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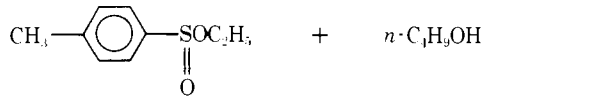
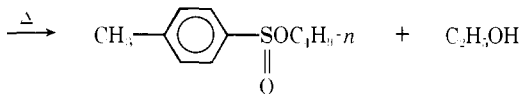
Nucleophilic Substitution at Sulfur. Kinetic Evidence for Inversion of Configuration at Sulfinyl Sulfur in Acid-Catalyzed Transesterification of Sulfinates

Sir:

In 1925 Phillips[1] prepared for the first time optically active levorotatory ethyl *p*-toluenesulfinate (*1*) and *n*-butyl *p*-toluenesulfinate (**2**) by kinetic resolution taking place when (−)-octanol-2 was heated with two molecular proportions of either racemic ethyl or *n*-butyl *p*-toluenesulfinate. Moreover, he stated that thermal transesterification of (−)-**1** with 1-butanol gives (+)-**2**. If one assumes, as Phillips did, that both (−) esters **1** and **2** obtained from kinetic resolution have the same configuration around sulfur, it follows that the conversion of (−)-**1** into (+)-**2** should occur with inversion of configuration. These experiments are considered to be the earliest evidence of the stereochemical course of substitution at chiral sulfur center.



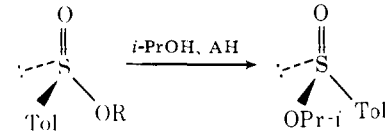
(−)-1, $[\alpha]_{546}$ −5.81° (ee, 2.6%)



(+)-2, $[\alpha]_{546}$ +0.32° (ee, 0.1%)

Recently, considerable progress has been made[2-5] in the synthesis of optically active sulfinates as well as in the determination of their optical purity and chirality at sulfur. This cast a new light on the experiments described by Phillips. First of all, the stereospecificity of the reaction shown above is extremely low (it does not exceed 5%), although, in accord with the original assumption by Phillips, the conversion of (−)-**1** into (+)-**2** is, indeed, accompanied by inversion.[6] However, in our hands the reaction of (−)-**1**, $[\alpha]_{589}$ −25.7°, with 1-butanol performed under the conditions described by Phillips resulted always in the formation of the completely racemic sulfinate ester **2**. Therefore, the desirability of exploring other experimental approaches to establish the steric course of the transesterification reaction of sulfinates was obvious.

Taking into account that hydrolysis of certain sulfinates and sulfites can be catalyzed by acids,[7] we have first investigated the stereochemistry of the reaction between optically active alkyl *p*-toluenesulfinates **3**, **4**, and **5** and isopropyl alcohol in the presence of strong acids (AH) like CF_3COOH, CF_3SO_3H, and $PhSO_3H$. The reaction was carried out at room temperature in isopropyl alcohol solution using equimolar amount of acid in respect to sulfinate. When the reaction was complete (see Table I) the usual workup (quenching with water, extraction, neutralization) gave isopropyl *p*-toluenesulfinate (**6**) which was isolated by distillation in yields of over 80%. The results obtained are summarized in Table I.



3, R = CH_3
4, R = $CH_2{=}CHCH_2$
5, R = $CH{\equiv}CCH_2$

6

As inspection of the results in Table I shows that, in contrast to the nonstereospecific reaction of **3**, sulfinate esters **4** and **5** undergo transesterification with predominant inversion of configuration, though the stereospecificity of these conversions was low. The highest stereospecificity (40%) of the reaction was observed for **5** in the presence of trifluoromethanesulfonic acid. In this context, it is interesting to note that both the acidic catalyst and the leaving alkoxy group have an influence on the stereospecificity of the considered reaction.

Most probably the great extent of racemization observed is due to the competitive symmetrical alkoxy-alkoxy exchanges in the starting and produced sulfinates. However, another possible way to account for these results is to assume that transesterification of sulfinates proceeds by an addition-elimination mechanism involving a dialkoxysulfurane intermediate which racemizes via permutational isomerization.[8]

In order to provide more rigorous evidence supporting the inversion in the transesterification of sulfinates as well as to gain better insight into mechanism of this reaction, we utilized the classical approach used by Hughes[9] to establish that inversion of configuration accompanies S_N2-type substitution. This approach, which consists of the comparison of the rate of racemization with that of isotopic exchange, has recently been successfully applied to phosphorus[10] and silicon[11] chemistry.

