[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

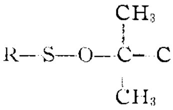
Derivatives of Sulfenic Acids. XXXVII. Studies of Sulfenyl Esters (Thioperoxides). Part 5. Thermal Decompositions[1]

BY ROBERT S. IRWIN[2] AND NORMAN KHARASCH

RECEIVED AUGUST 17, 1959

The pyrolysis of selected *t*-butyl esters of sulfenic acids, I, II, III, was studied. Compounds II and III yield isobutylene as the major volatile product, whereas I yields about 90% *t*-butyl chloride. No acetone was found in any case, showing that *t*-butoxy radicals are not involved, as might be expected by comparisons with peroxide pyrolyses. Other evidence suggests that the pyrolyses of I, II and III, under the conditions studied, do not involve homolysis of the –S–O– bond. A mechanism, which involves a cyclic transition state, analogous to that proposed for the pyrolysis of alkyl xanthates, is proposed.

Previous studies from this Laboratory have emphasized reactions of sulfenyl derivatives which have been clearly ionic in character. These have included the innumerable displacements of X, in RS-X, by nucleophiles, including olefins, acetylenes, aromatic hydrocarbon, alcohols, amines, thiols, epoxides and a variety of ionic reagents, such as thiocyanates, acetates, mercaptides, iodides, etc. While the group X, in RSX, has generally been chlorine, of a sulfenyl chloride, this is not a necessary limitation, for it can also be Br, SCN, I, SR, OR and many others.[3]



$$R{-}S{-}O{-}C(CH_3)_3$$

I, R = Cl_3C-
II, R = C_6H_5-
III, R = $2,4\text{-}(NO_2)_2C_6H_3-$

An equally broad area of study of sulfenyl derivatives concerns free radical scissions of R—S—X. Having clarified several major aspects of the ionic reaction mechanisms, we have now turned our major attention to reactions of R—S—X which may be free radical in character.

By analogy with the well-known homolytic scissions of dialkyl peroxides[4] and with homolytic

$$ROOR \longrightarrow 2RO\cdot$$

decompositions of disulfides,[5,6] one may predict that sulfenyl esters (RSOR′), also generally referred to as thioperoxides, may cleave at the —S—O— bond to give RS· and R′O· radicals

$$RSOR' \longrightarrow RS\cdot + R'O\cdot$$

The ability of these substances, in trace amounts, under photolytic conditions, to initiate vinyl polymerization,[7] which was also substantiated in our work, is suggestive of free radical behavior, as were also our initial observations on the pyrolytic decompositions of the sulfenyl esters.

The *t*-butyl sulfenyl esters generally decomposed only when heated above 120°. On the basis of limited examples, it appears that the order of stabilities of alkyl sulfenyl esters is primary > secondary > tertiary. For example, *t*-butyl trichloromethanesulfenate undergoes major decomposition above 120°, whereas the *sec*-butyl and *n*-butyl esters, respectively, decompose rapidly only above 184 and 210°. Because of the interest in *t*-butyl peroxides, we gave greatest attention, first, to the *t*-butyl sulfenyl esters, since these decomposed at quite moderate temperatures, and—in view of the extensive information available on the nature of *t*-butoxy radicals—it would be easy to establish whether —S—O— bond cleavage, to $t\text{-}C_4H_9O\cdot$, was involved.[8]

Compounds II and III (*t*-butyl benzenesulfenate and *tert*-butyl 2,4-dinitrobenzenesulfenate) were pyrolyzed at 120–135°. A nitrogen atmosphere was used to exclude air, since oxygen is undesirable in the possible presence of free radicals. The volatile products of pyrolysis were trapped, and—by gas chromatographic analysis—found to consist solely of isobutylene and a small amount of sulfur dioxide. The non-volatile residues were tars which could not be purified by adsorption chromatography.

If S—O bond homolysis had occurred in the above decompositions, one would expect to find the readily identifiable disulfides, which would result by dimerization of RS· radicals, as well as acetone—which would result by the well known decomposition of *t*-butoxy radicals, *via* the reactions

$$RS{-}O{-}C(CH_3)_3 \longrightarrow RS\cdot + \cdot OC(CH_3)_3$$
$$2RS\cdot \longrightarrow RSSR$$
$$\cdot OC(CH_3)_3 \longrightarrow \cdot CH_3 + (CH_3)_2C{=}O$$
$$2CH_3\cdot \longrightarrow C_2H_6$$

That S—O bond homolysis does not occur in the pyrolyses of I, II and III was also confirmed by the non-formation of any *t*-butyl alcohol or any 2,3-dimethyl-2,3-diphenylbutane when 5% solutions of the esters were pyrolyzed in cumene. Vaughan and co-workers have shown that these products result when *t*-butoxy radicals are generated in the presence of cumene. The products, in our study, obtained in the presence of cumene were the same as in its absence; that is, only isobutylene, sulfur dioxide and tar were found.

