

The catalyst employed (1.0 g. per 1.0 g. of olefin) was 5% palladium supported on calcium carbonate. The product was isolated by evaporation of the solvent and distillation of the residue. The hydrogen uptake was in each case theory  $\pm 2\%$ . The mixture of 2- and 3-phenyl-pentane isolated had an index of refraction of  $n_D^{25}$   $1.4860 \pm 0.0001$  (for pure 2-phenylpentane,  $n_D^{25}$  1.4858; for pure 3-phenylpentane,  $n_D^{25}$  1.4861<sup>4</sup>).

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## Neighboring Carbon and Hydrogen. XII. Internal Rearrangement in Solvolysis of 3-Phenyl-2-butyl *p*-Toluenesulfonate<sup>1</sup>

BY S. WINSTEIN AND KURT C. SCHREIBER

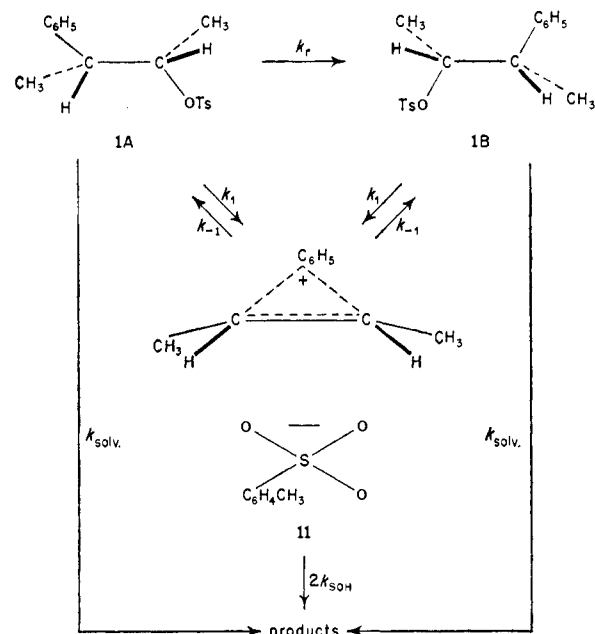
The same kind of polarimetric and titrimetric rate scrutiny as in the case of *exo*-norbornyl *p*-bromobenzenesulfonate has now been given the solvolysis of 3-phenyl-2-butyl *p*-toluenesulfonate IA. For the latter substance, polarimetric and titrimetric rate constants show good first order behavior, the polarimetric rates exceeding the titrimetric by factors of 2, 4.5–5, and 1.18 in ethanol, acetic acid and formic acid, respectively. Other details of the observed kinetics in the presence of added solutes show convincingly that the excess racemization is due to an internal phenomenon, and the results are discussed along with those for *exo*-norbornyl *p*-bromobenzenesulfonate. The rate of internal excess racemization of 3-phenyl-2-butyl *p*-toluenesulfonate is nearly as sensitive to change in solvent as the solvolysis rate, and there is suggested the probability of a common intermediate, essentially an ion-pair, for both internal racemization and solvolysis. This intermediate can give racemic *p*-toluenesulfonate by "internal return" or can go on to products. Analogous internal phenomena may be generally important in a number of connections.

The discovery that polarimetric rate constants were 1.4 to 3.5 times as large as titrimetric rate constants in the solvolysis of *exo*-norbornyl *p*-bromobenzenesulfonate<sup>2</sup> III brought to light a phenomenon of considerable importance to our understanding of molecular rearrangements. In principle, this kind of complication can be present in all studies of neighboring group participation.

The same kind of polarimetric and titrimetric scrutiny as in the case of *exo*-norbornyl *p*-bromobenzenesulfonate (III) has been given the solvolysis of 3-phenyl-2-butyl *p*-toluenesulfonate (IA). In this system, representing another symmetrical case, the rate<sup>3</sup> is convenient for extension of the measurements over a larger solvent range, including formic acid. Thus the system is especially worthwhile in seeking information on the nature of the reaction responsible for the excess racemization accompanying solvolysis. Further, the system represents a case of control of the stereochemistry<sup>4</sup> of replacement by neighboring phenyl.<sup>5</sup> However, the completeness of this control can be assessed more accurately with a knowledge of the excess racemization accompanying solvolysis. The results of the measurements on 3-phenyl-2-butyl *p*-toluenesulfonate are reported in this paper and discussed along with the results on *exo*-norbornyl *p*-bromobenzenesulfonate<sup>2</sup> and some related matters.

One of the optically active modifications of the 3-phenyl-2-butyl *p*-toluenesulfonate diastereomer labeled I by Cram<sup>4</sup> was obviously the material to be studied. Since the 3-phenyl-2-butyl acetates from the two diastereomeric types of toluenesulfonate (I and II) are very largely different,<sup>4</sup> it was already clear that any changes in the *p*-toluenesulfonate

concurrent with formation of acetolysis product would keep the toluenesulfonate I within the I classification. The phenomenon analogous to the one accompanying solvolysis of *exo*-norbornyl *p*-bromobenzenesulfonate<sup>2</sup> would, in the case of IA, also give rise to a racemization rate ( $k_\alpha$ ) in excess of a titrimetric solvolysis rate ( $k_t$ ).



