Pyrolysis of Cyclohexyl Trichloromethanesulfenate.—This compound decomposed at 200° during 5 hr. to form cyclohexyl chloride and thiophosgene, together with much tar and a small amount of two unidentified volatile components.

Pyrolysis of *t*-Butyl Trichloroacetate.—The ester[18] (9.6 g.), on heating at 130° for 3 hr., decomposed to form only isobutylene (1.46 g., 75%) and trichloroacetic acid (7.36 g.; 97%).

Ultraviolet Irradiation of t-Butyl Trichloromethanesulfenate.—The ester was recovered almost quantitatively after the pure liquid, or a 30% solution in isoöctane, or a 10% solution in cumene, had each been exposed to very intensive ultraviolet irradiation in a Vycor tube under an atmosphere of nitrogen.

Photo-induced Polymerization of Styrene in the Presence of *t*-Butyl Trichloromethanesulfenate.[19]—Fifty ml. of styrene, containing 0.132 g. *t*-butyl trichlormethanesulfenate, and a blank containing no sulfenyl ester, were illuminated, under identical conditions, with a Westinghouse A-H-4 mercury vapor lamp under an atmosphere of nitrogen. After 17 hours, the amount of polystyrene formed was determined by precipitating it with methanol, washing with methanol, filtering, and drying at 100°. The sample with sulfenyl ester showed 17% polymerization, while the one without added ester showed 4% polymerization of the styrene.

Acknowledgment.—We are indebted to Mr. William R. Wilcox, who carried out initial experiments on the pyrolysis of *t*-butyl 2,4-dinitrobenzenesulfenate, the results of which were significant for the work reported in this paper.

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[18] W. E. Scovill, R. E. Burk and H. P. Lankelma, THIS JOURNAL, **66**, 1039 (1944).

[19] T. Otsu, *J. Polymer Sci.*, **21**, 559 (1956).

LOS ANGELES 7, CALIF.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

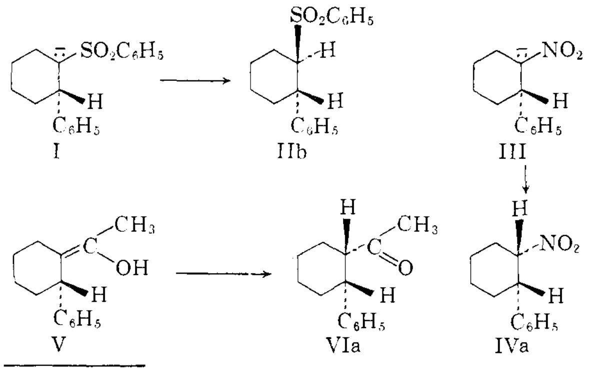
The Stereochemistry of Sulfone-stabilized Carbanions

BY HOWARD E. ZIMMERMAN AND B. S. THYAGARAJAN

RECEIVED SEPTEMBER 8, 1959

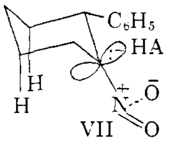
Cyclopropyl phenyl sulfone has been synthesized and its acidity compared with that of the acyclic analog isopropyl phenyl sulfone. The results of these experiments are considered in relation to the problem of the hybridization and geometry of a carbanion stabilized by the sulfone group.

In paper VII[1] of a series of publications dealing with the stereochemistry of proton transfer processes[2] there was reported the striking observation that protonation of the conjugate base (I) of 1-benzenesulfonyl-2-phenylcyclohexane (II) affords the *trans* isomer IIb of II as the kinetically preferred product. This result contrasts with the preferential formation of *cis*-1-nitro-2-phenylcyclohexane (IVa) from its conjugate base III[3] as well with the situation in ketonization of exocyclic enols and enolates where again the *cis* product is preferred.[4,5]

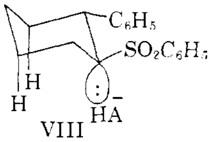


I IIb III V VIa IVa

The differing behavior of the nitro- and sulfone-stabilized anions is rationalized on the basis of dissimilar transition state geometries as illustrated



VII



VIII

It was suggested that electron delocalization from the carbon atom undergoing protonation is much more important in the nitro case than in the sulfone example. As a consequence, in the nitro transition state the carbon atom undergoing bonding is close to being sp^2-hybridized with the bonding electron pair being in a p-orbital. A p-orbital efficiently provides the required overlap with the nitro group, such overlap being needed for electron delocalization. In contrast, with delocalization less important in the sulfone case, the bonding electron pair becomes localized in a nearly sp^3 orbital with the resulting tetrahedral geometry.[6]

Evidence thus having been obtained that the *transition state* for protonation of the sulfone stabilized carbonaion is tetrahedral, it seemed of interest to consider the geometry of the *sulfone carbanion itself.* This question has been considered

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[1] H. E. Zimmerman and B. S. Thyagarajan, THIS JOURNAL, **80**, 3060 (1958).

[2] For the first paper of this series and an introduction to the problem of the stereochemistry of carbanion and enol protonation, see H. E. Zimmerman, *J. Org. Chem.*, **20**, 549 (1955); for paper IX see H. E. Zimmerman and A. Mais, THIS JOURNAL, **81**, 3644 (1959).

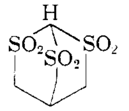
[3] H. E. Zimmerman and T. E. Nevins, *ibid.*, **79**, 6559 (1957).

[4] Note, for instance, ketonization of the enol of 1-acetyl-2-phenylcyclohexane which affords mainly the less stable *cis*-ketone [H. E. Zimmerman, *ibid.*, **79**, 6554 (1957)].

[5] The comparison of the nitro example with the sulfone anion case is valid since it has been shown (ref. 3) that it is indeed the conjugate base of the nitro compound rather than the *aci*-nitro tautomer which is being protonated in the transition state. Comparison with enol ketonization is less justified since only one of the several mechanisms operative under ordinary ketonization conditions involves protonation of the enolate anion.

[6] That sp^2 hybridization as in VII and sp^3 hybridization as in VIII should lead to preferential formation of *cis* and *trans* products, respectively, is clear when one considers that in VII the nitro group is in a plane symmetrical with respect to the two possible approaches of the proton donor and thus itself does not influence this approach; the less hindered attack is indicated in VII. On the other hand, the sulfonyl group in VIII has two possible conformations; the preferred one in which this large group is equatorial is illustrated in VIII. Evidence has been given (ref. 1) that as the size of HA increases, the relative energy of VIII is raised.

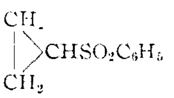
by Doering[7] who observed that the tricyclic sulfone IX is less acidic than its acyclic analog trisethylsulfonylmethane. It was pointed out that this difference could derive from strain in-



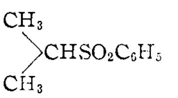
IX

curred in achieving the sp^2 hybridization of the bridgehead carbon atom which would be necessary if sulfone carbanions are indeed stabilized by electron delocalization (*i.e.*, resonance stabilized).