The formation of isobutylene, in high yield, can be accounted for best by assuming that the

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[2] Holder of a Fulbright travel grant and Visiting Research Associate, 1958–1959, from Queen's University, Northern Ireland.

[3] For a general discussion and leading references, *cf.* N. Kharasch, *J. Chem. Ed.*, **33**, 585 (1956), and chapters 30 and 32 in "Organic Sulfur Compounds," Vol. I, Edited by N. Kharasch, Pergamon Press, New York, N. Y., in press.

[4] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957.

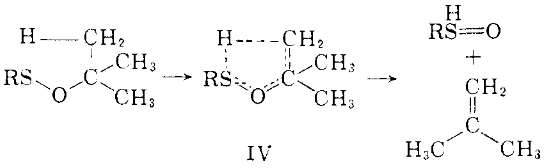
[5] A. J. Parker and N. Kharasch, *Chem. Revs.*, **59**, 583 (1959).

[6] R. G. R. Bacon, R. I. Guy, R. S. Irwin and T. Robinson, *Proc. Chem. Soc.*, in press.

[7] G. H. Birum and R. J. Kern, U. S. Patent 2,769,777 (1956); *C. A.*, **51**, 6215 (1957).

[8] J. H. Raley, F. F. Rust and W. J. Vaughan, THIS JOURNAL, **70**, 88, 1336 (1948).

initial breakdown occurs *via* a cyclic transition state, as



IV

which postulates formation of a molecule of RS(O)H. While this has a formal resemblance to a sulfoxide, it is undoubtedly a highly reactive intermediate, which at the elevated temperatures may lead to a tarry mixture and some sulfur dioxide (from sulfenic acid intermediates). Indeed, RS(O)H is one possible structure for a sulfenic acid, the elusive character of which has often been noted.[9] The formation of the cyclic transition state is, of course, only crudely indicated by structure IV, but is reasonable since unshared electrons on sulfur and oxygen are available for its stabilization.

A cyclic mechanism, as above, is similar to the one proposed for *cis* eliminations, with attendant olefin formation. Barton[10] has pointed out that a *cis*-hydrogen atom is suitably situated for the formation of a "planar" transition state with minimum activation energies in the case of 4-, 5- or 6-membered rings. The Chugaev decomposition of xanthates is also a good example of *cis* elimination, and its formulation by mechanisms analogous to the one shown above has already been recorded in the literature.[11] O'Connor and Nace[11] found a negative entropy of activation for the Chugaev reaction, which indicates that the transition state is highly ordered. The "π" electron resonance-stabilized transition state can be regarded as a hybrid of products and reactants, which can decompose to products by a further shift of atomic nuclei and redistribution of the non-localized electrons. As Hurd and Blunck correctly formulated in an early study,[12] the pyrolysis of alkyl carboxylates is also an intramolecular reaction which leads to olefins, and which may be formulated as proceeding by a similar cyclic mechanism.

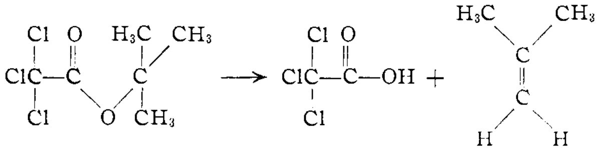
On the basis of the above mechanism, one would predict that alkyl sulfenates which have at least one α-hydrogen atom on the alkyl group should yield olefins on pyrolysis. Compounds II and III follow this pattern; but when R in I is trichloromethyl, a different behavior is observed, in that rather than an olefin (isobutylene), the alkyl chloride (*t*-butyl chloride) is the main product. Ester I gave 86% *t*-butyl chloride, whereas *sec*-butyl trichloromethanesulfenate and cyclohexyl trichloromethanesulfenates, respectively, gave the alkyl chlorides in considerably lower yields. The alkyl trichloromethanesulfenates are readily prepared and are generally quite stable liquids[13,14]; hence the variations in yields of product as a function of the nature of R could be extended without difficulty, but for the present work we chose instead to examine the *t*-butyl compound I in greater detail.