Polarimetric acetolysis rate constants determined at 50° or 75° indeed exceeded the previously determined titrimetric rate constants.<sup>3</sup> Table I lists the previously determined titrimetric rate constants,  $k_t$ , in acetic acid at a concentration of *ca.* 0.03 *M* and also titrimetric constants determined at the higher concentration (*ca.* 0.1 *M*) necessary for the polarimetric work. The agreement is good. Table II shows the good first order behavior of the data in a typical titrimetric run. Table I also

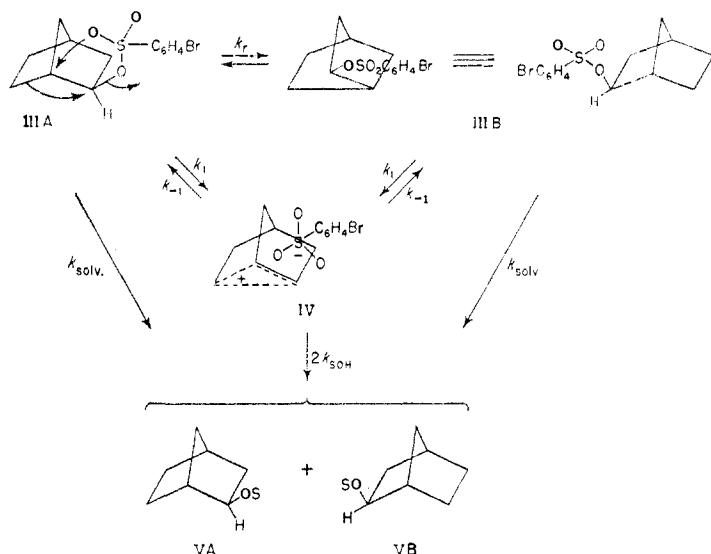
(1) Research supported by the Office of Naval Research.

(2) Winstein and Trifan, *THIS JOURNAL*, **74**, 1154 (1952).

(3) Winstein, *et al.*, *ibid.*, **74**, 1113 (1952).

(4) (a) Cram, *ibid.*, **71**, 3883 (1949); (b) Cram, *ibid.*, **71**, 3883 (1949).

(5) Winstein, Schreiber, Brown and Schlesinger, *ibid.*, **74**, 1140 (1952).



lists the first-order polarimetric rate constants,  $k_\alpha$ , calculated from equation (1), where  $t$  is the time and  $\alpha_0$ ,  $\alpha_\infty$  and  $\alpha$  are observed rotations at the

$$2.303 \log \frac{\alpha_0 - \alpha_\infty}{\alpha - \alpha_\infty} = k_\alpha t \quad (1)$$

commencement of observation, finally, and at the time  $t$ , respectively. Considering the small magnitude of the observed rotations in the polarimetric rate runs, very good adherence to first-order kinetics was observed. Figure 1 illustrates the straight line plots of  $\log [(\alpha_0 - \alpha_\infty)/(\alpha - \alpha_\infty)]$  vs.  $t$  for several runs.

Both polarimetric and titrimetric first-order rate constants for ethanolsysis of 3-phenyl-2-butyl *p*-toluenesulfonate were steady (Table I, Fig. 1), the ratio of  $k_\alpha/k_t$  (Table III) being 2.05 at  $74.91^\circ$ , lower than in the case of *exo*-norbornyl *p*-bromobenzenesulfonate. While the observed final rotation was zero in the polarimetric ethanolsysis, the necessary information on the rotations of the corresponding ethers is not available to decide to what extent simple inversion plays a part in the ethanolsysis.

In formolysis of 3-phenyl-2-butyl *p*-toluenesulfonate, the gap between  $k_\alpha$  and  $k_t$  is much reduced (Table I), but a definite difference remains between them, the ratio  $k_\alpha/k_t$  being 1.18 (Table III).

The available values of  $k_\alpha$  and  $k_t$  give the first order rate constants ( $k_\alpha - k_t$ ) of racemization of IA in excess of the rate of loss of activity due to solvolysis, and it is interesting to compare the calculated extents of racemization of still unsolvolyzed IA with the degree of racemization of IA recovered from partial acetolysis and formolysis by Cram.<sup>6</sup> This comparison is shown in Table V where the values of  $[\alpha]$  observed by Cram<sup>6</sup> are compared with the values calculated from equation (2). For these calculations,  $k_\alpha$  and  $k_t$  in AcOH, 0.228 *M* in sodium acetate

$$\ln [\alpha_0/\alpha] = (k_\alpha - k_t)t \quad (2)$$

were not available, the values at 0.1155 *M* NaOAc being employed. In formic acid,  $k_\alpha$  and  $k_t$  values

TABLE I

RATE CONSTANTS FOR SOLVOLYSIS OF 3-PHENYL-2-BUTYL *p*-TOLUENESULFONATE (IA)