As another approach to the problem it seemed of interest to investigate the acidity of cyclopropyl phenyl sulfone (X) in relation to that of the acyclic analog isopropyl phenyl sulfone (XI).



X



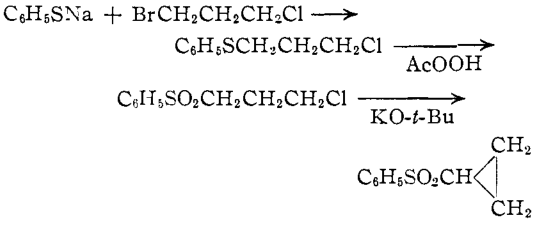
$$\begin{matrix} CH_3 & \\ & \rangle CHSO_2C_6H_5 \\ CH_3 & \end{matrix}$$

XI

In the event that sulfone carbanions are indeed stabilized by electron delocalization, there was reason to expect that the cyclopropyl compound X would be a weaker acid than XI, while in the event that delocalization is nil, it was anticipated that X would be a stronger acid than XI. This reasoning is discussed in connection with the results (*vide infra*).

Required for our study was a synthesis of the previously unknown cyclopropyl phenyl sulfone (X) along with that of the known[8] XI and also a means of comparing acidities of these compounds.

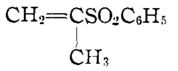
A convenient synthesis of cyclopropyl phenyl sulfone[9] was found in the potassium *t*-butoxide-catalyzed cyclization of γ-chloropropyl phenyl sulfone. This in turn was synthesized[10] by the following route.



$$C_6H_5SNa + BrCH_2CH_2CH_2Cl \longrightarrow C_6H_5SCH_2CH_2CH_2Cl \xrightarrow[AcOOH]{} C_6H_5SO_2CH_2CH_2CH_2Cl \xrightarrow[KO\text{-}t\text{-}Bu]{} C_6H_5SO_2CH\langle(CH_2)_2$$

X

One might concern himself with the possibility of the product being an unsaturated isomer of X such as XII, XIII or XIV. Formation of these acyclic isomers from an initially formed cyclopropyl phenyl sulfone or directly from γ-chloropropyl phenyl sulfone by *t*-butoxide-catalyzed processes is not mechanistically impossible. However, the evidence which follows clearly and decisively excludes such possibilities.



$$\begin{matrix} CH_2{=}CSO_2C_6H_5 \\ | \\ CH_3 \end{matrix}$$

XII

$CH_2{=}CHCH_2SO_2C_6H_5$

XIII

$CH_3CH{=}CHSO_2C_6H_5$

XIV

In the first place, compound X was found to be resistant to both bromine in carbon tetrachloride as well as to dilute permanganate as would be expected. Also, this compound exhibited an ultraviolet maximum at 219 mμ (log ϵ 4.07); interestingly, this is the absorption expected for a saturated alkyl phenyl sulfone. For example, methyl phenyl sulfone and *t*-butyl phenyl sulfone have been reported[11] to absorb at 217 mμ (log ϵ 3.83) and 216 mμ (log ϵ 3.94), respectively. On the other hand, the vinyl phenyl sulfones, vinyl phenyl sulfone[12] and 2-phenylcyclohexenyl phenyl sulfone[1] have been reported[1,12] to absorb at 225 mμ (log ϵ 4.1) and 226 mμ (log ϵ 4.3), respectively.

Also of interest was the infrared spectrum which contained only a doublet at 3.28 and 3.33 μ in the carbon–hydrogen stretching region; this contrasts with the spectrum of isopropyl phenyl sulfone which has bands at 3.29, 3.38, 3.42 and 3.50 μ. Absorption at 3.28 and 3.33 μ derives here from cyclopropane carbon–hydrogen stretching[13] as well as from aromatic carbon–hydrogen stretching.[14a] The lack of absorption at 3.38 and 3.50 μ, in a region characteristic of methyl and unstrained methylene carbon–hydrogen absorption,[14b] is further evidence in favor of the cyclopropane structure for X.

Finally, evidence was obtained by treatment of X with sodium deuteroxide in excess deuterium oxide and anhydrous dioxane. Mass spectrographic analysis[15] of the product showed this to contain 0.98 deuterium atom per molecule, a result compatible only with the cyclopropyl phenyl sulfone formulation for X. Since XIII and XIV should interconvert under the alkaline deuteration conditions and since in XIII the α-hydrogen atoms are exchangeable due to activation by the sulfone group while in XIV the γ-hydrogen atoms are vinylogously activated, one would predict XIII and XIV to afford a tetradeuterated product. Compound XII would be expected to exchange only very slowly since a relatively unstable simple allylic carbanion would have to be involved; with a stronger base this compound would exchange five hydrogen atoms.

The necessary cyclopropyl phenyl sulfone being available, it was possible to proceed with consideration of the acidity of this compound relative to isopropyl phenyl sulfone. This required a study of the position of equilibrium of a mixture of the two sulfones and their conjugate bases (equation 2 of Chart I).

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[7] W. v. E. Doering and L. K. Levy, THIS JOURNAL, **77**, 509 (1955).

[8] W. A. Baldwin and R. Robinson, *J. Chem. Soc.*, 1447 (1932).

[9] We have learned from Professor W. E. Truce of Purdue University that he has synthesized this compound independently but similarly.

[10] The synthesis of γ-chloropropyl phenyl sulfide and γ-chloropropyl phenyl sulfone employed a modification of procedures described by A. Kretow and J. Toropova, *J. Gen. Chem. U.S.S.R.*, **7**, 2009 (1937).

[11] E. Fehnel and M. Carmack, THIS JOURNAL, **71**, 231 (1949).

[12] C. C. Price and H. Morita, *ibid.*, **75**, 4747 (1953).

[13] V. Slabey, *ibid.*, **76**, 3604 (1954); in the present case, longer wave length absorption bands reported as characteristic of the cyclopropane ring were not helpful, since not only X but also isopropyl phenyl sulfone exhibited several bands in this general region.