In the pyrolysis of I it was shown, by gas chromatographic analysis, that the same volatile products were formed when compound I was decomposed as the liquid at 140°, as the vapor at 460°—by passage through a hot tube— or as a solution in cumene. As in the case of II and III, the last result suggests that the S–O bond is not cleaved homolytically. The decomposition products found in the volatile fraction were *t*-butyl chloride (86%), sulfur dioxide (45%), trichloromethanesulfenyl chloride (33%) and thionyl chloride (6%). Traces of hydrogen chloride and thiophosgene were also observed in the volatile fractions. Two other volatile components, present in trace amounts, were also noted but not identified. The residue consisted of a high-boiling liquid portion and some tar. A comparison pyrolysis of *sec*-butyl trichloromethanesulfenate at 200° showed the volatile products to consist of *sec*-butyl chloride (32%), thiophosgene (30%) and small amounts of sulfur dioxide and hydrogen chloride. In this case, however, no trichloromethanesulfenyl chloride was noted, but a high-boiling liquid and some tar was present in the residue.

The multiplicity of products observed in the pyrolysis of I suggests that a rather complex sequence of reactions must occur. While the nature of these can only be discussed in a hypothetical way at present, it seems apparent that the presence of the highly electronegative trichloromethyl radical causes a profound change in the nature of the decomposition products. In the liquid phase, at elevated temperatures, one possibility is the formation of an ion-pair, followed by a recombination which involves transfer of a chloride ion.

$$\mathrm{Cl_3C{-}S{-}O{-}C(CH_3)_3} \longrightarrow [(\mathrm{Cl_3CSO})^- + \mathrm{C(CH_3)_3}^+]$$
$$(\mathrm{Cl_2C{=}S{=}O}) + \mathrm{Cl{-}(CH_3)_3}$$

However, the formation of the same products from gas-phase pyrolysis, and the greater likelihood, in any case, favors a cyclic mechanism, as suggested above. The proposal of a cyclic transition state suggested the possibility that *t*-butyl trichloroacetate might also decompose to yield *t*-butyl chloride, but it was found (at 130°) that only isobutylene and trichloroacetic acid are obtained, which is consistent with the result anticipated on the basis of the Hurd–Blunck mechanism.



The geometry of the alkyl trichloromethanesulfenates permits the close approach of the C_1 atom in the alkyl group to a negatively charged chlorine atom; hence the formation of a cyclic transition state is favored. The formation of the latter is specially facilitated in the case of *t*-butyl trichloro-

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[9] *Cf.*, *e.g.*, N. Kharasch, S. J. Potempa and H. L. Wehrmeister, *Chem. Revs.*, **39**, 269 (1946); and T. C. Bruice and A. B. Sayigh, THIS JOURNAL, **81**, 3416 (1959).

[10] D. H. R. Barton, *J. Chem. Soc.*, 2174 (1949).

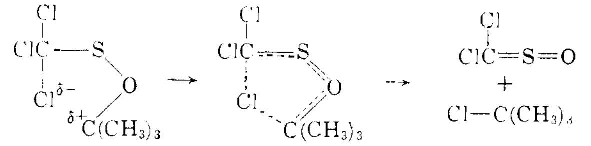
[11] G. L. O'Connor and H. R. Nace, THIS JOURNAL, **74**, 5454 (1952).

[12] C. D. Hurd and F. H. Blunck, *ibid.*, **60**, 2419 (1938).

[13] G. Sosnovsky, *J. Chem. Soc.*, 3139 (1956).

[14] R. Langford and N. Kharasch, *J. Org. Chem.*, **23**, 1694 (1958).

methanesulfenate, since the central carbon of the *t*-butyl group can carry an incipient positive charge, as indicated below.