Solvent	$t$ , °C.	Concn. ROTs mole/liter	Added salt	Proc.	Rotations, $\alpha^\circ$		$k$ , sec. <sup>-1</sup>
					Initial	Final	
EtOH <sup>a</sup>	74.92	0.02086	.....	Tit.	.....	.....	$(2.97 \pm 0.07) \times 10^{-5}$
EtOH <sup>a</sup>	74.91	.1239	.....	Pol.	-0.765	0.00	$(6.08 \pm 0.07) \times 10^{-5}$
HOAc <sup>4</sup>	49.60	.035	.....	Tit.	.....	.....	$2.38 \times 10^{-5}$
HOAc	49.61	.1048	.....	Tit.	.....	.....	$(2.42 \pm 0.04) \times 10^{-5}$
HOAc	49.61	.1048	.....	Pol.	.58	.00	$(1.11 \pm 0.07) \times 10^{-5}$
HOAc	49.61	.09572	0.30 <i>M</i> H <sub>2</sub> O	Tit.	.....	.....	$(4.01 \pm 0.06) \times 10^{-5}$
HOAc	49.61	.09572	.30 <i>M</i> H <sub>2</sub> O	Pol.	.53	.00	$(1.80 \pm 0.10) \times 10^{-5}$
HOAc <sup>4</sup>	74.71	.030	.....	Tit.	.....	.....	$4.95 \times 10^{-5}$
HOAc	74.91	.1089	.....	Tit.	.....	.....	$(5.15 \pm 0.07) \times 10^{-5}$
HOAc	74.91	.1089	.....	Pol.	.59	.00	$(2.27 \pm 0.10) \times 10^{-4}$
HOAc	74.86	.1156	.....	Pol.	.53	.00	$(2.25 \pm 0.10) \times 10^{-4}$
HOAc	74.91	.09566	.1155 <i>M</i> NaOAc	Tit.	.....	.....	$(6.72 \pm 0.16) \times 10^{-5}$
HOAc	74.91	.09566	.1155 <i>M</i> NaOAc	Pol.	.53	-.01	$(3.33 \pm 0.10) \times 10^{-4}$
HOAc	74.91	.08570	.0860 <i>M</i> NaOTs	Tit.	.....	.....	$(5.20 \pm 0.10) \times 10^{-5}$
HOAc	74.91	.08570	.0860 <i>M</i> NaOTs	Pol.	.45	.00	$(2.52 \pm 0.05) \times 10^{-4}$
HCOOH	24.98	.06960	.....	Tit.	.....	.....	$(2.28 \pm 0.03) \times 10^{-4}$
HCOOH	24.95	.06962	.....	Tit.	.....	.....	$(2.19 \pm 0.05) \times 10^{-4}$
HCOOH	25.40	.1052	.....	Pol.	.86	-.01	$(2.85 \pm 0.18) \times 10^{-4}$
HCOOH	25.12	.1161	.....	Pol.	3.92 <sup>b</sup>	-.04 <sup>b</sup>	$(2.65 \pm 0.12) \times 10^{-4}$

<sup>a</sup> Enantiomorph IB was used in these runs. <sup>b</sup> Measured in a 4-dcm. polarimeter tube.

The ratios of the  $k_\alpha/k_t$  from the data of Table I are summarized in Table III, which makes it clear that for acetolysis, the ratio of polarimetric to titrimetric rate constants is ca. 4.5–5.0 under the various conditions. This is somewhat larger than the ratio of 3.46 in the case of acetolysis of *exo*-norbornyl *p*-bromobenzenesulfonate<sup>2</sup> listed in Table IV.

from Table I were employed for lack of any values in solution containing added sodium formate. Considering the approximations involved, the small magnitude of the observed reading in the case of recovered toluenesulfonate from acetic acid, and the danger of further fractionation in working up the recovered ROTs, the agreement between cal-

(6) Cram, THIS JOURNAL, 74, 2129 (1952).

TABLE II

TITRIMETRIC ACETOLYSIS RATE OF 0.1089 *M* 3-PHENYL-2-BUTYL *p*-TOLUENESULFONATE AT 74.91°

Time, sec.	Ml. of 0.0451 <i>M</i> NaOAc	$10^4 k$ (sec. <sup>-1</sup> )
0	0.099	..
1050	0.348	5.18
3660	0.802	5.07
6000	1.273	5.22
10560	1.986	5.15
15720	2.617	5.12
22380	3.112	5.07
32160	3.848	5.21
∞	4.833	..

Mean  $5.15 \pm 0.06$ 

TABLE III

TREATMENT OF DATA FOR 3-PHENYL-2-BUTYL *p*-TOLUENESULFONATE

Solvent	<i>t</i> , °C.	$k_a/k_t$	$10^4 k_t$	$k_{-1}/k_{SOH}$
EtOH	74.91	2.05	1.55	1.05
HOAc	49.61	4.59	0.435	3.59
HOAc(H <sub>2</sub> O)	49.61	4.49	0.70	3.49
HOAc	74.91	4.41	8.7	3.41
HOAc(NaOAc)	74.91	4.96	13	3.96
HOAc(NaOTs)	74.91	4.85	10	3.85
HCOOH	25.0	1.18	1.9	0.18

TABLE IV

TREATMENT OF SOLVOLYSIS DATA FOR *exo*-NORBORNYL *p*-BROMOBENZENESULFONATE<sup>2</sup> AT 25°

Solvent	EtOH	AcOH	75% acetone
$k_a/k_t$	2.94	3.46	1.40
$10^4 k_{solv.}$	0.266	1.22	5.41
$10^4 k_r$	0.259	1.52	1.08
$10^4 k_l$	0.783	4.25	7.56
$k_{-1}/k_{SOH}$	1.94	2.46	0.40

TABLE V

COMPARISON OF OBSERVED<sup>6</sup> AND CALCULATED ROTATIONS OF IA RECOVERED FROM SOLVOLYSIS OF 0.164 *M* SOLUTION, 0.228 *M* IN BASE

Solvent	Time, min.	obsd. $[\alpha]$	calcd.
AcOH 75°	200	1.09	0.70
HCOOH 25°	43	13.9	14.7

culated and observed rotations is very satisfactory.

