S. Kushner for assistance in obtaining the nmr spectra and Dr. W. C. Baird, Jr., for a sample of *syn*-7-norbornenol. We are grateful to Professor S. Winstein for delaying the publication of his study (see adjoining communication) of the 7-norbornenyl cation so that our work could be published at the same time.

(10) Alfred P. Sloan Foundation Research Fellow.

(11) Supported (1964–1966) by a Fellowship (5-F1-GM, 23-26-302) from the National Institute of General Medical Sciences.

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Received April 30, 1966

Mechanisms of Thermal Racemization of Sulfoxides[1]

Sir:

It has long been known that sulfoxides suffer stereomutation on heating at elevated temperatures.[2] We now wish to report preliminary results of a study aimed at correlating the rates of racemization of optically active sulfoxides with their structures. We restricted our investigation to sulfoxides which are incapable of β elimination.[3] Salient results are collected in Table I.

Table I. Thermal Racemization of Sulfoxides, $RSOC_6H_4CH_3$-*p*[a]

R	Compd no.	Temp range, °C	k_R/k_{Ph}[b]	ΔH^*, kcal/mole	ΔS^*, eu
CH_3	**1**	240–260	0.24[c]	43	+3
p-$CH_3OC_6H_4$	**2**	210	0.60		
C_6H_5	**3**	200–220	1.0	39	0
p-$CF_3C_6H_4$	**4**	210	1.9		
o-$CH_3C_6H_4$	**5**	200–220	2.2	37	−2
α-$C_{10}H_7$	**6**	210	2.3		
2,4,6-$(CH_3)_3C_6H_2$	**7**	180–200	53.0[d]	34	−3
$C_6H_5CH_2$	**8**	135–155	2.8×10^3[e]	43	+24
$CH_2{=}CHCH_2$	**9**	50–70	5.6×10^5[f]	22	−9

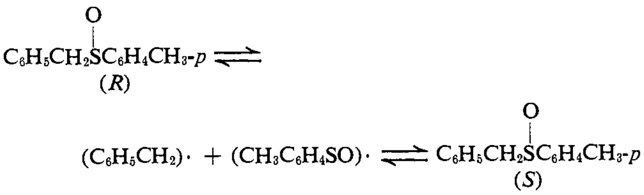
[a] In *p*-xylene or benzene. [b] First-order rate constant, k_R, of $RSOC_6H_4CH_3$-*p*, relative to that of phenyl *p*-tolyl sulfoxide, k_{Ph}, at 210° ($k_{Ph}^{210} = 3.19 \times 10^{-5}$ sec^{-1}); k_R^{210} values for **1** and **7–9** were obtained by extrapolation. [c] $k_R^{250} = 6.7 \times 10^{-5}$ sec^{-1}. [d] $k_R^{190} = 3.7 \times 10^{-4}$ sec^{-1}. [e] $k_R^{145} = 7.3 \times 10^{-5}$ sec^{-1} corrected for decomposition. [f] $k_R^{60} = 4.0 \times 10^{-4}$ sec^{-1}.

The rates of racemization of **1–7** are cleanly first order, and the racemized products are structurally identical with the starting materials.[4] While the rates are relatively insensitive to electronic effects, a steric factor appears to be operative, for the attachment of bulky groups to the sulfur atom leads to an increase in the rate of racemization. In the thermal racemization of sulfoxides the steric factor operates in the reverse direction from that observed[7] in the hydrogen chloride catalyzed racemization.

As the simplest working hypothesis, we assume that racemization of **1–7** proceeds by a *pyramidal inversion mechanism* and does not involve bond breaking. According to this model, the nonbonded repulsive interaction between the groups attached to the sulfur atom will be more important in the ground state than in the planar or near-planar transition state. This interpretation has its analogy in the B-strain hypothesis which has been invoked to account for the acceleration of solvolysis rates of tertiary halides.[8]

The thousandfold enhancement in rate of racemization of **8** over sulfoxides **1–7** is not accommodated within the framework of the above mechanism. It had previously been noted[9] that **8** was "more thermolabile" than the stereoisomeric 4-*t*-butylthiane 1-oxides, but no explanation for the accelerated rate of racemization was offered other than the comment that "conjugation between the tolyl and sulphoxide groups is possible" in **8**. However, as indicated above, such conjugation is incapable of accounting for the results since in **1–7** temperatures in excess of 180° are required to effect convenient measurements of racemization rates.

