

**STERIC INFLUENCE OF THE SULFONYL GROUP IN EQUILIBRATIONS OF UNSATURATED SULFONES. RAPID BROMINE-CATALYZED CIS-TRANS EQUILIBRATIONS<sup>1</sup>**

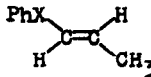
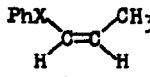
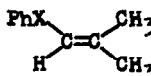
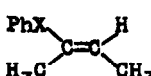
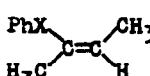
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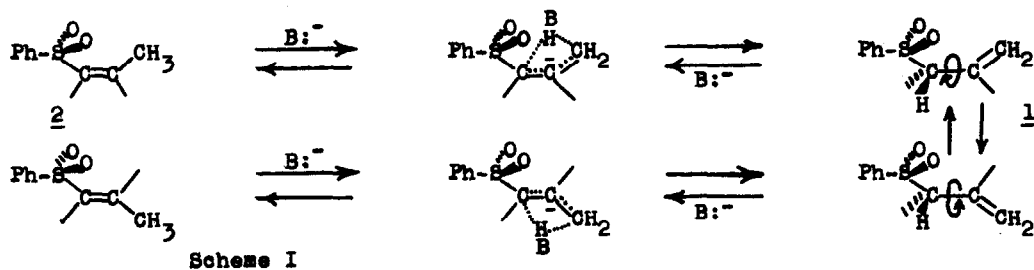
Base-catalyzed equilibrations of  $\beta,\gamma$ -unsaturated sulfones (1) -  $\alpha,\beta$ -unsaturated sulfones (2) afford predominantly trans-sulfonyl 2. When the structure of 2 necessitates a cis-sulfonyl juxtaposition with the  $\beta$  substituent (as in 2b), 1 predominates. These observations are undoubtedly related to the large steric requirement of the sulfonyl group and are illustrated by a comparison of sulfide and sulfone systems (Table I).<sup>2,3</sup> We have shown by D/H

**TABLE I. EQUILIBRATIONS<sup>a</sup> OF UNSATURATED SULFIDES<sup>b</sup> AND SULFONES<sup>c</sup>**

X	$\beta,\gamma$ -Unsaturated isomer, %	$\alpha,\beta$ -Unsaturated isomer, % <sup>d</sup>	
		<u>Trans</u> -PhX	<u>Cis</u> -PhX
	$\text{PhXCH}_2\text{CH}=\text{CH}_2$	 52	 48
S <sup>e</sup>	0		
SO <sub>2</sub>	( <u>1a</u> ) 28	( <u>2a</u> ) 69	( <u>2a'</u> ) 3
	$\text{PhXCH}_2\text{C}(\text{CH}_3)=\text{CH}_2$	 100	
S	0		
SO <sub>2</sub> <sup>f</sup>	( <u>1b</u> ) 70	( <u>2b</u> ) 30	
	$\text{PhXCH}(\text{CH}_3)\text{CH}=\text{CH}_2$	 54	 46
S	0		
SO <sub>2</sub>	( <u>1c</u> ) 0	( <u>2c</u> ) 100	( <u>2c'</u> ) 0

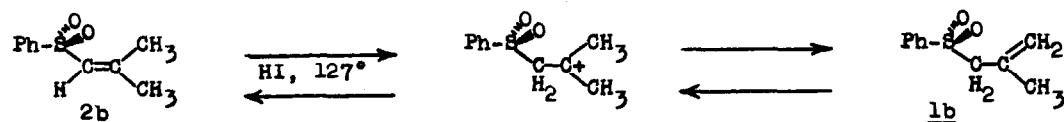
<sup>a</sup> Equilibrations were carried out in both directions; 0% indicates undetectable quantities (nmr). <sup>b</sup> t-BuOK-DMSO, 25°. <sup>c</sup> Et<sub>3</sub>N, 89°; pyridine, 115°; t-BuOK-t-BuOH, 25°. <sup>d</sup> Geometric assignments were verified, ref 3. <sup>e</sup> Cf. ref 4. <sup>f</sup> Equilibration also carried out in HI, 127°; the ratio of 1b:2b noted is an average, the individual values differing somewhat with the medium.

exchange studies that the cis-trans interconversions under these conditions are not direct but proceed through the  $\beta,\gamma$ -unsaturated isomer formed from the respective cis- and trans-allylic anions (illustrated for the sulfones in Scheme I).<sup>4</sup> This process accounts for the equilibration of all the isomeric species.