The racemization of the toluenesulfonate IA during solvolysis means that the fraction  $(1 - k_t/k_a)$  of the complete solvolysis product arises from already racemized toluenesulfonate, as derived previously.<sup>2</sup> This fraction amounts to 0.798 in acetic acid and 0.15 in formic acid. Thus only 20.2% of the solvolysis product in acetic acid arises from active starting material. Nevertheless this is sufficient to indicate the high degree of control of the stereochemical outcome of solvolysis by phenyl group participation.<sup>4,5,6</sup> Phenyl participation here competes very much better with solvent participation than in the case of benzylmethylcarbinyl *p*-toluenesulfonate,<sup>5</sup> where it is necessary to go to formic acid before retention of configuration is clearly dominant. The most recent results of Cram<sup>6</sup> on acetolysis of 3-phenyl-2-butyl *p*-toluenesulfonate indicate that acetolysis of I (or toluenesulfonate II<sup>4</sup>) gives a solvolysis product con-

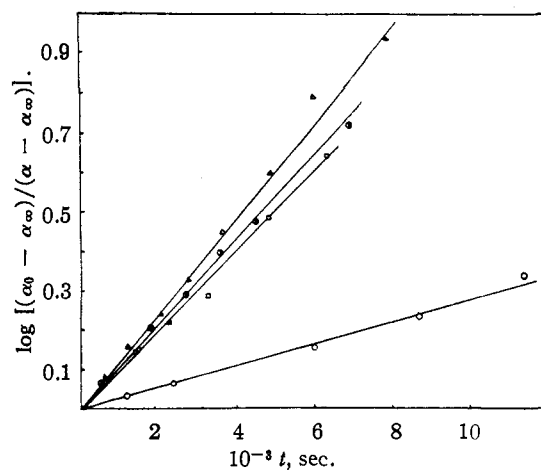
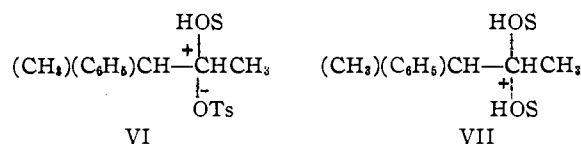
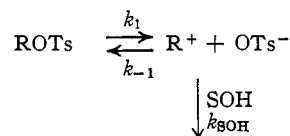


Fig. 1.—Polarimetric observation of solvolysis of 3-phenyl-2-butyl *p*-toluenesulfonate: O, EtOH, 75°; □, AcOH, 75°; ●, AcOH, 0.0860 *M* NaOTs, 75°; △, HCOOH, 25°.

taining 4–5% of material with the other diastereomeric configuration. Further, the optical activity of the solvolysis product from IA, multiplied by the factor  $k_a/k_t$  or  $1/0.202$  indicates a 3% content of enantiomorph IA. Thus the stereochemical result of acetolysis of IA to 3-phenyl-2-butyl acetate is largely racemization, with *ca.* 5% inversion and 3% retention. While other possibilities remain, it is perhaps simplest to ascribe the bulk of the 5% inversion and the 3% retention to ordinary solvent participation by way of the successive intermediates<sup>7</sup> VI and VII.



**Interpretation of Excess Racemization.**—In considering the nature of the process responsible for the excess racemization rate, measured by  $k_a - k_t$ , it is easily seen that it does not involve external *p*-toluenesulfonate ion. One possible way external *p*-toluenesulfonate ion, OTs<sup>-</sup>, could be responsible for this phenomenon is by the “mass-law effect”<sup>8</sup> or “external return.”<sup>7,9</sup> In this scheme, the



starting *p*-toluenesulfonate, ROTs, proceeds with a first order rate constant  $k_1$  to an intermediate R<sup>+</sup>, which is returnable to ROTs. The intermediate R<sup>+</sup>, which is actually or effectively internally compensated, reacts either with OTs<sup>-</sup> (rate constant  $k_{-1}$ ) to give racemic ROTs or with solvent, SOH (rate constant  $k_{SOH}$ ), either directly or after a prior unimolecular change, to give substitution or elimination products.

(7) Winstein, Grunwald and Jones, *THIS JOURNAL*, **73**, 2700 (1951).(8) Bateman, Church, Hughes, Ingold and Taher, *J. Chem. Soc.*, 979 (1940).(9) Young, Winstein and Goering, *THIS JOURNAL*, **73**, 1958 (1951).

