Pummerer Rearrangements of Sulfonium Salts[1a-c]

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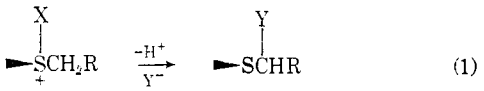
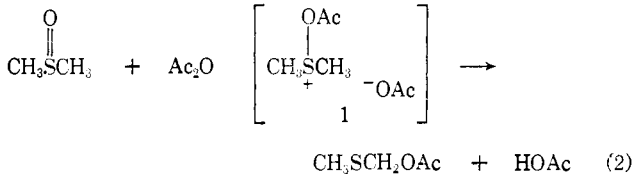
Abstract: Certain alkoxysulfonium salts rearrange under the influence of base to provide α-alkoxy sulfides. Treatment of alkoxysulfonium salts with sodium carboxylates in DMSO produced α-acyloxy sulfides; these same products were obtained by reaction of sulfoxides with acid anhydrides. All of these reactions are varients of the Pummerer rearrangement. Crossover products from carbon-14-labeling experiments, solvent effects, and substituent effects all point to a sulfur-stabilized carbonium ion as an intermediate in these reactions. In all cases it was found that migration proceeded to the least substituted α-carbon. It is suggested that the reaction is initiated by ylide formation and that this is the rate- and product-determining step. For the Pummerer reactions discussed in this paper, the following sequence is proposed: salt → ylide → sulfur-stabilized carbonium ion → product.

The Pummerer reaction,[2] which we suggest to be a general term for a class of reactions involving the reduction of a sulfonium sulfur with concomitant oxidation of the α-carbon, is illustrated in eq 1. Such



(1)

reactions have been the subject of much mechanistic speculation.[3] One of the most common examples of the Pummerer reaction is induced by the treatment of sulfoxides with anhydrides (eq 2).[2,4] It is generally

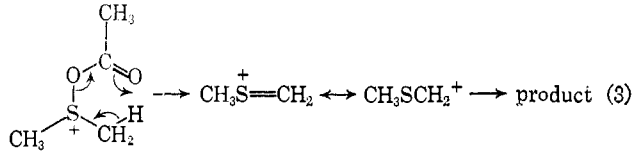


(2)

accepted that these reactions involve, as a first step, the formation of a sulfonium salt illustrated by **1**. The majority of the mechanistic proposals which have been suggested for the Pummerer rearrangement are illustrated below using a dimethylacetoxysulfonium salt.

Carbonium Ion Intermediate

Concerted cyclic elimination HOAc



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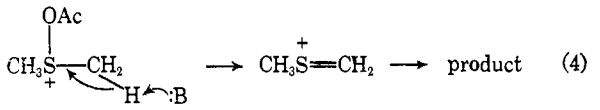
Concerted elimination of HOAc with external base



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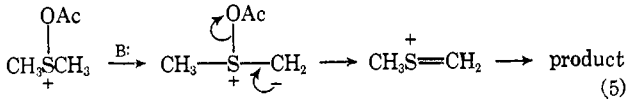
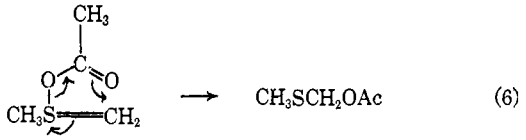
Ylide intermediate



(5)

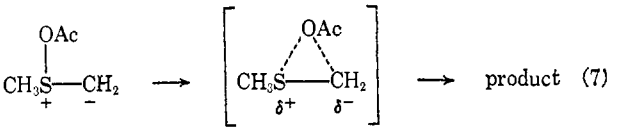
Internal Transfer of Acetoxy Group

Cyclic rearrangement



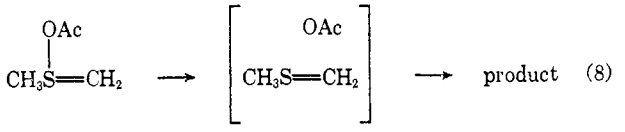
(6)

