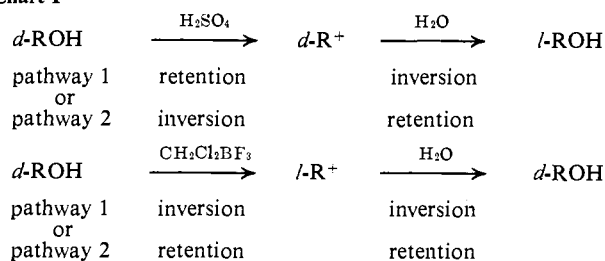


**Table II.** Stereochemistry of Formation and Capture of Phenylbiphenyl-1-(8-methylnaphthyl)carbonium Ion

Reagent	Initial [ $\alpha$ ]D, deg	Final [ $\alpha$ ]D, deg	Net optical <sup>a</sup> yield, %
H <sub>2</sub> SO <sub>4</sub>	-76	+58	77 inv
	+76	-69	91 inv
	-69	+58	84 inv
CH <sub>2</sub> Cl <sub>2</sub> -BF <sub>3</sub> Et <sub>2</sub> O	-24	+20	84 inv
	+74	+50	68 ret
	-23	-15	66 ret

<sup>a</sup> Difference from 100% is % racemic material.

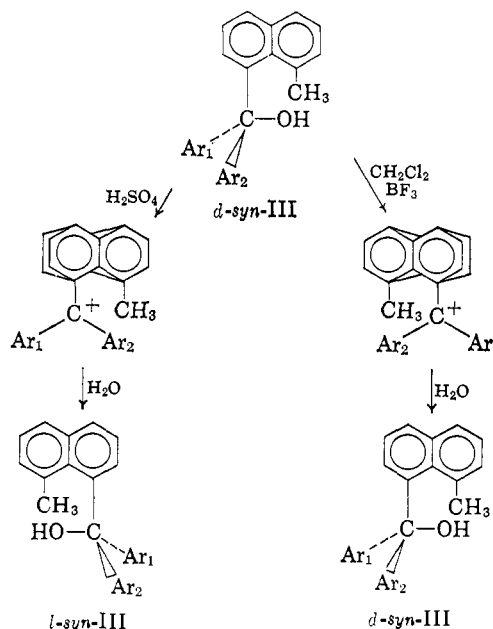
The stereochemical outcome was different when *d*-III was ionized in methylene chloride-boron trifluoride ether and quenched.<sup>8</sup> The recovered alcohol had [ $\alpha$ ]D +50° corresponding to 68% net retention (Table II). The methylene chloride solution showed no detectable rotation. However, a sulfuric acid solution obtained by extraction of the methylene chloride solution showed [ $\alpha$ ]<sub>365</sub> -1120°. The same result was achieved when the methylene chloride was removed *in vacuo* and the residue was dissolved in sulfuric acid. The results establish: (1) removal of water from ROH<sub>2</sub><sup>+</sup> in sulfuric acid has the opposite stereochemistry from R<sup>+</sup> capture by water in quenching; (2) naphthyl group rotation (inversion) through the plane of the central carbon and the two attached aryl groups must accompany *either* ionization in sulfuric acid *or* capture by water in quenching; (3) ionization in sulfuric acid has the opposite stereochemistry from ionization in methylene chloride; and (4) water capture of carbonium bisulfate and fluoroborate has the same stereochemistry. The allowed stereochemical pathways are summarized in Chart I. If

**Chart I**

pathway 1 is followed in sulfuric acid, pathway 1 must be followed in methylene chloride.

Our current working hypothesis is that pathway 1 is followed in sulfuric acid and methylene chloride (Chart II). Alcohol ionization is exothermic in sulfuric acid but endothermic in dilute acid (the reverse of quenching). Hammond's postulate<sup>9</sup> allows that the ionization transition state in sulfuric acid is more like the protonated alcohol (less cation character) than the transition state for quenching (more cation character). This reasoning suggests that water would attack the cation from the least hindered face (*anti* to methyl). Inversion of the naphthyl group occurs subsequently, affording the presumably more stable *syn*-III (Fisher-Hirschfelder models). Ionization in sulfuric acid involves loss of water from *syn*-III *without* naphthyl group inversion. Naphthyl group inversion accompanying ionization in methylene chloride may be forced by the steric requirements of the leaving group. Experiments

(9) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

**Chart II**

are in progress to further specify the mechanistic details of these intriguing transformations.

There is a parallel between the ionizations of III in sulfuric acid and methylene chloride-boron trifluoride and the ionizations of *cis*-7,8-dichlorocyclooctatriene-1,3,5 in fluorosulfonic and in methylene chloride-antimony pentafluoride.<sup>10</sup>

(10) R. Huisgen, C. Boche, and H. Huber, *ibid.*, **89**, 3345 (1967).