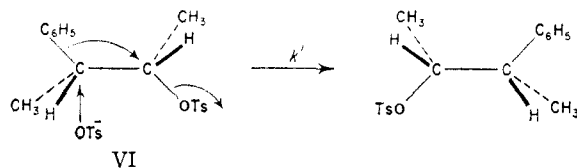
In such a scheme, involving external return, the instantaneous value of  $k_t$  is given by equation (3), where  $(\text{OTs}^-)$  is the *p*-toluenesulfonate ion concentration.<sup>10</sup>

Except for salt effects on the individual constants,  $k_\alpha$  would be insensitive to  $(\text{OTs}^-)$  ( $k_\alpha = k_t$ ). On the other hand,  $k_t$  would commence at a value equal to  $k_\alpha$

$$k_t = k_\alpha \frac{1}{1 + (k_{-1}/k_{\text{SOH}})(\text{OTs}^-)} \quad (3)$$

and decrease as  $(\text{OTs}^-)$  increases. This is certainly not in accord with the behavior of the solvolysis kinetics of 3-phenyl-2-butyl *p*-toluenesulfonate (IA) or *exo*-norbornyl *p*-bromobenzenesulfonate<sup>2</sup> (IIIA). The titrimetric rate constant begins much lower than  $k_\alpha$ , and shows no large drop in the early part of the titrimetric run as  $(\text{OTs}^-)$  is changing by large factors. The effect of added original  $\text{OTs}^-$  would be to greatly depress  $k_t$  but not  $k_\alpha$ . Further, addition of water or acetate ion to an acetic acid solvent would provide competitors of  $\text{OTs}^-$  for  $\text{R}^+$  and should tend to close the gap between  $k_\alpha$  and  $k_t$ . Actually, from the data in Tables I and III, addition of 0.30 *M* water at 50° leaves  $k_\alpha/k_t$  unchanged, although both  $k_\alpha$  and  $k_t$  are increased *ca.* 60%. Similarly, addition at 75° of 0.1155 *M* sodium acetate changes  $k_\alpha/k_t$  only little, if anything raising it slightly from 4.41 to 4.96. Similarly, 0.0860 *M* sodium *p*-toluenesulfonate gives about the same ratio of  $k_\alpha/k_t$  (4.85) as does sodium acetate. Certainly, return of an intermediate by external  $\text{OTs}^-$  is not appreciable under the range of conditions scrutinized.

Another possible way external  $\text{OTs}^-$  could be responsible for the gap between  $k_\alpha$  and  $k_t$  would be if it were involved in an  $\text{S}_{\text{N}}2'$  displacement<sup>3</sup> as symbolized in VI.

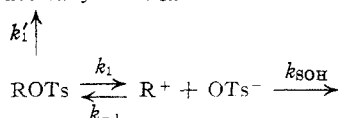


With  $k'$  the rate constant of formation of mirror image from IA by attack of  $\text{OTs}^-$ ,  $k_t$  would be insensitive to  $(\text{OTs}^-)$ , while  $k_\alpha$  would be given by equation (4). Thus

$$k_\alpha = k_t + 2k'(\text{OTs}^-) \quad (4)$$

it would begin, in a run, equal to  $k_t$  and climb. Also, added  $\text{OTs}^-$  should increase  $k_\alpha$  sharply. None of this behavior is observed. In a run where the half-life of racemization is *ca.* one-fifth of that of titrimetric solvolysis, and thus where most of the racemization occurs while  $\text{OTs}^-$  is building up to a fraction of its final value, the polarimetric rate

(10) The actual situation could be more complex, such as intermediates or products non-returnable to structurally identical ROTs



The simpler scheme suffices to make the required point that external  $\text{OTs}^-$  is not responsible.

constant is steady. Also, added  $\text{OTs}^-$  does not cause the enormous increase in  $k_\alpha$  to be expected on this basis.

Other conceivable formulations of the internal rearrangement involving toluenesulfonic or bromobenzenesulfonic acids or the combined action of  $\text{OTs}^-$  ( $\text{OBS}^-$ ) with either  $\text{AcOH}_2^+$  or  $\text{HOTs}$  ( $\text{HOBs}$ ) may also be eliminated on the basis of the kinetic evidence.

The available data both on 3-phenyl-2-butyl *p*-toluenesulfonate (IA) and on *exo*-norbornyl *p*-bromobenzenesulfonate (IIIA) then require an intramolecular interpretation of the  $k_\alpha/k_t$  ratio.

In considering the manner in which *exo*-norbornyl *p*-bromobenzenesulfonate (IIIA) and 3-phenyl-2-butyl *p*-toluenesulfonate (IA) undergo internal racemization, we may first consider an  $\text{S}_{\text{N}}1'$  type<sup>3</sup> internal cyclic rearrangement of IIIA to IIIB or IA to IB. This concerted double migration of arylsulfonate group and ring member in IIIA or phenyl group in IA represents conversion to the mirror image and thus racemization. If  $k_r$  is the specific rate constant of this process and  $k_{\text{sol}}$  is the rate constant for formation of products of solvolysis and elimination, then, for this interpretation,  $k_t$  would be equal to  $k_{\text{sol}}$  and  $k_r$  would be given by equation (5).

$$k_r = (k_\alpha - k_t)/2 \quad (5)$$

The values of  $k_r$  on this basis, calculated from the available data, are listed in Table III for 3-phenyl-2-butyl *p*-toluenesulfonate and in Table IV for *exo*-norbornyl *p*-bromobenzenesulfonate. In the case of 3-phenyl-2-butyl *p*-toluenesulfonate IA, sufficient data are available in acetolysis for comparison of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  for the presumed  $\text{S}_{\text{N}}1'$  process with the values calculated directly from the variation of  $k_t$  and  $k_\alpha$  with temperature. This comparison is shown in Table VI,  $\Delta H^\ddagger$  being closely similar ( $26.0 \pm 0.2$  kcal./mole), and  $\Delta S^\ddagger$  also ( $-2.4 \pm 0.9$  e.u.), whether calculated from  $k_t$ ,  $k_\alpha$  or  $k_r$ .

