P calcd." These values are, of course, sensitive to the choice of k_r and differ somewhat in some cases from the "S/P expl." values, which were based on earlier estimates of k_r .

Internal Rearrangement.—The internal rearrangement of III into IV which the data demand is still open to more than one kind of description, but, in line with the previous discussion,⁵ it seems



at present best described in terms of internal return^{5,7,9} On this basis an ion-pair type of intermediate such as VIII or IX is the one which can yield benzylmethylcarbiny *p*-bromobenzenesulfonate (IV) by internal return. We can have k' represent the sum of the first-order rate constants for reactions which either do not give return or do give some return, but only to very much more reactive bromobenzenesulfonates than III or IV. If k_1 represents the rate constant for formation from III of the intermediate which returns to IV (rate constant k_{-1}) or yields products and titrable *p*-bromobenzenesulfonic acid (rate constant k_{SOH}), then the measured k_r values (for III \rightarrow IV) are represented in equation 6, and the measured k_p values by equation 7.

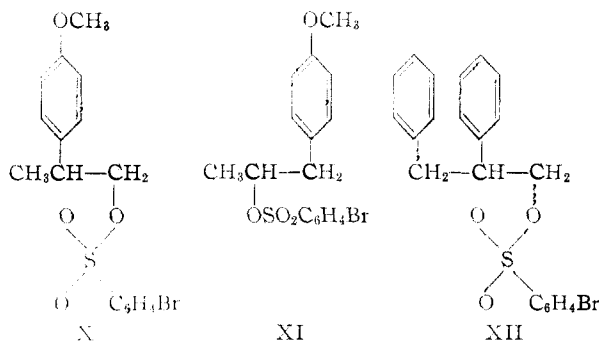
$$k_r = (k_1 k_{-1}) / (k_{-1} + k_{\text{SOH}}) \quad (6)$$

$$k_p = k' + [k_1 k_{\text{SOH}} / (k_{-1} + k_{\text{SOH}})] \quad (7)$$

Whether, on the present basis, the acetolysis of benzylmethylcarbiny *p*-bromobenzenesulfonate (IV) is also associated with internal return, cannot yet be answered. The extent to

which an intermediate from IV resembles or differs from intermediate VIII or IX from III in any solvent, taking into account the nearest and most important solvent molecules, we expect to decide from work now proceeding. An intermediate from IV can differ from one from III, and therefore internal return could be more important in one case than another.

It is interesting that the relative importance of the internal phenomenon is comparable in the several cases of acetolysis where internal rearrangement has been observed. Thus $(k_T + k_i)/k_T$ is *ca.* 3-4 for α,α -dimethylallyl chloride⁷ at 25°, k_a/k_t is 3.5 for *exo*-norbornyl *p*-bromobenzenesulfonate⁴ at 25° and *ca.* 4.5 for 3-phenyl-2-butyl *p*-toluenesulfonate⁵ at 50-75°, while $(k_p + k_r)/k_p$ is *ca.* 3-5 for 2-phenyl-1-propyl *p*-bromobenzenesulfonate (III) at 75-100°. The situation is similar with two analogs of III, namely, X and XII, as disclosed by preliminary work.



In acetolysis of 2-*p*-anisyl-1-propyl *p*-bromobenzenesulfonate (X) at 49.60°, the integrated first order rate constant begins in the region of $2 \times 10^{-5} \text{ sec.}^{-1}$ (k_p) and rises to $3.2 \times 10^{-5} \text{ sec.}^{-1}$ at 95% completion. The rate constant, k_s , of *p*-methoxybenzylmethylcarbinyl *p*-bromobenzenesulfonate (XI), not yet available, can be estimated at *ca.* $4 \times 10^{-5} \text{ sec.}^{-1}$ from the value for the *p*-toluenesulfonate,⁶ $1.20 \times 10^{-5} \text{ sec.}^{-1}$ at 49.72°. Thus the gap between k_p and k_s is very small. When a value for k_s of *ca.* $4.2 \times 10^{-5} \text{ sec.}^{-1}$ is used together with $k_p = 2 \times 10^{-5} \text{ sec.}^{-1}$ in equation 2, a plot of $\ln [a/(a-x)F_p]$ vs. t leads to a straight line. From this $(k_r + k_p)$ is *ca.* $5.60 \times 10^{-5} \text{ sec.}^{-1}$ so that $(k_r + k_p)/k_p$ is *ca.* 3.¹¹

The general climb in rate constant in acetolysis of 2,3-diphenyl-1-propyl *p*-bromobenzenesulfonate¹² (XII) suggests a comparable importance of internal rearrangement in this system, also.

