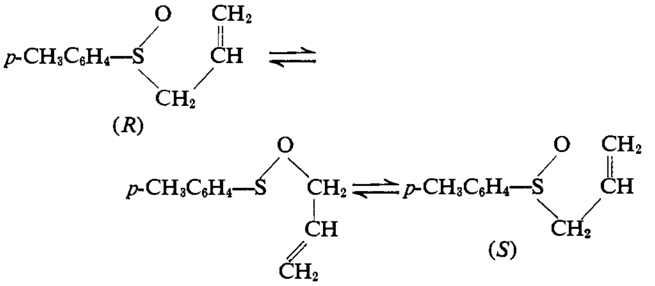
suggested by the observation[13] that α-naphthylcarbinyl *p*-tolyl sulfoxide is exceedingly photolabile under conditions where α-naphthyl *p*-tolyl sulfoxide and 2-(α-naphthyl)ethyl *p*-tolyl sulfoxide are completely stable. The large positive ΔS^* is in accord with the increase in degrees of freedom 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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Received April 5, 1966

Thermal Rearrangement of Sulfenates to Sulfoxides[1]

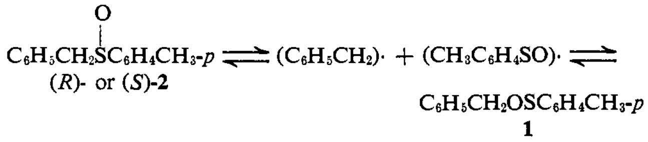
Sir:

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**.



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

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

[2] D. R. Rayner, E. G. Miller, P. Bickart, A. J. Gordon, and K. Mislow, *J. Am. Chem. Soc.*, **88**, 3138 (1966).

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This scheme provides a convenient rationalization for the rearrangement of **1** to **2**. The intermediacy of radicals is supported by two observations. First, a strong esr signal is observed[5] in naphthalene at 160° which decays in time to a steady-state signal. Second, partial decomposition occurs during the rearrangement, giving the same products which are observed in the thermal racemization[2] of **1**. As in the racemization reaction, leakage *via* a direct, intramolecular pathway cannot be ruled out at present.

Generation of stable radicals such as benzyl and *p*-toluenesulfinyl appears to be a prerequisite for the rearrangement: Thus methyl *p*-toluenesulfenate does not rearrange to *p*-tolyl methyl sulfoxide but instead pyrolyzes at *ca.* 200°, and benzyl methanesulfenate ($CH_3SOCH_2C_6H_5$) does not rearrange to benzyl methyl sulfoxide but instead decomposes at *ca.* 150° to give benzaldehyde and methyl mercaptan.[6] The sulfoxide–sulfenate equilibrium may also be implicated in the β elimination of sulfoxides and sulfenates.[7]

The small value of ΔS^* is somewhat surprising for a radical dissociation mechanism which is expected to exhibit a large positive ΔS^*;[2,8] this suggests that bond breaking is not significantly advanced in the transition state. From the values of ΔH^* and ΔS^* for the rearrangement (**1** → **2**) and racemization (of **2**) reactions, assuming microscopic reversibility, the driving force for the rearrangement, $\Delta G = \Delta\Delta G^*$, is of the order of 3 kcal/mole at 130°, in agreement with observation (less than 5% of **1** at equilibrium). The startling reversal in direction of the present rearrangement, as compared with the formally analogous Meisenheimer rearrangement, has its source in the formation of the strong S–O sulfoxide bond.[9] The strength of this bond may reside in its multiplicity[10] which in turn arises from back donation of the lone electron pairs on oxygen into the vacant d orbitals on sulfur.[11] This mechanism of bond strengthening is not available to the amine oxides. Similar arguments may also account for the direction of other O → S 1,2-shifts, such as the sulfoxylate → sulfinate[12] and sulfinate → sulfone[13] rearrangements, and for the direction of the thermal O → P 1,2-shift in the phosphinite → phosphine oxide rearrangement.[14]

A fuller discussion of these and related[15] rearrangements is reserved for the detailed paper.

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(5) We thank Drs. E. Wasserman, M. Gueron, and J. Turkevich for helpful discussions.

(6) This observation provides experimental support for the speculation by W. Carruthers, I. D. Entwistle, R. A. W. Johnstone, and B. J. Millard, *Chem. Ind.* (London), 342 (1966), that the pyrolysis of benzyl methyl sulfoxide to benzaldehyde and methyl mercaptan proceeds by way of benzyl methanesulfenate.

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

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Received April 5, 1966

Reversible Solvatochromic Shifts in Aqueous *t*-Butyl Alcohol Solutions[1,2] and Their Relationship to Thermochemical and Kinetic Properties

Sir:

We wish to report that certain electronic transitions show a solvent dependence in highly aqueous *t*-butyl alcohol that is closely related to the degree of structuredness of the medium and not to conventional solvent parameters. This medium effect produces reversible, bathochromic shifts which pass through an energy minimum at a composition of $X_{H_2O} \approx 0.96$.

Figure 1 portrays the most extreme effect of this kind which we have found so far: for one of Brooker's merocyanine dyes.[3] Adherence of ϵ_{max} to Beer's law was demonstrated in solvent compositions on both sides of the region of the reversal point.

In Table I are given data for various aromatic nitro compounds, most of which show the same effect to a smaller degree. Generally, these compounds have small, relatively soluble molecules with better characterized excited states than the larger dyes. To our knowledge, shift reversals have not been previously reported for these chemicals in any media. A number of other commercially obtained solvatochromic dyes of various kinds were examined. Some showed large spectral reversals and others showed none. Nearly all of them were so impure or badly characterized that we cannot say with confidence which component in the material was responsible for the inflection behavior and so will not report more than the qualitative result here. For example, a "quality" brand labeled naphthol blue yielded three components upon careful purification. All three of these unidentified materials gave shift inflections of over 29 mμ. Four blue-shifting (from *t*-butyl alcohol to water) dyes were examined: Brooker's dyes M-88[4] and IV,[5] quinaldine red, and sodium 2,6-dichlorobenzenone indophenol. None of these gave an inflection.

These observations are noteworthy because they are in harmony with a number of other facts about solvent–solute interactions in aqueous binary systems which have developed recently prompting us to perform the experiments described here.

Many physical properties of highly aqueous binary solutions pass through extrema in the region above

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(1) Solvent Effects in Organic Chemistry. IX. Previous paper is E. M. Arnett and G. W. Mach, *J. Am. Chem. Soc.*, **88**, 1177 (1966).

(2) Supported by National Science Foundation Grant GP 2014.

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