TABLE VI  
 $\Delta H^\ddagger$  AND  $\Delta S^\ddagger$  FOR REACTIONS OF IA IN AcOH

	$\Delta H^\ddagger$ , kcal./mole	$\Delta S^\ddagger$ , e.u.
From $k_t$	26.3	-2.9
From $k_\alpha$	25.9	-1.1
From $k_r$	25.8	-3.2

With variation of solvent,  $k_r$  shows a dependence on solvent similar to that of  $k_t$ . Comparing values in ethanol and acetic acid at 75° and values in acetic acid and formic acid at 25°,  $k_t$  shows the sequence: HCOOH, 3900; AcOH, 1.7; EtOH, 1. The sequence for  $k_r$  is: HCOOH, 740; AcOH, 5.6; EtOH, 1. Thus, logarithmically,  $k_r$  is seven- or eight-tenths as sensitive as  $k_t$  to ionizing power of solvent.

While a reaction proceeding by a cyclic mechanism may, of course, show a certain amount of sensitivity to medium changes due to increased polarity in the transition state, little is known regarding the magnitude of such effects in typical cases. In the present case,  $k_r$  shows a dependence on ionizing power so close to that of  $k_t$  as to question the existence of a path for  $k_r$  completely independent of the one for  $k_t$ . This suggests a common rate-deter-

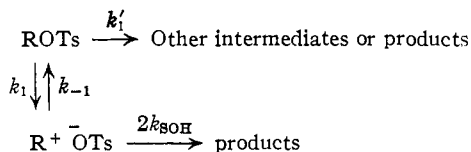
mining step for the over-all processes designated by  $k_r$  and  $k_t$ .

The common rate-determining step can be formulated as the ionization of IA to the ion-pair II (or of IIIA to IV) with a rate constant  $k_1$ . The "internal return" of this ion-pair either to initial or enantiomeric arylsulfonate (rate constant  $k_{-1}$  for each) or further separation of the ion pair with formation of solvolysis products (rate constant  $2k_{SOH}$ ) will give  $k_\alpha/k_t$  ratios greater than unity. On this basis  $k_1$  is equal to  $k_\alpha$  and the ratio of  $k_{-1}$  to  $k_{SOH}$  is given by equation (6).

$$k_{-1}/k_{SOH} = (k_\alpha/k_t) - 1 \quad (6)$$

The value of the ratio  $k_{-1}/k_{SOH}$  in the several solvents is given in Table IV for *exo*-norbornyl *p*-bromobenzenesulfonate IIIA and in Table III for 3-phenyl-2-butyl *p*-toluenesulfonate IA. In these terms, the reduction in  $k_\alpha/k_t$  due to a change from acetic acid solvent to 75% acetone or formic acid is due to a decrease in  $k_{-1}/k_{SOH}$ . This value for IIIA drops from 2.46 in acetic acid to 0.40 in 75% acetone, while for IA it drops from *ca.* 3.5 in acetic acid to 0.18 in formic acid.

The above scheme is oversimplified and should be expanded to



The rate constant  $k'_1$  sums up first order rate constants of reactions which are included in  $k_t$  and which do not proceed through materials which return to structurally identical ROTs. In this formulation,  $k_\alpha$ ,  $k_t$  and  $k_{-1}/k_{SOH}$  are given by equations 7, 8 and 9.  $k_{-1}/k_{SOH}$  from equation 9 differs from the value from equation 6 to the extent  $k'_1$  differs from zero. We can, however, use the values of  $k_{-1}/k_{SOH}$  from equation 6 for some of the discussion.

The general kind of decrease in the ratio  $k_{-1}/k_{SOH}$  with ionizing power of the solvent displayed by the values calculated from equation 6 and given in Tables III and IV is at least consistent with a

$$k_\alpha = k'_1 + k_1 \quad (7)$$

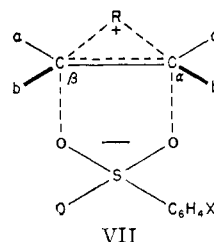
$$k_t = k'_1 + k_1 \frac{1}{1 + (k_{-1}/k_{SOH})} \quad (8)$$

$$k_{-1}/k_{SOH} = \frac{k_\alpha - k_t}{k_t - k'_1} \quad (9)$$

scheme involving internal return. The rate constant  $k_{-1}$ , being related to a reaction which makes a neutral molecule from an ion pair, will decrease<sup>8</sup> with increasing ionizing power of the solvent. The effect of solvent variation on  $k_{SOH}$  is not as easy to understand. The rate constant or sum of rate constants,  $k_{SOH}$ , is associated almost exclusively with formation of solvolysis product in the case of *exo*-norbornyl *p*-bromobenzenesulfonate (III)<sup>2</sup> and, at least very substantially with formation of solvolysis product in the case of 3-phenyl-2-butyl *p*-toluenesulfonate (I).<sup>4,6</sup> This formation of solvolysis product presumably requires the replacement of the bromobenzenesulfonate or *p*-toluenesulfonate ion part of the ion-pair II or IV by solvent