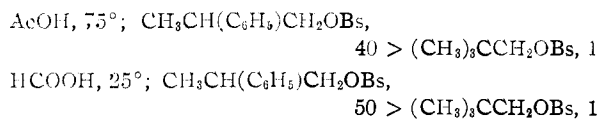
Ethanolysis and Formolysis.—In two other solvents, namely, absolute ethanol and formic acid, the solvolysis of 2-phenyl-1-propyl *p*-bromobenzenesulfonate (III) proceeds in a first-order fashion with no certain trend in the rate constants, which are summarized in Table VIII. Comparison of the rate constants of III in these solvents with those⁶ of IV shows that the failure to detect a trend is not largely due to a decreased gap in rate between III and IV, for the ratio of solvolysis rate

constants, IV:III is similar in ethanol and acetic acid and, while a little smaller, is still 9 in formic acid at 25°. In ethanol we ascribe the disappearance of the internal rearrangement phenomenon to solvent participation but shall defer more discussion of this matter until our investigation of the products and stereochemistry of solvolysis of III is more complete. In formic acid, the internal rearrangement has become sufficiently unimportant, relative to solvolysis, that a large trend in the solvolysis rate constant is no longer observed. In the case of 3-phenyl-2-butyl *p*-toluenesulfonate,⁵ the change from acetic acid to formic acid decreased very markedly the ratio of polarimetric to titrimetric rate constants. Analogously in the present case, the change from acetic to formic acid solvent would decrease the ratio of $(k_r + k_p)/k_p$ very markedly. This decrease was evidently sufficient to make the upward trend in rate constant [which can at most go from k_p originally to $(k_r + k_p)$ at infinity] during the portion of the reaction ordinarily scrutinized in a formolysis rate run too small to exceed ordinary random variations.

TABLE VIII
RATES OF ETHANOLYSIS AND FORMOLYSIS OF 2-PHENYL-1-PROPYL *p*-BROMOBENZENESULFONATE

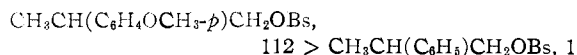
| Solvent | t , °C. | ROBs $10^2 M$ | $10^4 k$, sec. ⁻¹ |
|---------|-----------|---------------|-------------------------------|
| EtOH | 75.01 | 3.004 | 4.48 ± 0.08 |
| EtOH | 75.01 | 2.972 | 4.26 ± 0.09 |
| EtOH | 75.01 | 2.864 | 4.38 ± 0.06 |
| HCOOH | 24.96 | 5.374 | 3.31 ± 0.09 |
| HCOOH | 24.96 | 3.321 | 3.35 ± 0.16 |

Reactivity Considerations.—The rate data show that 2-phenyl-1-propyl *p*-bromobenzenesulfonate, with a primary leaving group, has a considerably enhanced reactivity to be ascribed to participation. Comparing $(k_p + k_r)$ with the rate constant for solvolysis of the corresponding neopentyl derivative^{3,13} (allowing a factor of 3 between a *p*-bromobenzenesulfonate and a *p*-toluenesulfonate), one obtains the sequences



These illustrate the rate enhancement even without consideration of correction factors previously discussed.³

The effect of a *p*-methoxy group in 2-phenyl-1-propyl *p*-bromobenzenesulfonate is very substantially rate-enhancing, as is expected. Comparing $(k_r + k_p)$ values in AcOH at 50° gives the sequence



This effect of the *p*-methoxy group corresponds to a ρ in Hammett's $\rho\sigma$ treatment¹⁴ of -7.65.

With the aid of the data presented in the present article and previously, it is possible again³ to illustrate the much decreased sensitivity of rate to α -methyl substitution for cases of participation.