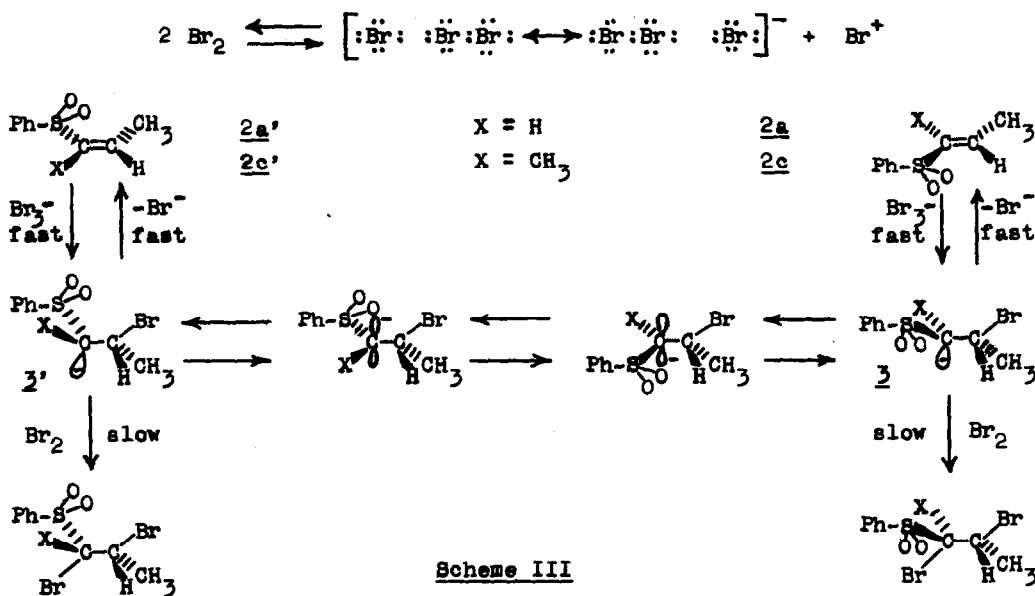
It can be concluded from the data in Table I and related results<sup>5</sup> that carbon-carbon double bonds are substantially more stabilized when substituted with sulfide ( $3p + R$ ) and alkyl ( $+I$ ) groups than with sulfonyl ( $-I$ ) groups and hydrogen atoms. Our data suggest that cis and trans isomers are electronically similar in stability and that the trans isomer predominates thermodynamically when the cis structure is sterically restricted. This restriction is strongly invoked by the bulky sulfonyl group but is much less noticeable in the sulfides.<sup>6</sup>

The sensitive interplay between electronic and steric factors is especially apparent in the equilibration of sulfones 1b/2b compared with that of the corresponding sulfides. The  $\beta,\beta$ -dimethyl substitution of the  $\alpha,\beta$ -unsaturated isomers is electronically stabilizing but sterically destabilizing; the former effect predominates in the sulfides (100%  $\alpha,\beta$  isomer) while the latter effect is the more influential in the sulfones (70%  $\beta,\gamma$  isomer, 1b). The steric factor and the innate stability of  $3^\circ$  carbonium ions probably account for the fairly rapid equilibration attained when 2b is treated with HI (Scheme II). Generally,  $\alpha,\beta$ -unsaturated sulfones undergo addition reactions with this reagent.<sup>7</sup>



Direct isomerization of cis-sulfonyl 2 to trans-sulfonyl 2 was found to proceed quantitatively in less than 4 min at  $25^\circ$  in  $\text{CCl}_4$  containing a small amount of  $\text{Br}_2$  (e.g., 0.9 mmol of 2, 1.0 mmol of  $\text{Br}_2$ , 24 g of  $\text{CCl}_4$ ). No trace of 1 was detected. The trans-sulfonyl isomers (2a, 2c) formed under these conditions continued to react with the  $\text{Br}_2$  very slowly forming mixtures of the respective threo and erythro dibromides;<sup>8</sup> complete reaction required ca. 30 hr. Robertson, et al., have presented substantial evidence indicating that addition

reactions of  $\alpha,\beta$ -unsaturated sulfones with  $\text{Br}_2$  are initiated by the nucleophilic attack of tribromide ion,  $\text{Br}_3^-$ .<sup>9</sup> We are suggesting, therefore, that the isomerizations as well as the addition reactions proceed with the formation of stable  $\beta$ -bromo- $\alpha$ -sulfonyl carbanions ( $\underline{2}$ ,  $\underline{2}'$ ) which should undergo rapid continuous inversion and rotation in nonpolar aprotic solvents,<sup>10</sup> allowing the two possible anti eliminations of bromide to occur. These rapid reversible processes constitute an equilibration leading to the thermodynamically favored trans-sulfonyl  $\underline{2}$ . The much slower irreversible reaction of  $\text{Br}_2$  with the equilibrating carbanions  $\underline{2}$  and  $\underline{2}'$ ,<sup>11</sup> would account for the non-stereospecific formation of diastereomeric dibromides<sup>12</sup> in a ratio that is kinetically controlled (Curtin-Hammett Principle<sup>13</sup>) regardless of the equilibrium concentrations of the two carbanions.<sup>14</sup> These processes are summarized in Scheme III.