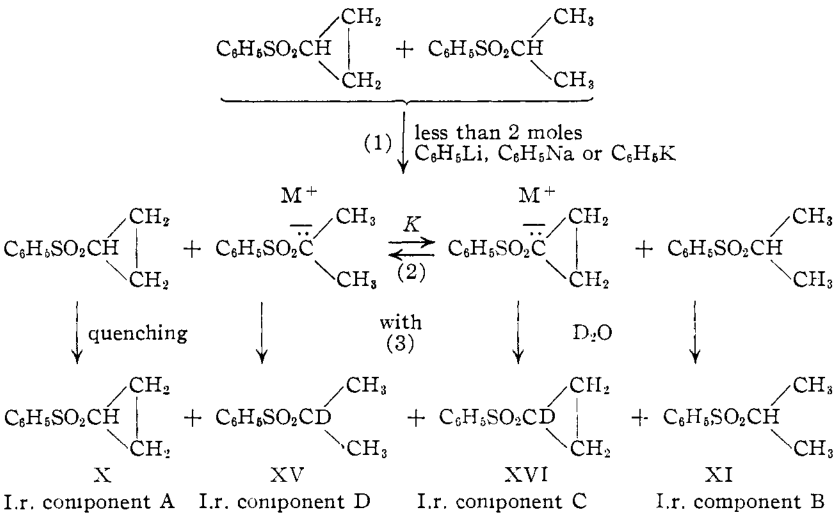
[14a] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 55. This absorption is also characteristic of olefinic carbon–hydrogen bonds.

[14b] Reference 14a, p. 13.

[15] Kindly run by S. Meyerson, Standard Oil of Indiana.

CHART I

DETERMINATION OF RELATIVE ACIDITIES



The anions were generated by treatment of a 1:1 mixture of the two sulfones with one of three strong bases—phenyllithium, phenylsodium and phenylpotassium—as depicted in equation 1 of Chart I. In each experiment the anionic mixture was allowed to equilibrate for a given time and then was quenched with deuterium oxide as indicated in equation 3 of Chart I; at the end of a 60-sec. reaction period the mixture of deuterated and undeuterated sulfones was washed free of base. The resulting four-component mixture—containing cyclopropyl phenyl sulfone (designated component A), isopropyl phenyl sulfone (B), cyclopropyl phenylsulfone-*α-d* (C) and isopropyl phenyl sulfone-*α-d* (D)—was then analyzed by an infrared procedure described in the Experimental section; as may be noted from Table V, analysis of seven synthetic mixtures indicated an average absolute error of ±2% units of any one component. The amount of each of the deuterated sulfones was taken to be equal to the quantity of the corresponding sulfone anion before quenching with deuterium oxide and similarly the amount of each of the undeuterated sulfones is considered to be that present before quenching. This assumption must, however, be justified.

One might concern himself about two serious possibilities. The first derives from the fact that on addition of deuterium oxide (equation 3) to the mixture of sulfone anions and sulfones there is generated deuteroxide anion which, being itself a base, might catalyze deuteration of cyclopropyl phenyl sulfone and isopropyl phenyl sulfone present in the mixture. The second troublesome possibility is that deuterium might be lost during the washing with water following quenching. Actually, proton removal from a sulfone by deuteroxide or hydroxide would be expected to be a slow process compared to the reaction of sulfone anions with deuterium oxide or water. This view was supported by the long period of reflux required to deuterate cyclopropyl phenyl sulfone and isopropyl phenyl sulfone on treatment with sodium deuteroxide–deuterium oxide.

Two further sources of evidence bearing on possible equilibration during or subsequent to quenching are available. In the first place, when either cyclopropyl phenyl sulfone or isopropyl phenyl sulfone was treated with somewhat more than one mole of phenyllithium and then was quenched and worked up in the usual manner, completely deuterated sulfone was obtained, thus excluding the possibility of loss of deuterium during washing. Secondly, in the runs made with the mixture of sulfones and less than two moles of the strong base, the extent of deuteration never exceeded that corresponding to the amount of strong base employed. Equilibration during quenching would have further increased the deuterium content.

Having been convinced that the distribution of deuterated and undeuterated sulfones corresponds to that of the sulfone anions and sulfones before quenching, one may proceed to the results of the equilibration experiments which are listed in Tables I and II.

TABLE I

RESULTS OF EQUILIBRATION OF LITHIUM CONJUGATE BASES

Run	Time before quenching	Relative amount[b] A	B	C	D	Extent of deuteration[c]	$\frac{B \cdot C}{A \cdot D}$
1	<1 sec.	36.9	40.7	18.3	13.6	0.29	1.1
2	5 sec.	33.5	36.3	24.5	15.7	.37	1.7
3	15 sec.	28.0	26.0	21.0	16.0	.41	1.2
4	30 sec.	36.2	34.4	17.5	15.6	.32	1.1
5	5 min.	24.9	26.2	29.8	26.7	.53	1.2
6	2 hr.	28.0	32.3	28.7	20.2	.45	1.6
7	17 hr.	36.2	24.6	19.6	10.6	.30	1.8
8[a]	2 hr.	36.4	45.3	19.3	13.3	.29	1.8

[a] Phenyllithium and cyclopropyl phenyl sulfone were allowed to react for 30 min. followed by addition of isopropyl phenyl sulfone. The mixture was quenched after an additional 2 hr. [b] 100 q_i as defined in Experimental section. [c] (C + D)/(A + B + C + D).

TABLE II

RESULTS OF EQUILIBRATION OF SODIUM AND POTASSIUM CONJUGATE BASES

Run	Time before quenching, hr.	Relative amount A	B	C	D	Extent of deuteration	$\frac{B \cdot C}{A \cdot D}$
9[a]	3	43.5	55.0	8.99	2.34	0.10	(4.8)
10[a]	6	32.6	34.8	20.1	10.7	.31	2.0
11[a]	16	31.5	23.3	1.22	2.22	.06	(0.41)
12[b]	13	54.6	10.1	23.0	5.28	.31	0.80
13[c]	3	46.4	62.9	48.1	24.3	.40	2.7

[a] Run with phenylsodium prepared from chlorobenzene. [b] Run with phenylsodium prepared from diphenylmercury. [c] Run with phenylpotassium.

Of these results it may be observed that runs made with phenyllithium as the base afford an average value of 1.4 ± 0.4 for K = (BC)/(AD), the equilibrium constant for equation 2 of Chart I.

There is no obvious dependence on the time of equilibration; and a similar value resulted when as in run 8 isopropyl phenyl sulfone was added only after ionization of cyclopropyl phenyl sulfone had been effected with phenyllithium. Thus equilibrium is very rapidly attained.

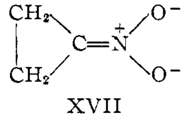
The results given in Table II for equilibration of sodium and potassium conjugate bases are less precise. Runs 9 and 11 are the least reliable, since due to the low extent of deuteration, the possible infrared analytical error of 2% units of each component is large compared to the quantity of some of the components. However, in runs 10, 12 and 13, where these errors are less troublesome, an average value of 1.8 ± 1.0 is obtained for K.

Thus it is observed that the equilibrium constant shows no large dependence either on the nature of the metal cation involved or on the homogeneity (in the case of the lithium experiments) or heterogeneity (as for the alkali metal runs) of the equilibration mixture.