In contrast to the racemization of **1–7**, the racemization of **8** is accompanied by decomposition. Three of the decomposition products have been identified as dibenzyl, *p*-tolyl *p*-toluenethiolsulfonate, and benzyl *p*-tolyl sulfide. The first two products arise from radical dimerization: it is known that arenesulfinyl radicals (ArSO) couple and rearrange to give thiolsulfonates.[10] The rate of racemization at 145° is about four times the rate of decomposition and in xylene a greater variety of pyrolysis products is noted than in benzene. These observations argue for the presence of radicals and suggest that **8** suffers racemization by a *homolytic dissociation mechanism*.



$$\underset{(R)}{C_6H_5CH_2\overset{O}{\overset{|}{S}}C_6H_4CH_3\text{-}p} \rightleftharpoons (C_6H_5CH_2)\cdot + (CH_3C_6H_4SO)\cdot \rightleftharpoons \underset{(S)}{C_6H_5CH_2\overset{O}{\overset{|}{S}}C_6H_4CH_3\text{-}p}$$

The activation parameters for the racemization of **8** support this conclusion. The low value of the bond dissociation energy of the carbon–sulfur bond, whose upper limit is 43 kcal/mole, is related to the stability of the two radicals, the one because it is a benzyl radical,[11] and the other because it is a *p*-toluenesulfinyl radical.[10,12] That the $ArCH_2$–S bond in sulfoxides of structure type **8** is notably weak had previously been

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(1) This work was supported by the National Science Foundation under Grants No. GP-757 and GP-3375.

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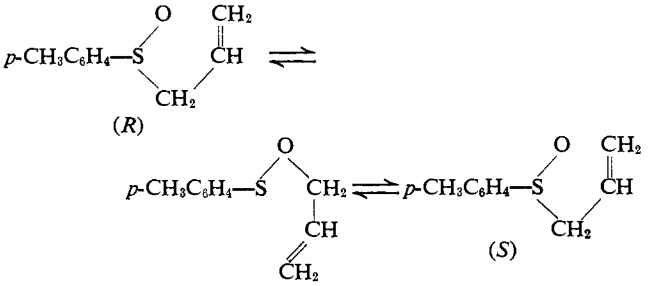
suggested by the observation[13] that α-naphthylcarbinyl p-tolyl sulfoxide is exceedingly photolabile under conditions where α-naphthyl p-tolyl sulfoxide and 2-(α-naphthyl)ethyl p-tolyl sulfoxide are completely stable. The large positive ΔS^* is in accord with the increase in degrees of freedom which accompanies fragmentation.[14] Kingsbury and Cram[3] have postulated a related radical mechanism in thermal sulfoxide elimination reactions.

The enormous increase in rate of racemization of **9** over any comparable sulfoxides is the result of a very low ΔH^* which more than compensates for the large negative ΔS^*. These observations, together with absence of decomposition at the temperatures of racemization, are readily accounted for by yet another pathway for racemization, in which the chiral sulfoxide is in mobile equilibrium with the achiral sulfenate, *i.e.*, a *cyclic rearrangement mechanism.*



Such a mechanism demands a low ΔH^* since bond-making and -breaking processes are concerted, and a negative ΔS^* because degrees of freedom are lost in the transition state.[14] The quantity of sulfenate at equilibrium is expected to be minute.[15]

The three mechanisms discussed in this communication do not exhaust the possibilities available for thermal stereomutation of sulfoxides, as will be discussed in a detailed paper.

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(16) Procter and Gamble Fellow, 1965–1966.

(17) Public Health Service Postdoctoral Fellow, on leave of absence from Manchester College, 1965–1966.

(18) National Aeronautics and Space Administration Fellow, 1965–1966.