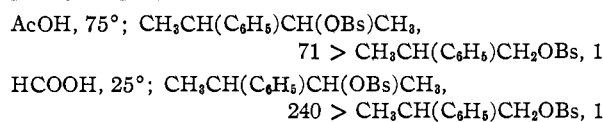
(11) In this system $(k_r + k_p) > k_s$ so that residual bromobenzenesulfonate, starting with pure X, approaches pure XI and the instantaneous rate constant approaches k_s .

(12) Kurt Schreiber, unpublished work.

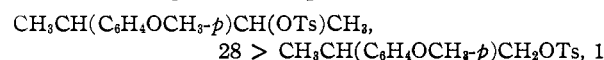
(13) S. Winstein and H. Marshall, *THIS JOURNAL*, **74**, 1120 (1952).

(14) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 183.

Comparison of 3-phenyl-2-butyl⁵ I (k_α) with 2-phenyl-1-propyl ($k_p + k_r$) gives the sequences



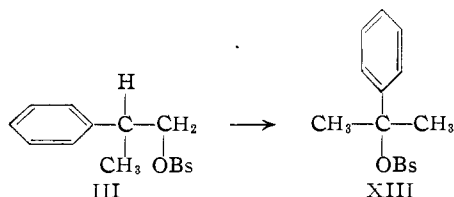
These show that introduction of an α -methyl group into 2-phenyl-1-propyl *p*-bromobenzenesulfonate increases rate by only a factor of *ca.* 10². This effect of an α -methyl group is even smaller when the substitution is in 2-*p*-anisyl-1-propyl *p*-bromobenzenesulfonate. Comparing k_t for 3-*p*-anisyl-2-butyl⁶ with k_p for 2-*p*-anisyl-1-propyl in AcOH at 50° gives the sequence



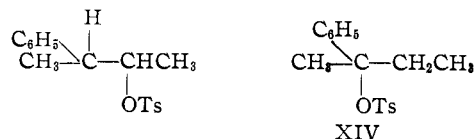
Complication Due to Internal Rearrangement.

For our understanding of molecular rearrangement, one of the worst complications arising from internal rearrangement is that the phenomenon may escape kinetic detection. For instance, consider the situation if, in the case of III, *S* had been very much more reactive in solvolysis; in other words $k_s \gg (k_r + k_p)$. Under these conditions, from the derivations in the Appendix, *S/P* would quickly reach the steady state value substantially equal to k_r/k_s and the solvolysis rate constant starting with pure *P* would very quickly reach the value ($k_p + k_r$). In fact the steady rate constant ($k_p + k_r$) could be reached before the first point in the kinetic run and then the measured steady rate constant would include reaction through *S* as an intermediate. Further, consider the hypothetical case where $k_s:k_r:k_p$ are of the order of 10⁵:10²:1. The steady rate constant, reached too soon to observe a drift, would be 101 times k_p and would measure solvolysis, 99% of which proceeded through the rearrangement product.

It is, of course, possible, in general, for a substance to rearrange to a number of isomers, depending on which one of the β -groups migrate in a Wagner-Meerwein rearrangement, even without bringing up the more complex possibility of coupled shifts. As derived in the appendix for one case of originally pure material giving solvolysis and irreversible rearrangement to other species, more reactive in solvolysis, each ratio S_n/P approaches a value R_n and the solvolysis rate constant approaches a definite final value. Now in such a case the S_n/P ratios approach their steady values at different rates. One or more of them may reach their steady values too soon to disturb the kinetics. Then, even the very initial solvolysis rate constant will be the sum of k_p and those k_r values relating to the S_n/P steady states so rapidly established. For example, in the case of 2-phenyl-1-propyl *p*-bromobenzenesulfonate III, rearrange-



ment to XIII involving hydrogen migration (see VI or VII) would yield such a reactive isomer that the k_r for this process would be included in the constant designated as k_p in the present work. Similarly in the case of 3-phenyl-2-butyl *p*-toluenesulfonate,⁵ rearrangement to the tertiary ester XIV would, for kinetic purposes, supply a con-



tribution to the titrimetric rate, included in the titrimetric rate constant, k_t .

