(*e.g.*, benzhydryl,[2a,d] allylic,[3] α-arylethyl,[4] and 2-phenyl-2-butyl[2b] *p*-nitrobenzoates).

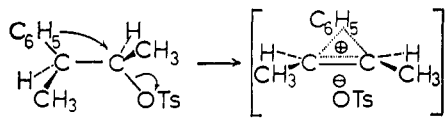
$$R^*OCOAr \xrightarrow{k_{eq}} R^*OC^*OAr \quad (1)$$

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.[5] 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[6] and II[7] 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.

$$ROSO_2Ar \xrightarrow{k_t} ROAc + ArSO_3H \quad (2)$$

$$R^*OSO_2Ar \xrightarrow{k_{eq}} R^*OS^*O_2Ar \quad (3)$$

$$(+)\text{-}ROSO_2Ar \xrightarrow{k_{rac}} (\pm)\text{-}ROSO_2Ar \quad (4)$$



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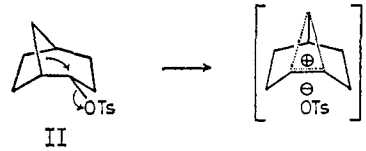

II

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-^{18}O- or sulfonyl-^{18}O-labeled ester and determining the ^{18}O distribution at various stages of the reaction. For each point, the isolated ester was cleaved at the S–O linkage[8] and the distribution determined from the ^{18}O content of the resulting alcohol.[2c] The total ^{18}O content of the ester remained constant throughout the reaction, and control experiments showed that the ^{18}O content of the alcohol corresponds to that of the ether oxygen in the ester.[9] 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 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[6b] and II[7] show only a normal salt effect with added lithium perchlorate. Thus, according to the "special-salt-effect" criterion,[6b] we are dealing with internal return in these cases.

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 10^5 sec^{-1} [a]	II 10^5 sec^{-1} [b]	II 10^5 sec^{-1} [c]
k_t	6.19 ± 0.07	0.322 ± 0.004	2.4[d]
k_{rac}[e]	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

[a] Concentration of I 0.095 *M*; sodium acetate concentration 0.12 *M*; temperature 74.91°. [b] Concentration of II 0.02–0.05 *M*; sodium acetate concentration 0.055 *M*; temperature 48.86°. [c] II, at 48.86°; solvent contained 0.10 *M* $LiClO_4$. [d] Average value; constant drifts from 2.0 × 10^{-5} to 2.6 × 10^{-5} at 65% reaction. [e] Determined from rates of loss of activity and solvolysis, *i.e.*, $k_{rac} = k_\alpha - k_t$.

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 $100k_{rac}/(k_{rac} + k_t) = 82\%$ 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[1]

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-

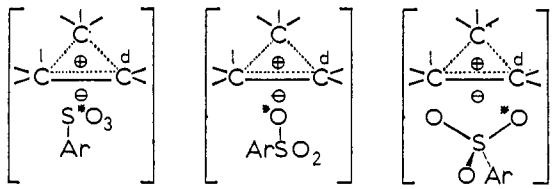
(1) This research was supported by the Air Force Office of Scientific Research (AFOSR-847-67).

(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).

tan-2-yl *p*-toluenesulfonate (II) results in incomplete oxygen equilibration. In these systems, first-order racemization of the unsolvolyzed ester (k_{rac}) provides an independent measure of total return, and for both I and II the first-order constant for oxygen equilibration (k_{eq}) is about $^1/_2k_{rac}$. From this it cannot be determined to what extent, or if any, oxygen equilibration occurs when the anion rebonds to the original carbon atom.

Possible orientations of the ions in intermediates derived from systems such as I or II are illustrated by III, IV, and V (the atom originally in the ether position is marked with an asterisk). The k_{eq}/k_{rac} ratios for these arrangements are also indicated. In each case the *d* and *l* carbon atoms are equivalent and ion-pair return gives racemic substrate. In III the three sulfonate oxygen atoms are equivalent and return gives equilibrated ester; thus $k_{eq}/k_{rac} = 1$. A process involving IV results in racemization (rearrangement) without oxygen equilibration, $k_{eq} = 0$. In V, which was suggested earlier,[2] two equivalent oxygen atoms are paired with the two equivalent carbon atoms. In this case, three of every four molecules re-formed by return corresponds to a mixture with one-third of the label in each of the three positions (*i.e.*, fully equilibrated), and the fourth has the original labeling pattern; thus $k_{eq}/k_{rac} = 0.75$.