Most interesting is the finding that the equilibrium constant for equation 2 of Chart I is not far from unity. This contrasts with two situations reported in the literature, one in which the cyclopropane ring shows enhanced acidity and the other in which it leads to depressed acidity.

Evidence is available that cyclopropane itself is considerably more acidic than a simple alkane. Morton[16] has shown that amylsodium is able to remove a proton from cyclopropane while metalation of other saturated hydrocarbons has not proved possible. Also, the interesting finding has been reported by Hart[17] that cyclopropyllithium does not add nucleophilically to ethylene in contrast to the addition of isopropyllithium reported by Bartlett, Friedman and Stiles.[18] The greater acidity of cyclopropane and enhanced stability of its conjugate base compared to acyclic systems seems to be a result of the greater *s* character of the carbon orbitals involved in bonding to the hydrogen atoms of cyclopropane.[19]

At the other end of the structural spectrum is the situation reported for nitrocyclopropane by Hass and Schechter[20]; here nitrocyclopropane is so much less acidic than 2-nitropropane that it is insoluble in strong aqueous base. This has been rationalized by these authors who attributed the weak acidity to internal strain[21] involved in formation of the anion which, to be stable, would have to receive a resonance contribution from structure XVII.



XVII

This is tantamount to saying that formation of an anion stabilized by delocalization of the electron pair and negative charge from the three-membered ring requires that the hybridization of the orbitals used for bonding ring carbon atoms together changes from $sp^{4.12}$ (*cf.* footnote 19) to a hybrid orbital less heavily weighted in *p*-character, since a *p*-orbital must then be reserved for overlap with the delocalizing group. Such a decrease in p-character is energetically unfavorable, since the inter-orbital angle (θ in Fig. 1), which is already greater than the 60° value which would maximize sigma overlap between ring carbon atoms, is increased further with such a change.

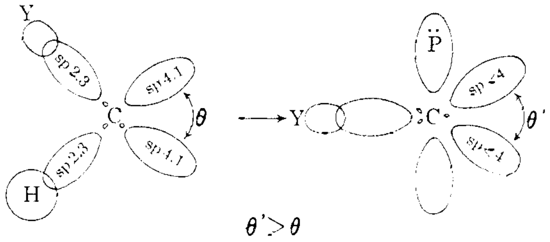


Fig. 1.—Ring carbon bearing the delocalizing group Y.

Having noted the enhanced acidity of cyclopropane anions where electron delocalization is unimportant and the contrasting inhibition of acidity of anions where acidity is dependent on such delocalization, one finds the case of cyclopropyl phenyl sulfone significant, since its nearly equal acidity compared to the acyclic analog means that the two effects have just cancelled one another. Thus one may conclude that in a carbanion stabilized by a sulfone group only some of the stabilization derives from electron delocalization and that there is only an approach to the planar geometry associated with such stabilization.

Experimental[22]

γ-Chloropropyl Phenyl Sulfide.—To a mixture of 94.2 g. (61.5 ml., 0.60 mole) of trimethylene chlorobromide and 100 ml. of dioxane in a 500-ml. flask equipped with glass paddle stirrer, reflux condenser and dropping funnel there was added dropwise with stirring a solution of sodium thiophenolate prepared from 55.1 g. (51.0 ml., 0.50 mole) of thiophenol, 22.0 g. (0.51 mole) of sodium hydroxide and 250 ml. of water. The addition was made over 40 min. during which time the temperature rose to 45°. The two- phase system was then stirred for an additional three hours. Following this, 200 ml. of water was added and the mixture hexane-extracted, the extracts dried over sodium sulfate and concentrated *in vacuo*. The residue was distilled to give two fractions of product: I, b.p. 79–80° at 0.7 mm., $n^{25}D$ 1.5721, weighing 17.69 g.; and II, b.p. 80–82° at 0.7 mm., $n^{25}D$ 1.5725, weighing 61.56 g. (total yield 86%) (reported[23] $n^{20}D$ 1.5752, b.p. 116–117° at 4 mm.).

γ-Chloropropyl Phenyl Sulfone.[10]—To a refluxing mixture of 18.7 g. (0.10 mole) of γ-chloropropyl phenyl sulfide and 70 ml. of acetic acid in a 300-ml. three-neck flask fitted with glass paddle stirrer, reflux condenser, dropping funnel and Glas-col heater was added 30.0 ml. (0.34 mole) of 30% hydrogen peroxide. The addition required 20 min., and during the latter half of this time Glas-col heating had to be lessened due to the exothermicity of the reaction. Refluxing was then continued for an additional 30 min. The mixture was cooled, diluted with 300 ml. of water and benzene-extracted. The benzene extracts were washed repeatedly

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[16] E. J. Lampher, L. M. Redman and A. A. Morton, *J. Org. Chem.*, **23**, 1370 (1958).

[17] H. Hart and J. M. Sandri, *Chemistry & Industry*, 1014 (1956).

[18] P. D. Bartlett, S. Friedman and M. Stiles, THIS JOURNAL, **75**, 1771 (1953).

[19] These orbitals have been estimated as being $sp^{2.28}$ while the orbitals used in joining ring atoms are $sp^{4.12}$; *cf.* L. L. Ingraham in "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 518, for a discussion and references.

[20] H. B. Hass and H. Schechter, *ibid.*, **75**, 1382 (1953).

[21] H. C. Brown and M. Gerstein, *ibid.*, **72**, 2926 (1950); H. C. Brown, R. S. Fletcher and R. B. Johannesen, *ibid.*, **73**, 212 (1959).

[22] All melting points were taken on a Fisher–Johns block whose thermometer had been checked with compounds of known melting point.

[23] W. Kirner and G. Richter, THIS JOURNAL, **51**, 3413 (1929).

with aqueous sodium thiosulfate until no color was obtained with starch–iodide paper. The benzene solution was then washed with water and dried over sodium sulfate; the dried solution was concentrated *in vacuo*. Distillation of the residue in a modified Claisen apparatus gave the following fractions: I, 2.30 g., b.p. 140–141° at 0.010 mm., $n^{25}\mathrm{D}$ 1.5467; II, 10.04 g., b.p. 137–140° at 0.005 mm., $n^{25}\mathrm{D}$ 1.5470; III, 4.47 g., b.p. 140–157° at 0.02–0.04 mm., $n^{25}\mathrm{D}$ 1.5467.

Anal. Calcd. for $C_9H_{11}SO_2Cl$: C, 49.43; H, 5.06. Found: C, 49.15; H, 4.65.

