

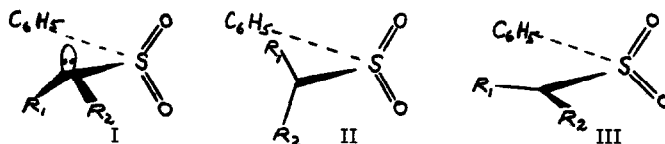
STEREOCHEMISTRY OF α -SULFONYL CARBANIONS

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(Received 19 April 1962)

A PREVIOUS note from this laboratory has reported the finding that phenyl 2-octyl sulfone undergoes base-catalyzed exchange of α -hydrogen in deuterated aqueous ethanol at a rate which is much faster than the rate of racemization.^{1,2} It can be concluded that a least 98 per cent of the benzene-sulfonyl methyl n-hexyl carbanions produced in these experiments are optically active and that asymmetry can be maintained until subsequent protonation. As expressed earlier,¹ two different possibilities must be considered in assigning stereochemistry to the asymmetric α -sulfonyl carbanion: (1) the anion is asymmetric because the charge-bearing α -carbon has a pyramidal



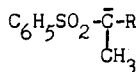
bonding arrangement (I) with a barrier to configurational inversion (analogous to the asymmetry about sulfur in $R_1R_2S=O$ and phosphorus in $R_1R_2R_3P$); (2) bonding to the α -carbon is essentially planar, but rotation about the $C_\alpha-SO_2$ bond from a minimum energy configuration which imparts molecular

¹ E.J. Corey and E.T. Kaiser, J. Amer. Chem. Soc. **83**, 490 (1961).

² Qualitatively similar results in other media have been reported independently by ^a D.J. Cram, D.A. Scott and W.D. Nielson, J. Amer. Chem. Soc. **82**, 6415 (1960); **83**, 3696 (1961) and by ^b H.L. Goering, D.L. Townes and B. Dittmer, J. Org. Chem. **27**, 736 (1962). However, the values of k_{exc}/k_{rac} vary more than a hundredfold depending on the solvent-base system.

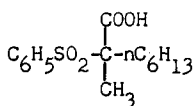
asymmetry (e.g. II) is restricted. Our results rule out structure III, a symmetric (optically inactive) molecular configuration.

We are now able to exclude possibility I on the basis of new data on exchange and racemization rates with phenyl 1,2,2-trimethylpropyl sulfone and the earlier results.¹ If asymmetric sulfone anions possess the geometry indicated by I, the rate of racemization of benzenesulfonyl t-butyl methyl carbanion (IV) should be far greater than that for benzenesulfonyl n-hexyl methyl carbanion (V) because of the effect of the t-butyl group to accelerate the pyramidal \rightarrow planar conversion.³ The tendency of these anions to racemize is expressible as the ratio $k_{\text{rac.}}/k_{\text{exc.}}$ which at 72.0° was found to

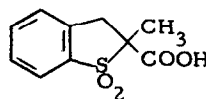


IV R=t-Bu

V R=n-C₆H₁₃



VI



VII

be 0.017 for the t-butyl substituted sulfone and 0.024 for the n-hexyl analog. The tetrahedral formulation (I) for such anions must therefore be rejected.

Another set of experiments independently allows exclusion of the pyramidal structure I. Decarboxylation of the α -carboxyl sulfones VI and VII occurs readily at 150-180° under base catalysis, with the carboxylate ions being the labile species. It can be assumed, therefore, that the sulfone anions are formed as primary products of this reaction. The decarboxylation of optically active VI either in ethanol-water (2:1) or without solvent afforded phenyl 2-octyl sulfone with about 97 per cent stereospecificity. Optically active VI⁴ was obtained via the cinchonidine salt, $[\alpha]_{\text{D}}^{25} + 22.1^\circ$ (ether). In sharp distinction, the decarboxylation of optically active

³ See, for example, H.C. Brown, *Rec. Chem. Progr.* **14**, 83 (1953); *Bull. Soc. Chim.* **7**, 980 (1956).