Return from III or V would give k_{eq}/k_{rac} ratios higher than the 0.5 observed for acetolysis of I and II.[3] This



$k_{eq}/k_{rac} = 1$ III $\quad$ $k_{eq}/k_{rac} = 0$ IV $\quad$ $k_{eq}/k_{rac} = 0.75$ V

means that return corresponds to a combination of IV (no mixing) and III or V, or both. The observed k_{eq}/k_{rac} ratio of 0.5 would obtain if one-half of the return were from III and one-half from IV, or if two-thirds were from V and one-third from IV.

It is important to distinguish between these possibilities because in one case (2:1 blend of V and IV) no scrambling occurs when the anion rebonds to the original carbon atom. This would indicate that ion-pair return in secondary alkyl systems that do not rearrange probably would not result in oxygen equilibration. On the other hand, if scrambling in I and II results from return from a 1:1 blend of III and IV, the same amount of equilibration occurs when the anion rebonds to the original carbon atom (no rearrangement) as for return with rearrangement.

To determine if equilibration involves return from III or V, or both, we have investigated return associated with acetolysis of optically pure (+)-*threo*-3-phenyl-2-butyl *p*-toluenesulfonate-sulfonyl-^{18}O ((+)-I-OS^{18}O$_2$Ar). One can distinguish between these possibilities from the amount of scrambling in each enantiomer of the racemic ester resulting from ion-pair return.

Optically pure (+)-I-OH, $[\alpha]^{21}D$ 31.6° (neat), was obtained as described earlier,[4] and the optical purity was confirmed by the method of Mislow and Raban.[5] The alcohol was converted to (+)-I-OS^{18}O$_2$Ar, $[\alpha]^{21}D$ 16.4° (benzene), by reaction with ^{18}O-labeled *p*-toluenesulfonyl chloride.[6] The active labeled ester (0.096 *M*) was solvolyzed in buffered acetic acid (0.12 *M* NaOAc) at 74.91° for a period (76.6 min) corresponding to 25% solvolysis, 51% racemization, and 29.8% oxygen equilibration of the unsolvolyzed ester. At this point, 34% of the (+) enantiomer and all of the (−) enantiomer have been formed by ion-pair return. The recovered ester was separated into optically pure (+) isomer and a racemic fraction by fractional recrystallizations (the active isomer is less soluble than the racemic modification). The ether-^{18}O content of the (+) isomer and racemic fraction was determined[3] and, from this, the ether-^{18}O content of the (−) isomer can be calculated.

Ether-^{18}O contents of the enantiomers in the recovered ester are shown in Table I together with calculated values for equilibration resulting from return from III (second column) and V (last column). In the first case, the amount of scrambling is the same for return to either carbon atom. The reason the calculated ether-^{18}O content for the (+) isomer is lower than that for the (−) isomer is 66% of the (+) isomer is unreacted sulfonyl-^{18}O-labeled starting material. If scrambling involves III, there must be an equal amount of return from IV (no scrambling) because $k_{eq}/k_{rac} = 0.5$. This is the reason the calculated value for the (−) isomer (0.525), all of which has been formed by return, is less than the equilibrium value, $(^2/_3)1.35 = 0.90$.

Table I. Ether-^{18}O Content of Enantiomers in the Unsolvolyzed Ester for Acetolysis of (+)-3-Phenyl-2-butyl *p*-Toluenesulfonate-sulfonyl-^{18}O (1.35 atom % excess) for 76.6 min at 74.9°[a]

	Ether-^{18}O content[b]		
Isomer	Observed[c]	Calculated for 1:1 return from III and IV	Calculated for 2:1 return from V and IV
(+) Isomer[d]	0.189 ± 0.002	0.180	0.052
(−) Isomer[d]	0.513 ± 0.005	0.525	0.900

[a] Gross ether-^{18}O content of isolated ester was 0.268 atom % excess. [b] Atom % excess ^{18}O. [c] Average and average deviation of three or more determinations. [d] All of the (−) isomer formed by return; 66% of the (+) isomer is unreacted sulfonyl-^{18}O labeled ester.