Cyclopropyl Phenyl Sulfone.—To a solution of sodium *t*-butoxide prepared from 2.76 g. of sodium and 60.0 ml. of *t*-butyl alcohol was added 21.9 g. of γ-chloropropyl phenyl sulfone, and the solution was stirred and refluxed for 6 hr. At the end of this time it was cooled, diluted with 200 ml. of water, ether extracted and the extracts washed with water, dried over sodium sulfate and concentrated under vacuum. Distillation of the residue afforded 12.6 g. of a colorless oil boiling at 128–130° at 0.01 mm. On cooling in ice this solidified to a colorless solid melting at 35–36°.

Anal. Calcd. for $C_9H_{10}SO_2$: C, 59.33; H, 5.53. Found: C, 59.07, 58.74, 58.60; H, 5.47, 5.50, 5.44.

The ultraviolet spectrum in 95% ethanol exhibited a maximum at 218 mμ (log ε 3.99) and much weaker bands at 264 and 271 mμ. The infrared spectrum contained only a doublet at 3.28 and 3.33 μ in the carbon–hydrogen stretching region. Strong absorption bands appeared at 7.59, 7.73, 8.68, 9.16, 11.23, 12.11, 13.10, 13.77, 14.52, 14.71 μ. The n.m.r. spectrum showed three types of hydrogen atoms, aromatic, aliphatic CH_2 and tertiary hydrogen.

Isopropyl Phenyl Sulfide.—To a mixture of 40.0 g. (1.0 mole) of sodium hydroxide pellets and 400 ml. of ethanol was added with stirring 110.0 g. (1.0 mole) of thiophenol. During the addition some heat was evolved, and the mixture was stirred for one hour during which time the sodium hydroxide pellets had dissolved. To this stirred solution was then added 123.0 g. (1.0 mole) of 2-bromopropane over a 20-min. period; heat was evolved and sodium bromide separated. After an additional 90 min. of refluxing the mixture was diluted with 1 l. of water and extracted with 1:1 ether–hexane. The extract was dried over sodium sulfate and concentrated *in vacuo*. Distillation of the residue yielded 11.65 g., b.p. 83° at 10.0 mm., $n^{25}\mathrm{D}$ 1.5436; and 120.64 g., 83° at 10.0 mm., $n^{25}\mathrm{D}$ 1.5439 (reported[11] b.p. 97° at 20 mm.).

Isopropyl Phenyl Sulfone.—To 76.0 g. (0.5 mole) of isopropyl phenyl sulfide dissolved in 100 ml. of acetic acid was added with stirring during 45 min. 249.0 ml. (1.0 mole) of peracetic acid solution (Becco 40% in acetic acid). The reaction mixture was cooled with an ice-bath during addition so that the temperature did not rise above 40°. After an additional hour the mixture was diluted with 1 l. of water, extracted with 1:1 benzene–hexane and the extracts thoroughly washed with saturated sodium thiosulfate solution and then with water. Concentration under vacuum followed by distillation of the residue afforded 1.88 g., b.p. 113° at 0.30 mm., $n^{25}\mathrm{D}$ 1.5293; and 68.25 g., b.p. 112–113° at 0.30 mm., $n^{25}\mathrm{D}$ 1.5302 (reported[8] b.p. 145–150° at 1 mm.). The infrared spectrum of this material was similar to that of cyclopropyl phenyl sulfone in possessing strong sulfone absorption bands in the 7.6 and 8.7 μ regions. Unlike the spectrum of cyclopropyl phenyl sulfone it exhibited carbon–hydrogen stretching bands at 3.29, 3.38, 3.42 and 3.50 μ.

Cyclopropyl Phenyl Sulfone-*α-d*.—To a solution of 6.0 g. of 98% deuterium oxide in 30.0 ml. of pure, anhydrous dioxane was added 0.60 g. of sodium. After complete reaction of the sodium 5.4 g. of cyclopropyl phenyl sulfone was added and the mixture was refluxed for 24 hr. The cooled solution was then diluted with water and ether extracted, the extracts washed to neutrality, dried over sodium sulfate and concentrated *in vacuo*. The infrared spectrum of the residual oil showed the presence of non-deuterated starting material; hence this material was recycled under conditions identical with those above. The resulting product was distilled to give 4.70 g. boiling at 112–114° at 0.005 mm. and melting at 35.5–36.0°. The infrared spectrum of the product possessed new absorption bands at 8.00, 9.60, 10.88 and 11.17 μ not present in the starting material; the spectrum lacked absorption at 12.71 μ characteristic of the starting material. Mass spectrographic analysis[15] indicated the monodeuterated species to constitute 97.9 ± 0.4% of the product. The ultraviolet spectrum possessed a maximum at 219 mμ (log ε 4.07) indicating no change in the absorbing system from that of undeuterated starting material. The n.m.r. spectrum showed only two types of hydrogen atoms.

Reaction of Cyclopropyl Phenyl Sulfone-*α-d* with Aqueous Sodium Hydroxide; Evidence against Skeletal Isomerization During Deuteration.—A mixture of 1.80 g. of cyclopropyl phenyl sulfone-*α-d* and a sodium hydroxide solution prepared from 0.20 g. of sodium and 2.00 ml. of water dissolved in 10.0 ml. of dioxane was refluxed for 24 hr. The cooled mixture was then diluted with 300 ml. of ether and the ether solution washed with water to neutrality, dried over sodium sulfate and concentrated *in vacuo*. The remaining oil weighed 1.7 g.; its infrared spectrum was identical with that of authentic cyclopropyl phenyl sulfone.

Isopropyl Phenyl Sulfone-*α-d*.—To a solution of sodium deuteroxide prepared from 0.60 g. of sodium, 6.0 ml. of 98% deuterium oxide and 30 ml. of anhydrous dioxane was added 5.4 g. of isopropyl phenyl sulfone. The mixture was refluxed for 24 hr., cooled, diluted with water and ether extracted. The extracts were washed to neutrality, dried over sodium sulfate and concentrated under vacuum. The residual oil was recycled under the same equilibrating conditions to yield a product distilling at 113° at 0.3 mm. Mass spectrographic analysis showed 94.0 ± 0.5% to consist of the monodeuterated species. The n.m.r. indicated absence of the tertiary hydrogen atom. The infrared spectrum showed an absence of the 7.92, 9.50 and 11.40 μ bands characteristic of isopropyl phenyl sulfone as well as the appearance of 8.41 and 10.86 μ bands characteristic of isopropyl phenyl sulfone-*α-d*.