The catalytic effect of sulfenyl esters in the photo-induced polymerization of olefins[6] was displayed by *t*-butyl trichloromethanesulfenate. A fourfold increase in the rate of polymerization of styrene was noted by irradiating the styrene solution containing 0.3%, by weight, of the sulfenyl ester. However, the sulfenyl ester appeared to be quite stable to powerful ultraviolet light, in the neat liquid state, and as solutions in isoöctane and cumene. In the latter, no *t*-butyl alcohol was detected, which would have indicated formation of $(CH_3)_3CO^\cdot$ radicals and hence indicate homolysis of the S–O bond. If these radicals are produced in the liquid state of the pure substance, or in presence of isoöctane or cumene, their rate of recombination must be much greater than that of hydrogen transfer from these hydrocarbons. The sensitivity of the styrene polymerization to radical initiation, however, makes this polymerization reaction useful as an indicator of the supposed free-radical initiators. An ionic initiation of polymerization by the sulfenyl derivative may also be postulated (involving sulfenium ions, RS^+), but the behavior in the present instance, under photolytic conditions, is more suggestive of free radical behavior.

The further study of these reactions and the stereochemical course of reactions in which R in Cl_3CSOR has a center of optical activity, as in the optically-active *sec*-butyl ester, is in progress.

Experimental

Preparation of Alkyl Sulfenates.—All materials used were anhydrous. To the sulfenyl chloride[14] (1.0 mole) and alcohol (1.1 moles), in ethylene chloride (1 liter) was added portionwise 1.1 moles of pyridine. The mixture became warm rapidly and pyridine hydrochloride separated. After standing about 12 hours, at room temperature, to ensure completeness of reaction,[15] the mixture was washed well with water and dried over anhydrous magnesium sulfate. Concentration of the solution, followed by cooling, in the case of *t*-butyl 2,4-dinitrobenzenesulfenate yielded the crude crystalline product which was crystallized from carbon tetrachloride as yellow prisms (m.p. 119°).[16] It was not possible to distil *t*-butyl benzenesulfenate (II) without decomposition, even under high vacuum. Hence, the crude, colorless liquid product was used in pyrolysis experiments.

The following alkyl trichloromethanesulfenates were also prepared. All of these were pleasant-smelling liquids, which—when pure—remained undecomposed on storage for months at room temperature, in darkness: **t-butyl**: 60%, b.p. 68–69° (3 mm.); λ_{max} 239,277 mμ; ϵ_{max} 444, 390 mμ; resp.; d^{25} 1.301, n^{25}D 1.4920. Calcd. for $C_5H_9Cl_3OS$: C, 26.8: H, 4.03. Found: C, 26.52; H, 3.88. ***sec*-butyl**: 75%, b.p. 79–80° (5 mm.), n^{52}D 1.4835, d^{25} 1.283. **isobutyl**: 60%, b.p. 63–64° (5 mm.), n^{25}D 1.4610, d^{25} 1.182. ***n*-butyl**: 75%, b.p. 83–84° (3 mm.), n^{25}D 1.4780, d^{25} 1.242. **cyclohexyl**: 70%, b.p. 117° (5 mm.), n^{25}D 1.5175, d^{25} 1.332. The last four compounds have been previously reported,[15] but the yields and physical constants on the purified samples of the compounds here prepared are given for comparison.

General Procedure for Pyrolyses.—Decompositions of known weights of the esters were effected in a 25-ml. flask, maintained at the desired temperature by an oil-bath on a hot-plate. A slow stream of dry nitrogen swept the volatile decomposition products, *via* a short Vigreux column and condenser, to three U-tubes, in series, the first of which was air-cooled and the other two were cooled in acetone–solid carbon dioxide traps. Traces of undecomposed ester were caught in the first U-tube and the remaining products were all collected in the second tube. No product was found in the third tube.

Since *t*-butyl 2,4-dinitrobenzenesulfenate (a solid) decomposed rather violently at 119°, the powdered solid was added slowly, from an addition bulb, to the hot flask.

Analysis of Products.—Volatile liquid products were identified by gas chromatography on three separate columns, of diisodecyl phthalate, silicone oil and polyethylene glycol, by comparison of the retention times of sample peaks with those of known compounds under the same conditions. A few of the minor components could not be identified. Experiments with synthetic mixtures of known composition showed that the ratio of peak areas corresponded closely to the ratio of the amounts of components, which simplified the obtaining of reasonably quantitative data for the unknown mixtures. The identities of alkyl chlorides and isobutylene were also confirmed by infrared spectra.

The high-boiling residues were fractionally distilled and/or chromatographed on silica gel and alumina. A considerable amount of this material always proved to be sulfur-containing tar, which resisted attempts to separate it into further components.