If equilibration involved return from V and IV—a 2:1 ratio would be required to give $k_{eq}/k_{rac} = 0.5$—there would be no equilibration for return to the original carbon atom and the rearrangement product (enantiomer) would be fully equilibrated; this is a consequence of a 2:1 ratio of rearrangement *via* V and IV. Thus, the calculated value for the (−) isomer in the last column is the equilibrium value. The reason the calculated value for the (+) isomer is not zero is because interconversion of enantiomers is reversible and 6% of the (+) isomer has at one time been (−) isomer.

(2) D. J. Cram, *J. Am. Chem. Soc.*, 74, 2129 (1952); S. Winstein and K. C. Schreiber, *ibid.*, 74, 2165 (1952).
(3) H. L. Goering and R. W. Thies, *ibid.*, 90, 2967 (1968).
(4) D. J. Cram, *ibid.*, 71, 3863 (1949).
(5) M. Raban and K. Mislow, *Tetrahedron Letters*, 4249 (1965); 3961 (1966); "Topics in Stereochemistry," Vol. 2, N. L. Allinger and E. L. Eliel, Ed., Interscience Publishers, Inc., New York, N. Y., 1967, p 216.
(6) S. Oae, K. Kitao, and Y. Kitaoka, *Tetrahedron*, 19, 827 (1963).

The observed ^{18}O content is in excellent agreement with values calculated for return with equal amounts of mixing in the two enantiomers (*i.e.*, return from III and IV). This means the observed equilibration to return ratio (k_{eq}/k_{rac}) applies for rebonding of the anion to the original carbon atom. In the present case only internal return is involved.[7] Thus it appears that, in secondary alkyl systems that do not rearrange, internal return will result in up to 50% sulfonate oxygen equilibration. In other work we are determining if external ion-pair return[8] results in complete equilibration.

It is not clear if one intermediate (a hybrid of III and IV) or if two or more intermediates are involved. Evidence for more than one intermediate in a similar case[3] suggests that ionization gives IV which is in equilibrium with III and it is the latter which is more capturable by lithium perchlorate (and solvent) and returns with equilibration.

(7) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2780 (1956).
(8) S. Winstein, P. E. Klinedinst, Jr., and G. C. Robinson, *ibid.*, **83**, 885 (1961).
(9) National Institutes of Health Predoctoral Fellow.

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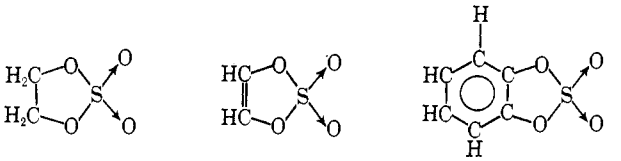
The Structure and Reactivity of Cyclic Esters. Ethylene Sulfate and Vinylene Sulfate

Sir:

Interest in five-membered cyclic esters of sulfur[1-4] and phosphorus[5-12] is keen because certain compounds of this class exhibit exceptional reactivity to solvolysis at the hetero atom when compared to their six-membered cyclic or acyclic analogs. For example, the rate enhancement has been estimated at 10^8 for alkaline hydrolysis of salts of ethylene phosphate over those of dimethyl phosphate.[5] This kind of kinetic acceleration has been attributed alternately to the effects of angle strain in five-membered rings and to 2p–3d π character in the oxygen–hetero atom bonds.[1,6,9] The search for a correlation between reactivity and structure has led to X-ray diffraction studies of two unsaturated phosphoric acid diesters, methyl ethylene phosphate[10] and methyl pinacol phosphate,[11] and more recently of an unsaturated cyclic diester, acetoinenediol cyclophosphate,[12] which is also known[12] to be highly reactive in solvolytic reactions.