Infrared Analysis of Four-component Mixtures of Cyclopropyl Phenyl Sulfone, Cyclopropyl Phenyl Sulfone-*α-d*, Isopropyl Phenyl Sulfone and Isopropyl Phenyl Sulfone-*α-d*.—For calibration purposes the spectra of the four pure compounds and seven synthetic mixtures of known composition were run in 0.1-mm. cells at a concentration of 50 mg./0.40 ml. of CS_2. The optical densities were recorded at the following four analytical wave lengths: 7.92 μ (characteristic of isopropyl phenyl sulfone), 8.40 μ (characteristic of cyclopropyl phenyl sulfone and isopropyl phenyl sulfone-*α-d*), 9.60 μ (characteristic of cyclopropyl phenyl sulfone and cyclopropyl phenyl sulfone-*α-d*) and 12.72 μ (characteristic of cyclopropyl phenyl sulfone). These values are listed in Table III.

From the optical densities determined for the four pure reference compounds the values of the 16 third-order determinants—Y'_{a}, Y'_{b}, Y'_{c}, Y'_{d}, Y''_{a}, Y''_{b}, Y''_{c}, Y''_{d}, Y'''_{a}, Y'''_{b}, Y'''_{c}, Y'''_{d}, $Y^{\prime\mathrm{v}}_{\mathrm{a}}$, $Y^{\prime\mathrm{v}}_{\mathrm{b}}$, $Y^{\prime\mathrm{v}}_{\mathrm{c}}$, $Y^{\prime\mathrm{v}}_{\mathrm{d}}$—and the fourth-order determinant X were obtained, these determinants being defined as:

$$Y'_{\mathrm{a}} = +\begin{vmatrix} D''_{\mathrm{b}} & D''_{\mathrm{c}} & D''_{\mathrm{d}} \\ D'''_{\mathrm{b}} & D'''_{\mathrm{c}} & D'''_{\mathrm{d}} \\ D^{\prime\mathrm{v}}_{\mathrm{b}} & D^{\prime\mathrm{v}}_{\mathrm{c}} & D^{\prime\mathrm{v}}_{\mathrm{d}} \end{vmatrix} \qquad Y''_{\mathrm{a}} = -\begin{vmatrix} D'_{\mathrm{b}} & D'_{\mathrm{c}} & D'_{\mathrm{d}} \\ D'''_{\mathrm{b}} & D'''_{\mathrm{c}} & D'''_{\mathrm{d}} \\ D^{\prime\mathrm{v}}_{\mathrm{b}} & D^{\prime\mathrm{v}}_{\mathrm{c}} & D^{\prime\mathrm{v}}_{\mathrm{d}} \end{vmatrix}$$

$$Y'''_{\mathrm{a}} = +\begin{vmatrix} D'_{\mathrm{b}} & D'_{\mathrm{c}} & D'_{\mathrm{d}} \\ D''_{\mathrm{b}} & D''_{\mathrm{c}} & D''_{\mathrm{d}} \\ D^{\prime\mathrm{v}}_{\mathrm{b}} & D^{\prime\mathrm{v}}_{\mathrm{c}} & D^{\prime\mathrm{v}}_{\mathrm{d}} \end{vmatrix} \qquad Y'_{\mathrm{b}} = -\begin{vmatrix} D''_{\mathrm{a}} & D''_{\mathrm{c}} & D''_{\mathrm{d}} \\ D'''_{\mathrm{a}} & D'''_{\mathrm{c}} & D'''_{\mathrm{d}} \\ D^{\prime\mathrm{v}}_{\mathrm{a}} & D^{\prime\mathrm{v}}_{\mathrm{c}} & D^{\prime\mathrm{v}}_{\mathrm{d}} \end{vmatrix}$$

$$\text{etc. and X} = \begin{vmatrix} D'_{\mathrm{a}} & D'_{\mathrm{b}} & D'_{\mathrm{c}} & D'_{\mathrm{d}} \\ D''_{\mathrm{a}} & D''_{\mathrm{b}} & D''_{\mathrm{c}} & D''_{\mathrm{d}} \\ D'''_{\mathrm{a}} & D'''_{\mathrm{b}} & D'''_{\mathrm{c}} & D'''_{\mathrm{d}} \\ D^{\prime\mathrm{v}}_{\mathrm{a}} & D^{\prime\mathrm{v}}_{\mathrm{b}} & D^{\prime\mathrm{v}}_{\mathrm{c}} & D^{\prime\mathrm{v}}_{\mathrm{d}} \end{vmatrix}$$

Here the superscripts (′,″,‴ and ′ᵛ) refer to the analytical wave lengths involved, 7.92, 8.40, 9.60 and 12.72 μ, respectively, while the subscripts (a, b, c and d) refer to the pure reference compounds—namely cyclopropyl phenyl sulfone (A), isopropyl phenyl sulfone (B), cyclopropyl phenyl sulfone-*α-d* (C), and isopropyl phenyl sulfone-*α-d* (D). Each third-order *Y* determinant is obtained by deleting that row and column of the *X* determinant corresponding to the superscript as well as subscript of *Y*, with the sign being positive or negative according to the even or odd sum of the numbers of the row and column deleted.

The relative concentrations (q_{a}, q_{b}, q_{c} and q_{d}) of the four components are then given for any mixture by the equations

$$q_{\mathrm{a}} = (C_{\mathrm{am}}/C_{\mathrm{a}}) = [D'Y'_{\mathrm{a}} + D''Y''_{\mathrm{a}} + D'''Y'''_{\mathrm{a}} + D^{\prime\mathrm{v}}Y^{\prime\mathrm{v}}_{\mathrm{a}}](1/X)$$

$$q_{\mathrm{b}} = (C_{\mathrm{bm}}/C_{\mathrm{b}}) = [D'Y'_{\mathrm{b}} + D''Y''_{\mathrm{b}} + D'''Y'''_{\mathrm{b}} + D^{\prime\mathrm{v}}Y^{\prime\mathrm{v}}_{\mathrm{b}}](1/X)$$

$$q_c = (C_{\mathrm{cm}}/C_{\mathrm{c}}) = [D'Y'_{\mathrm{c}} + D''Y''_{\mathrm{c}} + D'''Y'''_{\mathrm{c}} + D'^{\mathrm{v}}Y'^{\mathrm{v}}_{\mathrm{c}}](1/X)$$

$$q_d = (C_{\mathrm{dm}}/C_{\mathrm{d}}) = [D'Y'_{\mathrm{d}} + D''Y''_{\mathrm{d}} + D'''Y'''_{\mathrm{d}} + D'^{\mathrm{v}}Y'^{\mathrm{v}}_{\mathrm{d}}](1/X)$$

Here C_{am}, C_{bm}, etc., represent the concentration of components a, b, etc., in the given mixture while C_{a}, C_{b}, etc., are the concentrations at which the pure compounds were run during calibration; D', D'', etc., are optical densities of the given mixture at the four analytical wave lengths. Since the pure reference compounds were run at the same concentration, the q's give the relative concentration of the components.