#### NOTES AND REFERENCES

1. Taken in part from the PhD Dissertation of I. Sataty, Southern Illinois University, Carbondale, 1970.
2. C. Y. Meyers and I. Sataty, ACS National Meeting, Chicago, Sept. 1967, Abst. p. B 6; C. Y. Meyers, T. J. Doyle, M.-L. Hsu, and I. Sataty, ACS Regional Meeting, Manhattan, Kans., Oct. 1968, Abst. p. 41.
3. Isomer identification and determination of cis-trans ratios were based on the vinylic-proton coupling constants or the more general differential solvent shielding anisotropic effect, C. Y. Meyers and I. Sataty, Tetrahedron Letters,

4323 (1972). Geometric assignments to isomeric 2c (mp 50-51°) and 2c' and their respective nmr spectra, reported initially by Sataty (ref. 1), have recently been confirmed (ref. 14).

4. We are grateful to Dr. T. J. Doyle (PhD Dissertation, Southern Illinois University, Carbondale, 1971) for a portion of the data related to the isomerizations of allyl phenyl sulfide and propenyl phenyl sulfide.

5. D. E. O'Connor and W. I. Lyness, J. Amer. Chem. Soc., 86, 3840 (1964); C. D. Broadus, ibid., 90, 5504 (1968), and Accounts Chem. Res., 1, 231 (1968).

6. Even less steric restriction is exhibited by the corresponding ethers; e.g., cis-propenyl phenyl ether is thermodynamically more stable than the trans isomer by a factor of 68/32 (this study and M.-L. Hsu, Master's Thesis, Southern Illinois University, Carbondale, 1970).

7. This study and E. Rothstein, J. Chem. Soc., 684 (1934).

8. The diastereomeric dibromides were formed from 2a, for example, in a ratio of 39:61 determined by nmr ( $\delta$ , C<sub>6</sub>D<sub>6</sub>/TMS): 8.07-7.60 (m, o-Ph H), 7.44-7.03 (m, m- and p-Ph H), 5.20-4.63 (m,  $\alpha$  and  $\beta$  H), 1.84 (d,  $J$  = 6.4 Hz, CH<sub>3</sub> of one isomer), and 1.61 (d,  $J$  = 6.7 Hz, CH<sub>3</sub> of other isomer).

9. I. R. C. McDonald, R. M. Milburn, and P. W. Robertson, J. Chem. Soc., 2836 (1950); P. B. D. De La Mare and P. W. Robertson, ibid., 2838 (1950).

10. F. G. Bordwell, D. D. Phillips, and J. M. Williams, J. Amer. Chem. Soc., 90, 426 (1968); see also F. G. Bordwell, Accounts Chem. Res., 3, 281 (1970), and 5, 374 (1972).

11. The rapid eliminations from carbanions 3 and 3' relative to their reactions with Br<sub>2</sub> is consistent with the observation of F. G. Bordwell, J. Weinstock, and T. F. Sullivan, J. Amer. Chem. Soc., 93, 4728 (1971), that  $\beta$ -eliminations from sulfones that proceed via formation of  $\alpha$ -sulfonyl carbanions can be faster than  $\alpha$ -D/H exchange.

12. Non-stereospecific addition of bromine to  $\alpha,\beta$ -unsaturated sulfones was also observed by V. Baliah and Sp. Shanmuganathan, J. Phys. Chem., 63, 2016 (1959), and J. C. Phillips, M. Aregullin, M. Oku, and A. Sierra, Tetrahedron Letters, accompanying paper. We are grateful to Professor Philips for providing us with a copy of this manuscript.

13. See E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., New York, 1962, pp. 149 ff.

14. R. Andrisano, A. S. Angeloni, and A. Fini, Tetrahedron, 28, 2681 (1972), have reported that the  $\alpha$  carbanions of erythro and threo sulfones similar to 3 and 3' differ in stability.