Kinetic Appendix

Letting *P* and *S* denote the concentrations of primary and secondary isomer III and IV, respectively, equations 8 and 9 express dP/dt and dS/dt in terms of *P* and *S*.

$$dP/dt = -(k_r + k_p)P \quad (8)$$

$$dS/dt = k_r P - k_s S \quad (9)$$

Integration of equation 8 gives equation 10 for *P* as a function of time while substitution of this expression for *P* into equation 9 and solving the resulting differential equation yields equation 11 for *S* as a function of time. In equations

$$P = P_0 e^{-(k_r + k_p)t} \quad (10)$$

$$S = S_0 e^{-k_s t} + \frac{k_r P_0}{k_s - k_r - k_p} [e^{-(k_r + k_p)t} - e^{-k_s t}] \quad (11)$$

10 and 11, P_0 and S_0 denote initial values of *P* and *S*, respectively, to use the general case where a mixture of III and IV is solvolyzed. This gives for *S/P* the expression shown in equation 12.

$$\frac{S}{P} = \left[\frac{S_0}{P_0} - \frac{k_r}{k_s - k_r - k_p} \right] e^{-(k_s - k_r - k_p)t} + \frac{k_r}{k_s - k_r - k_p} \quad (12)$$

It is convenient to define *R*, R_0 and *A* by equations 13, 14 and 15 and thus to rewrite *S/P* from equation 12 in the form of equation 16.

$$R \equiv k_r / (k_s - k_r - k_p) \quad (13)$$

$$R_0 \equiv S_0 / P_0 \quad (14)$$

$$A \equiv k_s - k_r - k_p \quad (15)$$

$$S/P = (R_0 - R)e^{-At} + R \quad (16)$$

From equation 16, F_p , the mole fraction of primary ester III in the remaining ester at any time, *t*, is given by equation 17 and from this equation and equation 2

$$F_p = \frac{1}{(R_0 - R)e^{-At} + R + 1} \quad (17)$$

the instantaneous first order rate constant, $(dx/dt)/(a - x)$, is given by equation 18.

$$k = (dx/dt)/(a - x) = k_s - \frac{(k_s - k_p)}{(R_0 - R)e^{-At} + R + 1} \quad (18)$$

For the general case where originally pure *P* isomerizes irreversibly to a number, *n*, of more reactive species, S_1, S_2, \dots, S_n , each with a solvolysis rate constant $k_{s1}, k_{s2}, \dots, k_{sn}$, an analogous treatment is possible. *P* is given

$$P = P_0 e^{-(k_p + \sum_1^n k_r)t} \quad (19)$$

$$S_n = \frac{k_{rn} P_0}{k_{sn} - k_p - \sum_1^n k_r} \left[e^{-(k_p + \sum_1^n k_r)t} - e^{-k_{sn}t} \right] \quad (20)$$

$$\frac{S_n}{P} = \frac{k_{rn}}{k_{sn} - k_p - \sum_1^n k_r} \left[1 - e^{-(k_{sn} - k_p - \sum_1^n k_r)t} \right] \quad (21)$$

as a function of time by equation 19, the concentration of any one of the isomers, S_n , by the general equation 20 and S_n/P by equation 21.

Where k_{S_n} is greater than $(k_p + \sum_1^n k_r)$, S_n/P approaches the value R_n defined by equation 22.

$$R_n \equiv \frac{k_{rn}}{k_{S_n} - k_p - \sum_1^n k_r} \quad (22)$$

Defining A_n by equation 23, S_n/P becomes

$$\left(k_{S_n} - k_p - \sum_1^n k_r\right) \equiv A_n \quad (23)$$

expressible by equation 24

$$\frac{S_n}{P} = R_n [1 - e^{-A_n t}] \quad (24)$$

When all the ratios S_n/P have become equal to the R_n values, the fractions of P , S_1 , etc., in the remaining toluenesulfonate are given by equations 25 and 26. The rate

$$F_P = \frac{1}{1 + \sum_1^n R_n} \quad (25)$$

$$F_{S_n} = \frac{R_n}{1 + \sum_1^n R_n} \quad (26)$$

constant for solvolysis at that time will be given by equation 27.

$$k = \frac{dx/dt}{a-x} = \frac{1}{1 + \sum_1^n R_n} [k_p + R_1 k_{S_1} + R_2 k_{S_2} + \dots R_n k_{S_n}] \quad (27)$$