TABLE III

OPTICAL DENSITIES OF PURE COMPOUNDS AND SYNTHETIC MIXTURES AT FOUR ANALYTICAL WAVE LENGTHS

Material run	D'	D''	D'''	D'^{v}
Cyclopropyl phenyl sulfone	0.0362	0.2965	0.3565	0.2403
Isopropyl phenyl sulfone	.3565	.0434	.0315	.0177
Cyclopropyl phenyl sulfone-*α-d*	.0969	.0531	.3872	.0506
Isopropyl phenyl sulfone-*α-d*	.0555	.4202	.0223	.0200
Synthetic mixt. 1	.1107	.2480	.1738	.0969
Synthetic mixt. 2	.0969	.2676	.1612	.0458
Synthetic mixt. 3	.1457	.2076	.1675	.0339
Synthetic mixt. 4	.0757	.2076	.3096	.1089
Synthetic mixt. 5	.1337	.1904	.1904	.0706
Synthetic mixt. 6	.1871	.1107	.1904	.0531
Synthetic mixt. 7	.0835	.2528	.1675	.0862

Table IV lists the values of (Y/X) for each component and wave length, as determined from the calibration spectra, while Table V gives the results of analysis of the seven synthetic mixtures, taking the percentage of each component i as directly equal to $100q_i$.

TABLE IV

VALUES OF (Y/X) USED IN ANALYZING MIXTURES

Component	Wave length λ'	λ''	λ'''	λ'^{v}
A	−0.1869	−0.1973	+0.6271	+5.3634
B	+2.8626	− .3954	−0.8306	+1.2888
C	−0.05178	+ .06689	+3.2206	−4.8527
D	−0.1573	+2.5514	+0.1213	−3.3044

Reaction of Isopropyl Phenyl Sulfone with Phenyllithium Followed by Deuterium Oxide Quenching.—A solution of 0.92 g. (5.00 mmole) of isopropyl phenyl sulfone in 20.0 ml. of anhydrous ether was treated with 6.0 ml. (5.54 mmole) of a stock solution of 0.924 *N* phenyllithium. The clear yellow-brown solution was stirred under nitrogen at room temperature for 2 hr. and then treated with 1.00 ml. of 98% deuterium oxide, stirred for 1 min., diluted with water, extracted with ether, and the extracts washed to neutrality with water and dried over sodium sulfate. Concentration *in vacuo* left 0.73 g. of oil whose infrared spectrum showed complete deuteration to form isopropyl phenyl sulfone-*α-d*.

Reaction of Cyclopropyl Phenyl Sulfone with Phenyllithium Followed by Deuterium Oxide Quenching.—A solution of 0.91 g. (4.99 mmoles) of cyclopropyl phenyl sulfone dissolved in 20.0 ml. of anhydrous ether was treated as in the preceding experiment with 6.0 ml. (5.54 mmoles) of 0.924 *N* phenyllithium solution in ether. In this case the conjugate base of the sulfone separated from solution and addition of 12.0 ml. more anhydrous ether did not effect solution. At the end of 2 hr. stirring at room temperature 1.00 ml. of 98% deuterium oxide was added and the reaction mixture was worked up as in the preceding experiment, yielding 0.81 g. of oil whose infrared spectrum was that of cyclopropyl phenyl sulfone-*α-d* and lacked absorption bands typical of starting material.

In another experiment 0.91 g. of cyclopropyl phenyl sulfone in 25.0 ml. of anhydrous tetrahydrofuran was treated with 6.0 ml. of 0.924 *N* phenyllithium in ether. In this case no precipitation of the conjugate base occurred, and the reaction mixture was stirred for 2 hr. at room temperature. Quenching with 1.00 ml. of deuterium oxide and working up as before afforded 0.86 g. of product whose infrared spectrum indicated complete deuteration.

TABLE V

ANALYSES OF SYNTHETIC MIXTURES

Mixture	Component	Actual comp., %	Calcd. comp., %
1	A	37.7	34.1
	B	22.1	19.9
	C	8.6	10.0
	D	31.6	31.6
2	A	12.2	7.4
	B	8.9	9.7
	C	26.6	31.0
	D	52.4	53.6
3	A	0.0	0.8
	B	19.6	23.6
	C	39.9	38.1
	D	40.5	41.5
4	A	34.4	33.5
	B	0.0	1.8
	C	45.8	47.9
	D	19.6	19.6
5	A	23.0	19.7
	B	22.5	24.0
	C	28.2	27.6
	D	26.3	25.5
6	A	13.3	10.9
	B	40.2	40.2
	C	35.5	35.3
	D	11.1	10.1
7	A	35.6	29.2
	B	12.7	11.1
	C	11.1	13.4
	D	39.6	36.7

Competitive Ionization of Cyclopropyl Phenyl Sulfone and Isopropyl Phenyl Sulfone to Afford Lithium Conjugate Bases under Equilibrium Conditions.—A solution of 1.00 g. of each of the two sulfones in 30.0 ml. of anhydrous tetrahydrofuran was treated with 7.00 ml. of 0.924 *N* phenyllithium solution in ether; there was no separation of solid material. At the end of 5 min., 1.00 ml. of 98% deuterium oxide was added and the mixture was worked up as in the preceding experiments, yielding 1.70 g. of oil. Analysis by quantitative infrared (*vide supra*) gave $K = (q_bq_c/q_aq_d) = 1.2$.

In similar fashion runs were made with varying times of reaction with the phenyllithium solution before quenching with deuterium oxide. These results are given in Table I. In run 1 a Y-shaped tube leading into stirred deuterium oxide under nitrogen and leading from two dropping funnels, one containing phenyllithium solution and the other the 1:1 mixture of the sulfones in tetrahydrofuran. From the volume rate of flow of tetrahydrofuran through the Y-tube and the dimensions of the tube, it was calculated that contact time before quencing was less than 1 second. In run 8, the tetrafuran contained only cyclopropyl phenyl sulfone, and 30 min. after addition of the phenyllithium solution the isopropyl phenyl sulfone was added. The mixture was then stirred for 2 hr. before quenching with deuterium oxide.