(1) E. T. Kaiser, M. Panar, and F. H. Westheimer, *J. Am. Chem. Soc.*, **85**, 602 (1963).
(2) E. T. Kaiser, I. R. Katz, and T. F. Wulfers, *ibid.*, **87**, 3781 (1965).
(3) O. R. Zaborsky and E. T. Kaiser, *ibid.*, **88**, 3084 (1966).
(4) E. B. Fleischer, E. T. Kaiser, P. Langford, S. Hawkinson, A. Stone, and R. Dewar, *Chem. Commun.*, 197 (1967).
(5) J. Kumamoto, J. R. Cox, Jr., and F. H. Westheimer, *J. Am. Chem. Soc.*, **78**, 4858 (1956).
(6) P. C. Haake and F. H. Westheimer, *ibid.*, **83**, 1102 (1961).
(7) J. R. Cox, Jr., R. E. Wall, and F. H. Westheimer, *Chem. Ind.* (London), 929 (1959).
(8) A Eberhard and F. H. Westheimer, *J. Am. Chem. Soc.*, **87**, 253 (1965).
(9) D. A. Usher, E. A. Dennis, and F. H. Westheimer, *ibid.*, **87**, 2320 (1965).
(10) T. A. Steitz and N. W. Lipscomb, *ibid.*, **87**, 2488 (1965).
(11) M. G. Newton, J. R. Cox, Jr., and J. A. Bertrand, *ibid.*, **88**, 1503 (1966).
(12) D. Swank, C. N. Caughlan, F. Ramirez, O. P. Madan, and C. P. Smith, *ibid.*, **89**, 6503 (1967).

In the sulfur series, ethylene sulfate (I) hydrolyzes in base with about 14% S–O bond cleavage, while dimethyl sulfate is hydrolyzed exclusively at carbon. While highly indicative, this case unfortunately cannot permit comparison of relative rate constants for attack of hydroxide ion at the sulfur atom beyond establishing a lower limit (~300). However, more



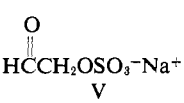
I II III

recent solvolytic studies[2] on catechol cyclic sulfate (III) have shown this compound to hydrolyze 2×10^7 times faster than its open-chain analog, diphenyl sulfate, and in fact considerably faster than ethylene sulfate. Studies described here show that vinylene sulfate (II) hydrolyzes in base nearly as rapidly as III.

Structural studies of the cyclic esters of sulfuric acid have not hitherto been reported, although a comparison[4] has been made recently of the structures of five- and six-membered cyclic sulfonates. We now describe the molecular and crystal structures of ethylene sulfate (I) and vinylene sulfate (II).

Vinylene sulfate was prepared using the following reactions. Ethylene sulfate[13] was chlorinated in refluxing carbon tetrachloride (CCl_4) using chlorine and a GE sunlamp to give 1,2-dichloroethylene sulfate (IV) which was isolated by vacuum distillation and recrystallized from CCl_4–hexane as a white solid, mp 47–49°.[14] The dechlorination of V was effected by using magnesium in refluxing tetrahydrofuran. The solvent was subsequently removed and II was isolated in 50% yield by steam distillation. Recrystallization from CCl_4 and sublimation gave pure II, mp 51.5–52°.

The alkaline hydrolysis of vinylene sulfate (II) was conducted in a thermostated cell at 25° in solutions maintained at constant pH values by means of a Radiometer automatic titrator and at an ionic strength of 0.5 by the addition of sodium perchlorate. The hydroxide ion concentrations employed ranged from 1.59×10^{-5} to 5.01×10^{-5} M, and the initial concentration of sulfate II ranged from 3.56×10^{-4} to 11.54×10^{-4} M. Calculation of the second-order rate constant for the hydroxide ion catalyzed hydrolysis of II from the pseudo-first-order constants measured in various runs gave a value of 8.33 M^{-1} sec^{-1}. The corresponding rate constant for III is 18.8 M^{-1} sec^{-1} (see ref 2). The product of the hydrolysis of II in sodium hydroxide solution was isolated and identified as sodium glycolaldehyde monosulfate (V), a hygroscopic solid.



V

Our X-ray studies indicated that I and II crystallize isomorphously in the space group F2dd with eight

(13) A modified procedure of J. Brunken (West German Patent 1,049,870 (1959)) was used.
(14) All new compounds exhibited satisfactory analytical and spectral properties.