To this end we have (a) synthesized optically active sulfinate **3** containing ^{14}C in the methoxy group by the asymmetric reaction shown in eq 1 and (b) measured the rate of racemization of **3** and isotopic methoxy-methoxy exchange in methanol in the presence of trifluoroacetic acid.

The racemization and isotopic exchange measurements[12] were carried out under exactly the same conditions using a methanol solution of sulfinate (+)-**3** (12.37×10^{-2} mol/L) and trifluoroacetic acid (17.52×10^{-2} mol/L). The results obtained are shown in eq 2.

Table I. Acid-Catalyzed Reaction of (−)-*S*-Alkyl *p*-Toluenesulfinates with Isopropyl Alcohol

compd	starting sulfinate $[\alpha]_{589}$,	starting sulfinate ee, %	catalyst	reaction time, h	sulfinate **6** $[\alpha]_{589}$, deg	sulfinate **6** ee, %	stereospecificity
3	−19.35	9.3	CF_3SO_3H	75	0	0	0
4	−15.6	10.7	CF_3COOH	98	0	0	0
4	−15.6	10.7	CF_3SO_3H	18	+2.0	1	9.2
4	−15.6	10.7	$C_6H_5SO_3H$	2.5	+1.7	0.9	7.9
5	−4.4	4.0	CF_3COOH	72	+0.3	0.15	3.8
5	−24.2	21.7	CF_3SO_3H	41	+17.6	8.7	40

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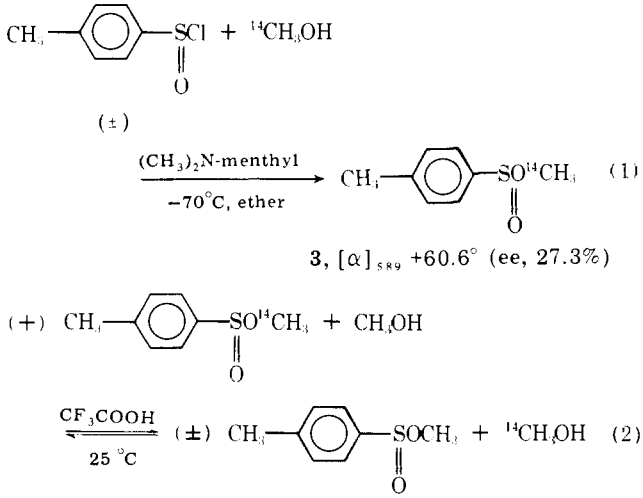
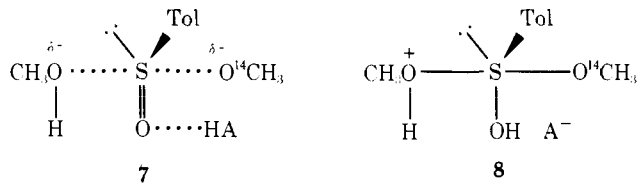


$$k_{rac} = (6.25 \pm 0.01)\ 10^{-5}\ s^{-1}$$
$$k_{ex} = (2.94 \pm 0.04)\ 10^{-5}\ s^{-1}$$

The fact that **3** loses its optical rotation practically twice as fast as it loses the radioactive methoxy group proves unequivocally that the methoxy–methoxy exchange at sulfinyl sulfur proceeds stereospecifically with net inversion of configuration. This result is compatible with the simple bimolecular S_N2-S substitution for exchange involving a transition state (**7**) or with the mechanism involving a transient sulfurane intermediate (**8**).[13] If the latter mechanism is true, the postulated dialkoxysulfurane (**8**) would have a high barrier for the Berry-type pseudorotation since positions of all substituents at sulfur in trigonal bipyramid are most convenient from the point of view of apicophilicity. Therefore, **8** should undergo decomposition much faster than pseudorotation to give nucleophilic substitution product in a stereospecific manner.



7 **8**

Full kinetics of the acid-catalyzed transesterification of sulfinates is being investigated.