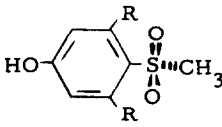
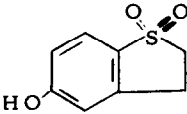
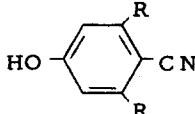
⁴ Satisfactory analytical data have been obtained.

cyclic acid VII under similar conditions gave completely racemic sulfone. The dextro isomer of VII⁴ $[\alpha]_{5460}^{25} + 59.0^\circ$ (ethanol) m.p. 161-162^o was prepared via the brucine salt. If the asymmetry of sulfone anions were due to pyramidal bonding to the α -carbon atom with a barrier to inversion, approximately the same degree of stereospecificity would be expected for the decarboxylation of VI and VII. The experimental results refute this possibility.^{5,6} It should be noted that the planar α -carbanion derived from VII must be optically inactive and requires total racemization.

Guided by the evidence that carbanions such as IV and V owe their asymmetry to a preferred rotational orientation about the α -carbon-sulfur bond as shown in II, we now inquire as to the reasons for the difference in stability between the anions II and III. Although this might arise from differences in overlap between the $p(C_\alpha)$ orbital and the SO_2 molecular orbitals no support for such a possibility has been found either in the most recent calculations of overlap integrals⁶ or in qualitative data on anion stability as summarized in Table 1.

TABLE 1

pK_a Values in H₂O at 25^o

		
VIII ^{7a} R=H 7.72	X 7.81	XI ⁸ R=H 7.95
IX ^{7b} R=CH ₃ 8.13		XII ⁸ R=CH ₃ 8.21

⁵ As asymmetric solvation (ref. 2^a) effects were generally important with sulfone anions the decarboxylation products of VII would be expected to show some optical activity.

⁶ Recent X-ray studies of tetramethylsulfamide, $(CH_3)_2NSO_2N(CH_3)_2$, show that the bonds to a given nitrogen in this compound are almost coplanar and lead to the conclusion that the planar form of the α -carbanions would

The sulfone X,⁴ m.p. 157.5-158.5° prepared from 5-methoxythianaphene⁹ in three steps, possesses the fixed geometry corresponding to anion III whereas the sulfones VIII and IX should prefer the conformation shown (analogous to II) to minimize interference with ortho groups. The data indicate a negligible angular overlap dependence especially when an allowance is made for non-overlap effects using the nitriles XI and XII as models. Thus, the difference between orientations II and III does not arise from differences in overlap of molecular orbitals.

Another possibility to account for the preference of configuration II over III is the occurrence of repulsive exchange interactions of the same type which cause staggered ethane to be more stable than the eclipsed form. Such interactions are expected to be serious for second-row elements of higher covalency. For a sulfone anion this effect can be estimated in the following way. Interaction is taken as proportional to the orders of the S-O and C-S bonds with assigned values of 2 and 1 respectively. The components of these values along an axis parallel to the axis of the p-orbital on the anionic α -carbon atom are calculated taking both OSO and $C_{\alpha}SC_{\alpha}$ angles as 120° for simplicity. The repulsion involving the C_{α} -S π -electrons and the RSO_2 group for the orientations II and III are then given by $3 \cos 30^{\circ} = 2.6$ and $4 \cos 30^{\circ} = 3.5$. The assumption that this repulsive interaction will be more important than those involving the more remote C_{α} - C_{β} σ -bond electrons, leads to the hypothesis that orientation III might be less stable than II because of this effect.¹⁰

6 (Contd.)

not represent a significant barrier to inversion. T. Jordan, W. Smith and W.N. Lipscomb, Tetrahedron Letters 2, 37 (1962).

7 This value compares closely with those previously measured ($pK_a = 7.83$)
^a F.G. Bordwell and G.D. Cooper, J. Amer. Chem. Soc. 74, 1058 (1952);
^b H. Kloosterziel and H.J. Baker, Rec. Trav. Chim. 72, 185 (1953).