to give a new solvated cationic species which eventually results in solvolysis product. If this process can be treated pretty much as the separation of an ion pair,  $k_{SOH}$  will be predicted to increase with ionizing power of the solvent, based on the suggestion of Professor J. G. Kirkwood to one of us (S.W.) that free energy of activation will be affected by solvent changes like free energy of dissociation of ion-pairs. Thus  $k_{-1}/k_{SOH}$  would decrease as ionizing power increased.

However, it is not clear to what extent geometrical factors and others, such as nucleophilic character of the solvent, would play a part in the removal of the anionic part of the ion-pairs II and IV. As pointed out previously,<sup>7</sup> the first intermediate in solvolysis may have appreciable covalent character to linkages to a solvent molecule and to the leaving group. In the formulated bridged cation-arylsulfonate ion-pairs II and IV, there may be appreciable covalent character to the cation-anion interaction, depending on the geometry of the cationic portion. If the hybridization of orbitals on  $C_\alpha$  and  $C_\beta$  were such as to leave the  $\begin{array}{c} a \\ \diagdown \\ C \\ \diagup \\ b \end{array} - \begin{array}{c} a \\ \diagup \\ C \\ \diagdown \\ b \end{array}$  skeleton planar<sup>11</sup> as shown in VII, this appears the most favorable to covalent character to the cation-anion interaction (VII). If



the general geometry of the  $\begin{array}{c} a \\ \diagdown \\ C \\ \diagup \\ b \end{array} - \begin{array}{c} a \\ \diagup \\ C \\ \diagdown \\ b \end{array}$  skeleton is similar to that in cyclopropane<sup>12</sup> or ethylene oxide,<sup>13</sup> this would be less favorable to covalent character to the cation-anion interaction.<sup>14</sup>

The range of solvent, over which the internal rearrangement of I and III has been studied, is still too meager to make any generalizations with regard to the effect of solvent on  $k_{-1}/k_{SOH}$  and we hope to contribute on this point later. Both for I and III,  $k_{-1}/k_{SOH}$  is smaller in ethanol than in acetic acid, but it is not clear how much of this is due to back-side intervention of ethanol.

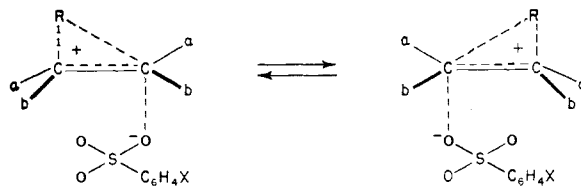
While more work is proceeding on the phenomenon of internal rearrangement and its inter-

(11) *E.g.*, (a) Dewar, *J. Chem. Soc.*, 406 (1946); (b) Dewar, *Faraday Soc. Disc.*, 2, 50 (1947).

(12) (a) Coulson and Moffitt, *Philosophical Mag.*, 40, 1 (1949) (b) Walsh, *Trans. Faraday Soc.*, 45, 179 (1949).

(13) L. L. Ingraham, Ph.D. Thesis, U.C.L.A., 1949.

(14) It must be noted that, in the kinetic arguments, II, IV or VII may be replaced by a dynamic mixture of two unsymmetrical species.



pretation, the available evidence somewhat favors the interpretation involving internal return<sup>7,9</sup> of the ion-pairs II and IV in the case of IA and IIIA, respectively. If the interpretation proves valid, then cases such as IA and IIIA with 2 carbon atom reaction centers represent a special device for the study of internal return,<sup>7,9</sup> which in cases with one reactive carbon atom center are usually not discernible.

**Internal Rearrangements.**—Internal rearrangements are apparently going to be of general importance in a number of connections. The observation of internal rearrangement in connection with solvolysis of IA and IIIA recalls the related isomerization of  $\alpha,\alpha$ -dimethylallyl chloride to  $\gamma,\gamma$ -dimethylallyl chloride which occurs in acetolysis.<sup>9</sup> While "internal rearrangements" may be quite common in the allylic field, one finds in very few of the available possible<sup>15</sup> examples any convincing evidence that this type of mechanism contributes.<sup>16</sup> A case where intramolecular rearrangement does appear to play a part is the dilute acid-catalyzed rearrangement-hydrolysis of propenylethynylcarbonyl acetate. Here, rearrangement is actually more rapid than hydrolysis at temperatures above 80°, the indications being strong that intramolecular rearrangement is a factor.<sup>17</sup>

In the Wagner-Meerwein rearrangement, internal rearrangement is apparently fairly widespread. In addition to the cases of IA and IIIA, unsymmetrically substituted systems are considered in the following article.<sup>18</sup> Whether internal rearrangement plays any role in the classical case of rearrangement of camphene hydrochloride to isobornyl chloride requires investigation. Some contribution of this internal rearrangement in many of the solvents investigated is still compatible with the available facts.<sup>19</sup> In solvolyzing solvents like ethanol-methanol, internal rearrangement of camphene hydrochloride to isobornyl chloride competes little, if at all, with solvolysis, judging by the work of Meerwein and van Emster.<sup>20</sup> In alkaline alcoholic solution camphene hydrochloride samples gave analyses up to 90–93% camphene hydrochloride. The development of isobornyl chloride during solvolysis of camphene hydrochloride would, of course, contribute to a low analysis under Meerwein and van Emster's conditions.