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(6) The chirality at sulfur and optical purity of *n*-butyl *p*-toluenesulfinate (**2**) has been estimated as follows: (−)-*S*-menthyl *p*-toluenesulfinate, $[\alpha]_{589}$ −202°, was treated with *N,N*-diethylaminomagnesium bromide to give (+)-(*S*)-*N,N*-diethyl *p*-toluenesulfinamide, $[\alpha]_{589}$ +100°, which on treatment with 1-butanol in the presence of benzenesulfonic acid gave (−)-(*S*)-*n*-butyl *p*-toluenesulfinate (**2**), $[\alpha]_{589}$ −130° (ee, 70.4%). The ee value has been estimated chemically by means of the conversion of (−)-(*S*)-**2** into methyl *p*-tolyl sulfoxide, $[\alpha]_{589}$ +104.3° (ee, 70.4%).
(7) See, for example, J. G. Tillet, *Chem. Rev.*, **76**, 747 (1976).
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(12) The rate of racemization of **3** was measured with a Perkin-Elmer 241 MC photopolarimeter. The pseudo-first-order rate constant was calculated from the equation $\log(\alpha_0/\alpha_t) = kt/2.303$. The isotopic exchange experiments were carried out in sealed ampules which contained 0.5 mL of the solution. The samples were frozen at −78 °C before and after reaction. The reactants were separated by extraction in the system toluene (3 mL) and water (10 mL). The radioactivity of the organic phase was measured by the liquid scintilation method. The rate constant for the exchange was determined from the equation $\log[(I - I_\infty)/(I_0 - I_\infty)] = k_{ex}t/2.303$ where I_0, I, and I_∞ are the count rates of the sample at times 0, t, and $t = \infty$, respectively. The value of I_∞ was obtained experimentally for $t_\infty = 10\tau_{1/2}$.
(13) Addition–elimination mechanism for substitution at sulfur in sulfinates is preferred by Kice: J. L. Kice and Ch. A. Walters, *J. Am. Chem. Soc.*, **94**, 590 (1972).

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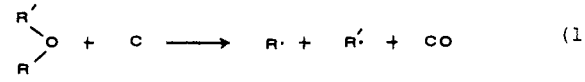
A Novel Rearrangement in the Reaction of Carbon Atoms with Furan

Sir:

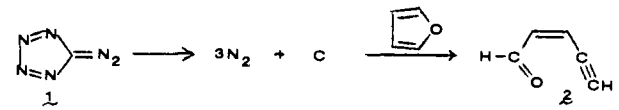
The reactions of atomic carbon with substrates containing heteroatoms are generally thought to involve initial attack of the electron-dificient carbon at the most electronegative atom.[1] Thus simple ethers are attacked on oxygen to effect deoxygenation with the concurrent formation of a pair of radicals (eq 1).[2] We report here that the reaction of carbon atoms with the



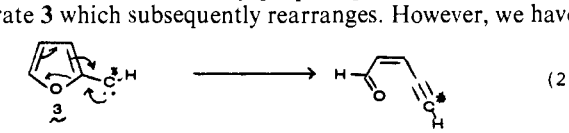
(1)

aromatic ether furan takes an entirely different course which is apparently dictated by the electron distribution in the highest occupied molecular orbital (HOMO).

When atomic carbon was generated by the pyrolysis of 5-diazotetrazole[3,4] (**1**, 9.8×10^{-2} mmol) in the presence of gaseous furan (1.17 mmol), the major volatile organic product was *cis*-2-penten-4-ynal (**2**, 1.3×10^{-2} mmol). The fact that only trace amounts of carbon monoxide and acetylene are formed in this system indicates that deoxygenation is not an important pathway.



The unsaturated aldehyde **2** has previously been obtained in the rearrangement of the 2-furfurylcarbene, **3** (eq 2).[5] Thus one could rationalize the formation of **2** in the reaction of carbon atoms with furan by proposing a C–H insertion to generate **3** which subsequently rearranges. However, we have



(2)

reported that atomic carbon is selective in its C–H insertions and invariably prefers the weakest C–H bond.[4] Since vinylic C–H bonds are rather strong and other sites are available for reaction, it does not seem likely that a C–H insertion by atomic

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