Experimental

2-Phenyl-1-propyl *p*-Bromobenzenesulfonate.—2-Phenylpropionaldehyde (8 g., 0.06 mole), was reduced with lithium aluminum hydride (1.2 g., 0.03 mole) in 70 ml. of anhydrous ether. The reaction mixture was poured into ice-water containing 6 *N* sulfuric acid, and the carbinol was isolated in the usual way. The residue (8 g.) from removal of ether from the ethereal solution of the carbinol was not purified, but immediately treated with 60 cc. of anhydrous pyridine and 16 g. of *p*-bromobenzenesulfonyl chloride. The reaction mixture was allowed to stand in the refrigerator for 24 hours; then it was worked up in the usual way to yield 15.2 g. (73%) of 2-phenyl-1-propyl *p*-bromobenzenesulfonate, m.p. 81.5–82.5°. The equivalent wt. of this material in acetolysis was within 1.0% of theory.

Anal. Calcd. for $C_{15}H_{16}O_3SBr$: C, 50.71; H, 4.26. Found: C, 50.84; H, 4.46.

Benzylmethylcarbonyl *p*-Bromobenzenesulfonate.—This material was the same as previously described.⁶

2-*p*-Methoxyphenyl-1-propyl *p*-Bromobenzenesulfonate.—2-Anisylpropionaldehyde⁶ was reduced with lithium aluminum hydride. To a solution of crude 2-anisyl-propanol (5.4 g., 0.0326 mole) in pyridine (32 cc.) was added bromobenzenesulfonyl chloride (8.3 g., 0.0326 mole) with cooling and the mixture was allowed to stand overnight in the refrigerator. Isolation in the usual way yielded 5.2 g. (42%) of 2-anisyl-1-propyl bromobenzenesulfonate, m.p. 87–88°.

Anal. Calcd. for $C_{15}H_{17}O_4SBr$: C, 49.88; H, 4.44. Found: C, 49.87; H, 4.29.

Diphenylguanidinium *p*-Bromobenzenesulfonate.—A solution of 1.5 g. (0.0063 mole) of *p*-bromobenzenesulfonic acid in 100 ml. of dry ether was added with shaking to a solution of 1.4 g. (0.0065 mole) of diphenylguanidine in 50 ml. of dry ether. The mixture was kept overnight in the refrigerator. Then the crystals were filtered, washed with cold ether and dried to yield 3.5 g. (90%) of material; m.p. after recrystallization from acetonitrile, 180.5–181.3°.

Anal. Calcd. for $C_{19}H_{18}N_3O_3SBr$: C, 50.90; H, 4.05. Found: C, 50.84; H, 4.16.

Isolation of Benzylmethylcarbonyl *p*-Bromobenzenesulfonate (IV) from Partial Solvolysis of 2-Phenyl-1-propyl *p*-Bromobenzenesulfonate (III).—A solution of 2-phenyl-1-propyl *p*-bromobenzenesulfonate (24 g., 0.0675 mole) in dry acetic acid (1 l.) was heated at 99.7° for 95 minutes, cooled in ice and poured into a separatory funnel containing water (1 l.), Skellysolve "F" (500 cc.) and ether (500 cc.). The aqueous layer was once extracted with a 1:1 mixture of ether–Skellysolve F. The combined organic layers were neutralized with 10% potassium carbonate solution and dried over potassium carbonate. After concentrating to ca. 200 cc. and cooling in ice, 7.8 g. of fairly pure III, m.p. 79.5–82° were obtained. On further concentration to ca. 50 cc. there was obtained a second crop (3.2 g.), m.p. 75–79°, which still consisted largely of III. After removal of the remaining solvent and standing in the freezing unit of a refrigerator for several days, a third crop (2.4 g.), m.p. 61–75°, was obtained. This contained a substantial amount of IV.

Procedure for Kinetic Measurements.—In acetolysis¹⁵ and ethanolysis,⁸ the general procedure was the one previously described. Lithium perchlorate was prepared and used in acetolysis runs as reported previously.¹⁶ In formolysis, the titration procedure was the one used before,¹³ the solvent was 0.08% in water by Karl–Fischer titration, and the ampoule technique was employed.

LOS ANGELES 24, CALIF.

RECEIVED JUNE 11, 1951

(15) S. Winstein, E. Grunwald and L. Ingraham, *THIS JOURNAL*, **70**, 821 (1948).

(16) S. Winstein and R. Adams, *ibid.*, **70**, 838 (1948).