(19) National Science Foundation Cooperative Predoctoral Fellow, 1963–1964.

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Received April 5, 1966

Thermal Rearrangement of Sulfenates to Sulfoxides[1]

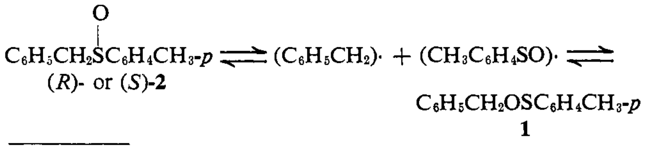
Sir:

In order to account for the facile racemization of allyl p-tolyl sulfoxide, we proposed an equilibrium between the sulfoxide and allyl p-toluenesulfenate.[2] In previous attempts to effect a thermal rearrangement of allyl phenyl sulfoxide, no allyl benzenesulfenate was observed,[3] even though the S → O shift in a thermal sulfoxide → sulfenate rearrangement is formally analogous to the N → O shift in the Meisenheimer rearrangement.[4] We now report evidence for facile O → S allyl and benzyl shifts in sulfenate → sulfoxide rearrangements. Thus, *the driving force of the rearrangement is in a direction opposite to that of the formally analogous Meisenheimer rearrangement.*

Reaction of p-toluenesulfenyl chloride with lithium allyl alcoholate in ether at room temperature yields allyl p-tolyl sulfoxide *directly.* The rearrangement in this case proceeds by a concerted 1,3-allylic shift, as indicated by the observation that reaction of p-toluenesulfenyl chloride with lithium crotyl alcoholate affords 1-methylallyl p-tolyl sulfoxide, whereas reaction with lithium 1-methylallyl alcoholate yields crotyl p-tolyl sulfoxide. A related observation was recorded by Kleinschmidt and Cope for the Meisenheimer rearrangement.[4]

Reaction of p-toluenesulfenyl chloride with lithium benzyl alcoholate in glyme at room temperature, or with benzyl alcohol in carbon tetrachloride in the presence of pyridine, yields benzyl p-toluenesulfenate (**1**). Sulfenate **1** rearranges at temperatures above 110° to give benzyl p-tolyl sulfoxide (**2**). The rearrangement proceeds even at room temperature: samples of neat **1** on standing for several months deposit crystals of **2**. The rearrangement proceeds with essentially complete conversion: after 9.5 hr in benzene (sealed tube under nitrogen) at 130°, less than 5% of starting **1** is left; conversely, starting with **2**, conversion to **1** takes place to the extent of less than 5% under identical conditions. Rates and equilibrium positions are conveniently measured either by the decrease of the methylene nmr signal of **1** (τ 5.38 in benzene) or by the increase of the methylene nmr signal of **2** (τ 6.35 in benzene). First-order rate constants determined by either method are essentially the same. Typically, at 130°, $k_1 = 2.4 \times 10^{-4}$ sec^{-1} as measured by the decrease in **1** and 2.0×10^{-4} sec^{-1} as measured by the increase in **2**. From rates measured over the temperature range of 110–130°, values of the activation parameters were found to be $\Delta H^* = 29$ kcal/mole and $\Delta S^* = 0 \pm 2$ eu.

Evidence had been adduced that the thermal racemization of **2** proceeds by a homolytic dissociation mechanism, which involves radical intermediates.[2] In the colligation step the methylene carbon atom of the benzyl radical may combine either with the sulfur atom or with the oxygen atom of the p-toluenesulfinyl radical to form, respectively, the sulfoxide **2** or the sulfenate **1**.



$$\underset{(R)\text{- or }(S)\text{-}\mathbf{2}}{C_6H_5CH_2\overset{\overset{O}{|}}{S}C_6H_4CH_3\text{-}p} \rightleftharpoons (C_6H_5CH_2)\cdot + (CH_3C_6H_4SO)\cdot \rightleftharpoons \underset{\mathbf{1}}{C_6H_5CH_2OSC_6H_4CH_3\text{-}p}$$

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(1) This work was supported by the National Science Foundation under Grant No. GP-3375.

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