Reaction of Isopropyl Phenyl Sulfone with Phenylsodium Followed by Deuterium Oxide Quenching.—A 200-ml. flask with doubly indented sides was fitted with a Morton type high speed stirrer (13,000 r.p.m.) dropping funnel and reflux condenser; also, it was provided with a positive pressure atmosphere of nitrogen purified by benzophenone ketyl in *p*-xylene followed by a gas washing bottle containing mineral oil. Surmounting the condenser was a short capillary tube of sufficient length to maintain positive pressure but short enough to ensure sweeping out of the system. To the flask was added 0.92 g. (0.04 mole) of sodium and 15.0 ml. of isooctane, and the sodium was dispersed with refluxing of the solvent by Glas-col with high speed stirring. The dispersion was cooled to 45–50° and 2.26 g. (0.02 mole) of chlorobenzene in 15.0 ml. of thiophene-free benzene was added over an hour with high speed stirring; the mixture was then stirred for an additional 2 hr. At the end of this time the mixture was jet black. To the mixture containing phenylsodium was added a solution of 2.20 g. (0.012 mole) of isopropyl phenyl sulfone in 15.0 ml. of pure benzene, and the mixture was stirred for 14 hr. At the end of this time 4.0 ml. of 98% deuterium oxide was added with external cooling to avoid a temperature rise. Stirring was continued for one minute after the addition, and the mixture was then poured into 300 ml. of ether. The ether solution was washed to neutrality with water, dried over sodium sulfate and concentrated *in vacuo*, affording 1.8 g. of product which on infrared analysis was found to be 99.6% deuterated.

Reaction of Cyclopropyl Phenyl Sulfone with Phenylsodium Followed by Deuterium Oxide Quenching.—With the same apparatus described in the preceding experiment a dispersion was prepared from 2.76 g. (0.12 mole) of sodium and 80.0 ml. of isoöctane. To this was added at 35° a solution of 6.76 g. (0.06 mole) of chlorobenzene in 30.0 ml. of isoöctane. The addition was made over 1 hr. and stirring was continued for an additional 2 hr. To the bluish-black dispersion was added a solution of 4.36 g. (0.024 mole) of cyclopropyl phenyl sulfone in 30 ml. of anhydrous thiophene-free benzene. The mixture was stirred for 7.5 hr. At the end of this period the mixture was quenched by adding 4.00 ml. of 98% deuterium oxide with careful cooling to prevent a temperature rise; the product, weighing 3.96 g., was obtained as in the previous experiment. Quantitative infrared analysis indicated this to be 87.1% deuterated.

Competitive Ionization of Cyclopropyl Phenyl Sulfone and Isopropyl Phenyl Sulfone to Afford Sodium Conjugate Bases under Equilibrium Conditions.—Using the same apparatus as in the preceding two experiments 0.23 g. (0.01 mole) of sodium was dispersed in 10.0 ml. of isoöctane. The first 7 drops of a solution of 0.56 g. (0.005 mole) of chlorobenzene in 10.0 ml. of dry benzene were added at 70–75° and the remainder at 35–40° during 15 min. The mixture was then stirred for an additional 2 hr., and then a solution of 0.50 g. each of cyclopropyl phenyl sulfone and isopropyl phenyl sulfone and 10.0 ml. of dry benzene was added to the jet black phenylsodium dispersion. The mixture was then stirred for 3 hr. Following this, 1.0 ml. of 98% deuterium oxide was added with cooling and worked up as before. Quantitative infrared analysis indicated $q_a = 0.435$, $q_b = 0.550$, $q_c = 0.0899$ and $q_d = 0.0238$.

In a second run the same procedure was followed except that 0.276 g. (0.012 mole) of sodium, 0.678 g. (0.006 mole) of chlorobenzene and 0.0027 mole of each of the sulfones was used; also, in this run the time of stirring between addition of the sulfones and quenching with deuterium oxide was extended to 6 hr. Quantitative infrared analysis indicated $q_a = 0.326$, $q_b = 0.348$, $q_c = 0.201$ and $q_d = 0.107$.

The procedure of run two was followed in run three except that the time before quenching was extended to 16 hr. Here $q_a = 0.315$, $q_b = 0.233$, $q_c = 0.0122$ and $q_d = 0.0222$.

Competitive Ionization with Phenylsodium Generated from Diphenylmercury.—A dispersion of 0.138 g. (0.006 mole) of sodium in 10.0 ml. of isoöctane prepared as before was treated hot with the first few drops of a solution of 1.06 g. (0.003 mole) of diphenylmercury in 20.0 ml. of dry benzene. The rest of the diphenylmercury solution was added over 20 min. at room temperature. The mixture was then stirred for 6 hr. Following this a solution containing 0.50 g. each of cyclopropyl phenyl sulfone and isopropyl phenyl sulfone in 10.0 ml. of dry benzene was added and stirring was continued for 13 hr. After quenching with 1.00 ml. of deuterium oxide, the mixture was worked up as usual to afford 0.56 g. of material subjected to quantitative infrared analysis: $q_a = 0.546$, $q_b = 0.101$, $q_c = 0.230$ and $q_d = 0.0528$.

Competitive Ionization with Phenylpotassium.—To 0.24 g. (0.006 mole) of potassium dispersed in 10.0 ml. of isoöctane was added during 20 min. 1.06 g. (0.003 mole) of diphenylmercury dissolved in 20.0 ml. of anhydrous benzene. The mixture turned jet black, and stirring was continued for 2 hr. To the phenylpotassium thus produced was added a solution of 0.50 g. each of cyclopropyl phenyl sulfone and isopropyl phenyl sulfone in 10.0 ml. of dry benzene, and stirring was continued for 3 hr. more. Quenching with 1.00 ml. of deuterium oxide with external cooling and the usual workup afforded 0.72 g. of product analyzing as $q_a = 0.464$, $q_b = 0.629$, $q_c = 0.481$ and $q_d = 0.243$.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Relative Nucleophilic Character of Several Mercaptans toward Ethylene Oxide[1]

BY JAMES P. DANEHY AND CHARLES J. NOEL[2]

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Pseudo-first order rate constants have been determined for the reactions in buffered aqueous solutions of ethylene oxide with twelve different mercaptans. Values for the rate constants increase with increasing *p*H over a *p*H range characteristic for each mercaptan. With the single exception of thiophenol, plots of k *vs.* $[RS^-]/[RSH]$ are linear. Thus, the mercaptide ion is the reactive species, and the slopes of the straight lines afford a relative measure of the intrinsic reactivities of the various mercaptide ions with respect to ethylene oxide. Values for the dissociation constants of thirteen mercaptans have been determined at 20° and, in five cases, at 30 and 40° as well. In general, the higher the value for pK_a for the mercaptan, the greater the intrinsic reactivity toward ethylene oxide. However, *o*-aminothiophenol has a uniquely high intrinsic reactivity and constitutes the major exception to this generalization.

Introduction

There are several references, mostly preparative in nature, to the formation of hydroxyalkyl thioethers by the reactions of mercaptans with epoxides.[3] Searles[4] studied the reactions of thiophenol and of several aliphatic mercaptans with trimethylene oxide and found that the reactions proceeded smoothly in alkaline solution to give good yields of 3-hydroxypropyl sulfides while poor yields were obtained in acidic solution. Berbe[5] made a kinetic study of the reactions of hydrogen sulfide and of 2-mercaptoethanol with ethylene oxide and with propylene oxide. He claimed that the expected product is a catalyst for

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