(11) This work was supported by National Science Foundation Grants GP 3537 and GP 6406.

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### Tosylate Oxygen Scrambling Associated with Ion-Pair Return<sup>1</sup>

Sir:

The relationship between structure and rates of ionization is of considerable importance in mechanistic investigations of carbonium ion processes. Unfortunately, in most cases, ionization rates cannot be determined from rates of solvolysis because the amount of ion-pair return is unknown.

In earlier investigations<sup>2,3</sup> it was found that ion-pair return associated with solvolysis of carboxylic esters results in randomization of the carboxyl oxygen atoms. Thus oxygen equilibration of <sup>18</sup>O-labeled esters (eq 1) is a method for measuring re-formation of substrate by ion-pair return.<sup>3</sup> A unique feature of this method is that it is applicable in systems in which the alkyl group does not racemize or rearrange; however, it is limited to reactive systems that undergo alkyl-oxygen cleavage

(1) This research was supported by the Air Force Office of Scientific Research (AFOSR-847-67) and the National Institutes of Health (G.M. 14134); presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Abstract S38.

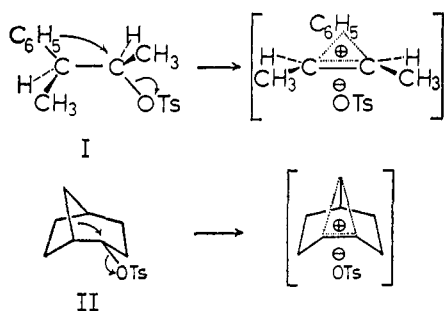
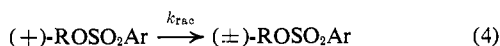
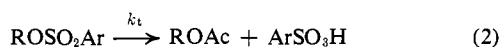
(2) (a) H. L. Goering, R. G. Briody, and J. F. Levy, *J. Am. Chem. Soc.*, **85**, 3059 (1963); (b) H. L. Goering and S. Chang, *Tetrahedron Letters*, 3607 (1965); (c) H. L. Goering and J. F. Levy, *J. Am. Chem. Soc.*, **84**, 3853 (1962); (d) A. F. Diaz and S. Winstein, *ibid.*, **88**, 1318 (1966).

(3) H. L. Goering, J. T. Doi, and K. D. McMichael, *ibid.*, **86**, 1951 (1964).

(e.g., benzhydryl,<sup>2a,d</sup> allylic,<sup>3</sup>  $\alpha$ -arylethyl,<sup>4</sup> and 2-phenyl-2-butyl<sup>2b</sup> *p*-nitrobenzoates).



We have now extended our studies to alkyl *p*-toluenesulfonates to determine to what extent ion-pair return results in scrambling of the sulfonate oxygen atoms. Sulfonate oxygen equilibration has been observed in the 1-aryl-2-propyl system.<sup>5</sup> However, equilibration was not correlated with an independent measure of ion-pair return. In our work we have compared rates of oxygen equilibration ( $k_{eq}$ , eq 3) and racemization ( $k_{rac}$ , eq 4) of the unsolvolyzed ester for acetolysis of *threo*-3-phenyl-2-butyl *p*-toluenesulfonate (I) and *endo*-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate (II). Earlier work had shown that I<sup>6</sup> and II<sup>7</sup> give symmetrical carbonium ions and, thus, reaction 4 is an independent measure of total return. It had also been shown that in each case substantial return is involved and that reactions 2 and 4 are first order.



Rate constants for reactions 2–4 for acetolysis of I and II are given in Table I. The first-order constants were steady and reproducible; in each case the constants are average values for several independent experiments. Oxygen equilibration (eq 3) was followed by starting with ether-<sup>18</sup>O- or sulfonyl-<sup>18</sup>O-labeled ester and determining the <sup>18</sup>O distribution at various stages of the reaction. For each point, the isolated ester was cleaved at the S–O linkage<sup>8</sup> and the distribution determined from the <sup>18</sup>O content of the resulting alcohol.<sup>2c</sup> The total <sup>18</sup>O content of the ester remained constant throughout the reaction, and control experiments showed that the <sup>18</sup>O content of the alcohol corresponds to that of the ether oxygen in the ester.<sup>9</sup> Both ether-labeled and sulfonyl-labeled II gave the same results.

The data show that oxygen equilibration is associated with ion-pair return. However, equilibration is slower than racemization (i.e.,  $k_{rac} > k_{eq}$ ). This means that

(4) Unpublished work by G. Sandrock.