1,2 shift



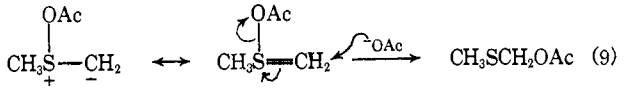
(7)

Homolytic dissociation-recombination[5]



(8)

Nucleophilic Displacement of Ylide



(9)

During the course of our study of alkoxysulfonium salts we observed a similar α migration.[6] For example, α-methoxyethyl phenyl sulfide (**3**) along with

(1) (a) Part XIV in the series "Chemistry of Sulfoxides and Related Compounds." (b) Part XII: C. R. Johnson, J. E. Keiser, and J. C. Sharp, *J. Org. Chem.*, in press. (c) We gratefully acknowledge support by the National Science Foundation (Grant No. GP-5944). (d) Alfred P. Sloan Research Fellow, 1965–1968. (e) National Aeronautics and Space Administration Trainee, 1965–1967.

(2) R. Pummerer, *Ber.*, 42, 2282 (1909); 43, 1401 (1910); see also J. A. Smythe, *J. Chem. Soc.*, 95, 349 (1909).

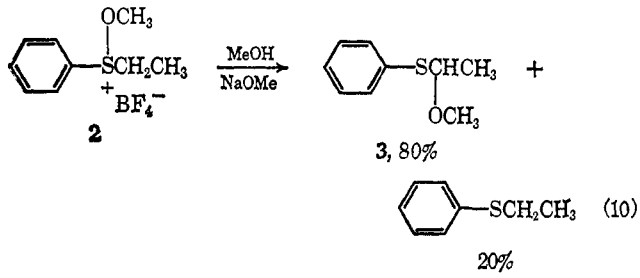
(3) (a) S. Oae, T. Kitao, S. Kawamura, and Y. Kitaoka, *Tetrahedron*, 19, 817 (1963); (b) S. Oae and M. Kise, *Tetrahedron Letters*, 2261 (1968); (c) H. D. Becker, G. J. Mikol, and G. A. Russell, *J. Am. Chem. Soc.*, 85, 3410 (1963); (d) H. D. Becker, *J. Org. Chem.*, 29, 1358 (1964); (e) W. J. Kenney, J. A. Walsh, and D. A. Davenport, *J. Am. Chem. Soc.*, 83, 4019 (1961); (f) D. Walker and J. Leib, *Can. J. Chem.*, 40, 1242 (1968); (g) F. G. Bordwell and B. M. Pitt, *J. Am. Chem. Soc.*, 77, 572 (1955); (h) W. E. Parham and M. D. Bhawsar, *J. Org. Chem.*, 28, 2686 (1963).

(4) L. Horner and P. Kaiser, *Ann.*, 626, 19 (1959).

(5) Should this mechanism obtain, the dissociation–recombination must occur within the solvent cage, otherwise carbon dioxide should be evolved from the reaction mixture.

(6) C. R. Johnson and W. G. Phillips, *J. Org. Chem.*, 32, 1026 (1967).

some phenyl ethyl sulfide was formed when phenylethylmethoxysulfonium fluoroborate (**2**) was subjected to sodium methoxide in methanol. Deuterium-labeling



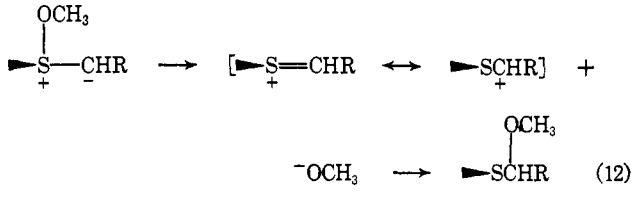
2 **3**, 80% 20% (10)

experiments revealed that the collapse to carbonyl compounds proceeds *via* a cyclic transition state involving a sulfur ylide (pathway a). The preponderance of the α-rearrangement product (pathway b) appeared, based on substituent effects, to be a function of the stability of the carbonium ion formed by elimination of alkoxide from the ylide intermediate.