Internal phenomena may prove to be important in pinacol type rearrangements as well. In this class of rearrangement is included the one illustrated by



(15) (a) Hughes, *Trans. Faraday Soc.*, **34**, 185 (1938); (b) Young, Nozaki and Warner, *THIS JOURNAL*, **61**, 2564 (1939); (c) Baife and Kenyon, *Trans. Faraday Soc.*, **37**, 721 (1941); (d) Braude, *Quart. Reviews*, **4**, 404 (1950).

(16) Catchpole, Hughes and Ingold, *J. Chem. Soc.*, 8 (1948).

(17) Braude, *ibid.*, 794 (1948).

(18) Winstein and Schreiber, *THIS JOURNAL*, **74**, 2171 (1952).

(19) Nevell, de Salas and Wilson, *J. Chem. Soc.*, 1188 (1939).

(20) Meerwein and van Emster, *Ber.*, **55**, 2500 (1922).

(21) Meerwein and Wortman, *Ann.*, **435**, 190 (1924).

The internal phenomenon is, of course, possible with neighboring functional groups. Thus, in the case of mutarotation-solvolysis of  $\Delta^5$ -cholestene dibromide, in 1:1  $\text{CHCl}_3$ :AcOH for example, involving bromine both as a neighboring and a leaving group, Dr. C. A. Grob<sup>22</sup> has shown that mutarotation is faster than solvolysis, and does not involve external bromide ion.

**Reactivity Considerations.**—The rate data reported here permit more comparison of the ratio of reactivities in solvolysis of 3-phenyl-2-butyl toluenesulfonate to that of the 2-butyl ester. The ratio of rates, using  $k_t$  for 3-phenyl-2-butyl, which was 1:1.8 in AcOH<sup>3</sup> at 50° (and which extrapolates to 1:2.5 at 25°) becomes 4.4:1 in HCOOH at 25°. If internal return is not a factor with 2-butyl, the use of  $k_\alpha$  for 3-phenyl-2-butyl would give a more reliable comparison. Using  $k_\alpha$ , the ratio of reactivities is 1.9 in AcOH at 25° and 5.2 in HCOOH at 25°. Thus the change from acetic to formic acid introduces a gain in relative reactivity of 3-phenyl-2-butyl compared to 2-butyl, probably, in part at least, due to the more limiting<sup>7</sup> character of the solvolysis of the latter in formic acid.

The relative solvolysis rates of 3-phenyl-2-butyl and benzylmethylcarbonyl *p*-toluenesulfonates were 4.0:1 in AcOH at 50° (*ca.* 5:1 at 25°) and 16:1 in HCOOH at 25°. Using  $k_\alpha$  for 3-phenyl-2-butyl may or may not give a better estimate of the reactivity ratio, depending on whether there is internal return in the case of benzylmethylcarbonyl *p*-toluenesulfonate<sup>18</sup>; this gives the ratio of *ca.* 20:1 both in AcOH and HCOOH. At any rate the effect of a  $\beta$ -methyl group is to enhance rate by a factor of *ca.* 20 in formic acid as a solvent.

## Experimental

3-Phenyl-2-butyl *p*-toluenesulfonate (IA) was kindly furnished by Dr. Donald Cram of these laboratories.

**Kinetic Measurements.**—Solvents, acetic acid<sup>23</sup> containing a trace of acetic anhydride, absolute ethanol<sup>3</sup> and formic acid<sup>24</sup> were prepared as previously described. The formic acid contained 0.08% water as determined by Karl Fischer titration. Sodium acetate solutions in acetic acid were prepared from sodium carbonate, while sodium toluenesulfonate solutions were prepared from solutions of sodium acetate and *p*-toluenesulfonic acid. In each case, acetic anhydride equivalent to the water produced in reaction was added. The solution of 0.30 *M* water (0.55%) in acetic acid was analyzed by Karl Fischer titration.

For the kinetic runs, the procedure was the usual one for the titrimetric rates.<sup>23,3,24</sup> For the polarimetric rates at 50° and 75°, the ampoule technique used with *endo*-norbornyl *p*-toluenesulfonate<sup>25</sup> was employed, a 1-dm. tube being used for the polarimeter readings. For the polarimetric rates in formic acid at 25°, the 4-dm. jacketed tube<sup>2</sup> was used.

Solvolysis was followed to 70–95% completion. Good first order behavior was observed in all runs, the mean deviation in the constants obtained from the integrated first order expression being shown in Table I.

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(22) C. A. Grob, unpublished work.

(23) Winstein, Grunwald and Ingraham, *THIS JOURNAL*, **70**, 821 (1948).

(24) Winstein and Marshall, *ibid.*, **74**, 1120 (1952).

(25) Winstein and Trifan, *ibid.*, **74**, 1147 (1952).