8 G.W. Wheland, R.M. Brownell and E.C. Mayo, J. Amer. Chem. Soc. 70, 2492 (1948).

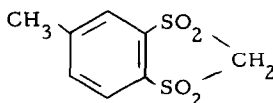
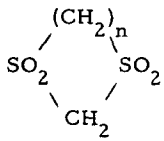
9 A.V. Sunthakar and B.D. Tilak, Proc. Indian Acad. Sci. 33A, 35 (1951).

10 This hypothesis is not inconsistent with the results given in Table 1 on phenol dissociation since repulsion effects would not be very different in corresponding phenol and phenoxide ion structures.

The relative stability of II might be further increased by an unequal distribution of π -electrons in the C_{α} -S bonds such that the electron density is concentrated in the π -region which is more removed from the oxygens of the SO_2 group, i.e. on the side of the obtuse rather than the acute OSO angle.¹¹

If the $p(C_{\alpha})-SO_2$ orientation expressed in II is more stable than that given by III, the difference ought to be detectable by measurement of ionization constants of cyclic sulfones for which preferred conformations are available. In Table 2 are presented data on a series of 1,3-disulfones.⁴

TABLE 2
pK_a Values in H₂O at 25°

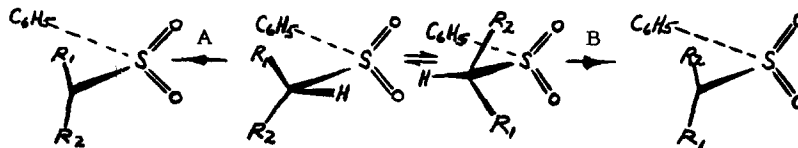
$(CH_3SO_2)_2CH_2$	12.50		12.63
	n=2 13.9 (approx.) n=3 12.61 n=4 11.75 n=5 10.99	$(C_6H_5SO_2)_2CH_2$	11.21

In agreement with expectation, the 8-membered cyclic anion (which in the sterically more probable conformation corresponds to the geometry of II) is relatively more stable than the 5-membered cyclic anion (corresponding to orientation III). In addition, there seems to be a gradual variation in the series between these extremes as expected from consideration of molecular models.

It is necessary at this point to comment on the stereochemistry of

¹¹ The peculiar relative arrangement of the two $N(CH_3)_2$ groups in tetramethylsulfamide (ref. 6) might be explained in this way. However, this geometry might also be controlled by intramolecular steric effects. Such steric effects provide still another possible interpretation of the difference in stability of the II- and III-type orientations as has already been pointed out (ref. 6).

formation of asymmetric anions having the geometry II from optically active sulfones. Starting from a sulfone of given configuration at the asymmetric α -carbon atom, either antipodal anion might be formed by proton removal, as indicated:



At present the predominant manner of proton transfer, A or B, is not known, but it is clear that there must be a large rate difference; this could originate from one or more of the following factors: (1) a purely steric effect operating because of a difference in non-bonded interactions in the transition states for paths A and B; (2) σ -bond eclipsing effects in the transition state; (3) unequal distribution of π -bonding electrons in the C_α -S bond relative to the nodal plane through the C_α -S axis as discussed above. (Since the electron density would be greater on the side of the π -nodal plane opposite the SO_2 oxygens, proton transfer from that side might be favored, i.e. path B.) The striking sensitivity of $k_{exc.}/k_{rac.}$ of phenyl 2-octyl sulfone to the nature of the base and/or medium^{2a} may be an indication of the operation of steric factors and an indication that in certain systems racemization may be due to simultaneous operation of processes A and B.¹²

Acknowledgments - We are indebted to the National Institutes of Health for financial support, to Dr. W.N. Lipscomb for helpful discussions and to Dr. R.S. Breslow for providing the aromatic, cyclic 1,3-disulfone. N.S.F. Fellowships to T.H.L. (1960-62) are also acknowledged.

¹² This differs from our previous conclusion¹ that the more important course of racemization (in aqueous ethanol) is anion isomerization rather than non-specific proton transfer. It now appears from subsequent work both in our system and those of Gram^{2a} that the isotope effect for proton transfer is actually too low to allow practical application of the kinetic distinction between these processes which is possible in theory.