Pathway a

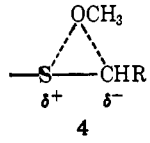
(11)

Pathway b



(12)

However a transition state **4** involving direct intramolecular transfer could not be eliminated from consideration.



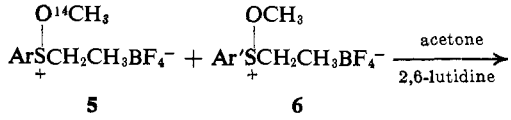
4

In this paper[7] we describe details which interrelate the rearrangements of acetoxy- and alkoxysulfonium salts and provide new and significant mechanistic insights into the mechanism of the Pummerer reactions.

Results

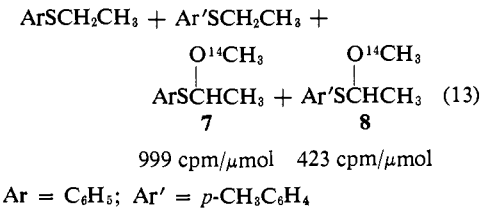
An obvious approach to probe into the mechanism of these reactions is to inquire as to the intermolecular or intramolecular nature of the transfer of the group from sulfur to carbon. For such an investigation we chose a mixed salt system in which one of the salts had been tagged with a methyl group and the other with a carbon-14 label and examined the reaction mixture for crossover products.

(7) This work has been reported in part in preliminary form: C. R. Johnson, J. C. Sharp, and W. G. Phillips, *Tetrahedron Letters*, 5299 (1967).



5 **6**

1389 cpm/μmol



(13)

999 cpm/μmol 423 cpm/μmol

Ar = C_6H_5; Ar′ = p-$CH_3C_6H_4$

For this experiment, phenylethylmethoxysulfonium-*O*-^{14}C fluoroborate (**5**) and *p*-tolylethylmethoxysulfonium fluoroborate (**6**) were selected since we had previously shown that salts of this structure tend to react *via* pathway b as opposed to pathway a when treated with base. In addition the products formed from these salts are volatile enough to be separated by vapor phase chromatography (vpc). Since the experiment requires a solvent–base system which would not exchange with the alkoxysulfonium salts (prior exchange would scramble the label) acetone and 2,6-lutidine were employed.

Phenylethylmethoxysulfonium-*O*-^{14}C fluoroborate (**5**) was mixed with 1 equiv of *p*-tolylethylmethoxysulfonium fluoroborate (**6**) and added to 2,6-lutidine in dry acetone. Four products were obtained: phenyl ethyl sulfide and *p*-tolyl ethyl sulfide (formed *via* pathway a) plus α-methoxyethyl phenyl sulfide (**7**) and α-methoxyethyl *p*-tolyl sulfide (**8**) (formed *via* pathway b). The compounds were separated by vpc, collected, characterized, and analyzed for carbon-14. As indicated in eq 13, both hemithioacetals were found to contain carbon-14.

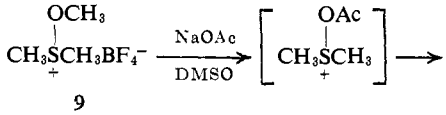
Two control experiments were run. First it was established that 2,6-lutidinium fluoroborate (a byproduct) does not catalyze the scrambling of the label between the two thioacetals **7** and **8**. When 1 equiv of labeled methyl alcohol was added to a mixture of phenyl ethyl sulfide and unlabeled **7** in the presence of 1 equiv of 2,6-lutidinium fluoroborate, the recovered thioacetal **7** contained no carbon-14. Secondly, it was established that the label was not scrambled between the two thioacetals during the chromatography.

These results provide obligatory evidence that alkoxy groups escape to solution in the α-rearrangement reaction. In such an experiment scrambling of the label would not be expected to be statistical since the ions should be short lived and a certain amount of ion-pair return is to be expected.

When phenylethylmethoxysulfonium fluoroborate (**5**) is treated with sodium methoxide in methyl alcohol the products are thioacetal (four parts) and phenyl ethyl sulfide (one part) (eq 10). When the less polar tetrahydrofuran (THF) is used as solvent with sodium hydride as the base, the sole product is phenyl ethyl sulfide. As can be seen from Figure 1, the percentage of acetal formed in this reaction increases as a linear function of the methyl alcohol concentration in methyl alcohol–THF mixtures.