Pyrolysis of *t*-Butyl 2,4-Dinitrobenzenesulfenate.—This ester melted with vigorous decomposition at the melting point, 119°. Isobutylene and a trace of sulfur dioxide, but no acetone, were the only volatile products. The solid residue was an intractable gum, quite insoluble in all organic solvents except acetone, and contained sulfur. No bis-(2,4-dinitrophenyl) disulfide was detected. A 5% solution of the ester, in cumene, decomposed at a slower rate (*ca.* 3 hr.) at 120°, but gave exactly the same products; no *t*-butyl alcohol was found.

Pyrolysis of *t*-Butyl Benzenesulfenate.—The crude ester (*cf.* above) was kept in a highly-evacuated flask for 2 hours to remove all volatile substances. Decomposition of this pretreated ester occurred readily at 120°, with the formation of isobutylene and sulfur dioxide, as well as much tar. The same result was obtained for a solution in cumene; no *t*-butyl alcohol was detected.

Pyrolysis of *t*-Butyl Trichloromethanesulfenate.—The ester (18.37 g.) was decomposed at 140° during 4 hr. (initial decomposition began at 120°). An unpleasant smelling, fuming orange liquid collected in the cold trap. By distillation, this was separated into a fraction of b.p. less than 80° (8.46 g.) and a higher-boiling orange liquid. The former contained *t*-butyl chloride (6.7 g., 86% of theoretical), sulfur dioxide (1.18 g., 45%), thionyl chloride (0.59 g., 6%) and traces of hydrogen chloride and thiophosgene. There were also two unidentified components, in very minor amount. The higher boiling fraction was trichloromethanesulfenyl chloride (2.49 g., 33%), b.p. 146°, identified as the sulfenmorpholide,[17] m.p. 56°, and by infrared spectrum. The black non-volatile residue consisted of tar and a yellow, odorous liquid, b.p. 75–140° (13 mm.), which resisted further separation.

The same products were obtained by pyrolysis of the vapor at 460°, when the liquid was distilled at 1 mm., through a tube packed with glass beads, heated in a furnace.

Pyrolysis of *sec*-Butyl Trichloromethanesulfenate.—The sulfenate (9.74 g.) decomposed in 3 hr. at 200° to form *sec*-butyl chloride (1.43 g., 32% of theory), thiophosgene (1.51 g., 30%) some hydrogen chloride and sulfur dioxide. A considerable amount of tar, and two minor, unidentified compounds, but no carbonyl or hydroxyl compounds were also found.

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[15] In a previous paper [R. B. Langford and N. Kharasch, *J. Org. Chem.*, **23**, 1694 (1958)] it was suggested that a negative starch-iodide test indicated the completeness of reaction. This test is, however, invalid in the presence of pyridine, which presumably complexes the iodine. We are indebted to Dr. F. A. Drahowzal for calling this to our attention.

[16] A general procedure for characterizing alcohols with 2,4-dinitrobenzenesulfenyl chloride was described by N. Kharasch, D. P. McQuarrie and C. M. Buess, THIS JOURNAL, **75**, 2658 (1953).

[17] R. S. Hawley, U. S. Patent 2,553,774 (1951); *C. A.*, **45**, 6792 (1951).

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

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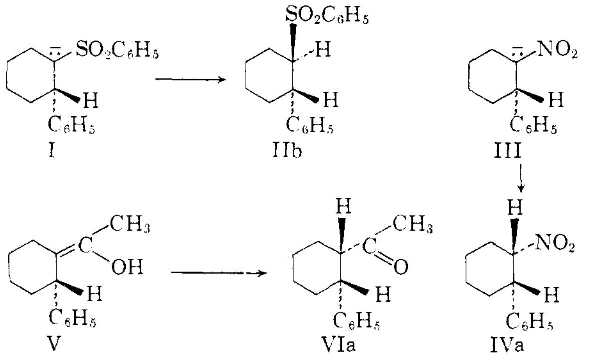
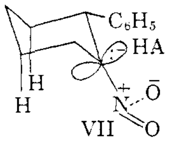
Cyclopropyl phenyl sulfone has been synthesized and its acidity compared with that of the acyclic analog isopropyl phenyl sulfone. The results of these experiments are considered in relation to the problem of the hybridization and geometry of a carbanion stabilized by the sulfone group.

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]

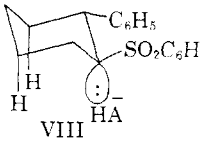


I IIb III V VIa IVa

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.