(5) D. B. Denney and B. Goldstein, *J. Am. Chem. Soc.*, **79**, 4949 (1957).

(6) (a) D. J. Cram, *ibid.*, **74**, 2129 (1952); S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2165 (1952); D. J. Cram and J. A. Thompson, *ibid.*, **89**, 6766 (1967); (b) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2780 (1956).

(7) H. L. Goering and G. N. Fickes, *ibid.*, **90**, 2848 (1968); G. N. Fickes, Ph.D. Thesis, University of Wisconsin, 1965.

(8) W. D. Closson, P. Wriede, and S. Bank, *J. Am. Chem. Soc.*, **88**, 1581 (1966).

(9) See also J. E. Nordlander and W. J. Kelly, *J. Org. Chem.*, **32**, 4122 (1967).

**Table I.** Rate Constants for Solvolysis ( $k_t$ ), Oxygen Equilibration ( $k_{eq}$ ), and Racemization ( $k_{rac}$ ) for Acetolysis of *threo*-3-Phenyl-2-butyl *p*-Toluenesulfonate (I) and *endo*-Bicyclo[3.2.1]octan-2-yl *p*-Toluenesulfonate (II)

	I 10 <sup>5</sup> sec <sup>-1</sup> <sup>a</sup>	II 10 <sup>5</sup> sec <sup>-1</sup> <sup>b</sup>	II 10 <sup>5</sup> sec <sup>-1</sup> <sup>c</sup>
$k_t$	6.19 ± 0.07	0.322 ± 0.004	2.4 <sup>d</sup>
$k_{rac}$ <sup>e</sup>	15.5 ± 0.5	1.47 ± 0.02	6.02 ± 0.07
$k_{eq}$	8.19 ± 0.09	0.70 ± 0.02	2.33 ± 0.04

<sup>a</sup> Concentration of I 0.095 M; sodium acetate concentration 0.12 M; temperature 74.91°. <sup>b</sup> Concentration of II 0.02–0.05 M; sodium acetate concentration 0.055 M; temperature 48.86°. <sup>c</sup> II, at 48.86°; solvent contained 0.10 M LiClO<sub>4</sub>. <sup>d</sup> Average value; constant drifts from 2.0 × 10<sup>-5</sup> to 2.6 × 10<sup>-5</sup> at 65% reaction. <sup>e</sup> Determined from rates of loss of activity and solvolysis, i.e.,  $k_{rac} = k_{\alpha} - k_t$ .

some return occurs without oxygen equilibration and, thus,  $k_{eq}$  does not correspond to total return. In buffered acetic acid  $k_{eq}/k_{rac} \approx 0.5$  for both substrates. Both I<sup>6b</sup> and II<sup>7</sup> show only a normal salt effect with added lithium perchlorate. Thus, according to the "special-salt-effect" criterion,<sup>6b</sup> we are dealing with internal return in these cases.

The last column in Table I shows data for acetolysis of II in the presence of 0.1 M lithium perchlorate. The normal salt effect is larger percentagewise for  $k_t$  than for  $k_{rac}$  and, as a result, ion-pair return is decreased from 100 $k_{rac}/(k_{rac} + k_t) = 82\%$  in buffered acetic acid to 72% in the presence of lithium perchlorate, or, to put it another way, part of the return is eliminated by the lithium perchlorate. The salt also reduces, but does not eliminate, oxygen equilibration associated with return ( $k_{eq}/k_{rac}$  drops from 0.47 ± 0.02 to 0.39 ± 0.01). From this it seems that that part of the return eliminated by lithium perchlorate would otherwise give completely equilibrated substrate.

This suggests that ion-pair intermediates that return with different amounts of oxygen equilibration are involved—the intermediate that returns with most equilibration is diverted by lithium perchlorate. Thus, even though there is no apparent special salt effect, it appears that species which differ in degree or kind are involved in the return.

(10) National Institutes of Health Predoctoral Fellow.

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### On Sulfonate Oxygen Scrambling as a Criterion for Ion-Pair Return<sup>1</sup>

Sir:

We wish to report evidence that internal return in which a *p*-toluenesulfonate ion rebonds to the original carbon atom is accompanied by about 50% randomization of the sulfonate oxygen atoms. This is significant because existing methods for detecting ion-pair return are not applicable to secondary alkyl systems that do not rearrange.

The preceding communication reports that ion-pair return associated with acetolysis of *threo*-3-phenyl-2-butyl *p*-toluenesulfonate (I) and *endo*-bicyclo[3.2.1]oc-

(1) This research was supported by the Air Force Office of Scientific Research (AFOSR-847-67).