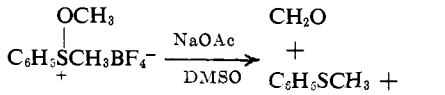
A reaction analogous to that of acetic anhydride and

dimethyl sulfoxide was observed when dimethylmethoxysulfonium fluoroborate (**9**) was treated with sodium acetate in DMSO; acetoxymethyl methyl sulfide was formed in 43% yield (eq 14). By analogy to rapid alkoxy interchange[6] an intermediate acetoxysulfonium salt should be initially formed; this is the same intermediate which has been postulated to exist in the anhydride–sulfoxide reaction. An alternate mechanism not invoking an acyloxysulfonium salt is considered unlikely since S-methyl salts of this type react almost entirely *via* pathway a to give the parent sulfide. Similar reactions were observed to occur when salt **9** was treated with the sodium salts of propionic, benzoic, and *p*-nitrobenzoic acids. Carboxylates of lower nucleophilicity such as those derived from bromoacetic and trifluoroacetic acid did not produce α-acyloxy sulfides.



9

$$\xrightarrow[\text{DMSO}]{\text{NaOAc}} \left[\begin{array}{c}\text{OAc}\\ |\\ \text{CH}_3\overset{+}{\text{S}}\text{CH}_3\end{array}\right] \longrightarrow \underset{43\%}{\text{CH}_3\text{SCH}_2\text{OAc}} \quad (14)$$



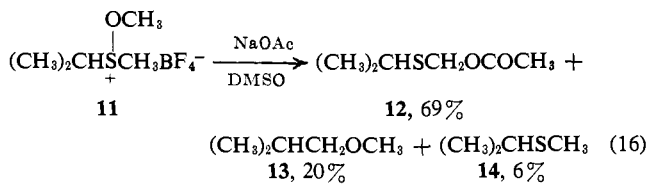
10

$$\xrightarrow[\text{DMSO}]{\text{NaOAc}} \underset{82\%}{\text{CH}_2\text{O} + \text{C}_6\text{H}_5\text{SCH}_3} + \underset{11\%}{\text{C}_6\text{H}_5\text{SCH}_2\text{OAc}} + \underset{7\%}{\text{C}_6\text{H}_5\text{SCH}_2\text{OCH}_3} \quad (15)$$

The reaction of acetate ion with phenylmethylmethoxysulfonium fluoroborate (**10**) is illustrated in eq 15. These results question Torssell's suggestion that alkoxysulfonium salts are not involved in the oxidation of alcohols with DMSO–acetic anhydride mixtures. Torssell[8] found that dimethylisobutoxysulfonium tetraphenylborate gave only traces of carbonyl compounds when treated under DMSO–acetic anhydride conditions for the oxidation of alcohols. However as noted by Goldman and Albright,[9] he did not add acetate ion which is present in the oxidation mixture as a by-product. Our data suggest that acetate can act as a base to promote the conversion of alkoxysulfonium salts to carbonyl compounds.

In order to access the factors governing the orientations of α rearrangements the reactions of an unsymmetrical dialkylsulfonium salt were investigated. As anticipated when isopropylmethylmethoxysulfonium fluoroborate was treated with sodium methoxide in methanol the only sulfur-containing product obtained was isopropyl methyl sulfide. On the other hand when this same salt was treated with sodium acetate in DMSO acetoxymethyl isopropyl sulfide was formed along with methoxymethylisopropyl sulfide and methyl isopropyl sulfide (eq 16). It is important to note that the acetate migrated to the least-substituted carbon atom as did the methoxy group suggesting similar mechanisms for their formation. (A small amount of a highly volatile fourth product, possibly isopropyl mercaptan, was also formed in this reaction.)

The reaction of isopropyl methyl sulfoxide with



11

$$\xrightarrow[\text{DMSO}]{\text{NaOAc}} \underset{\textbf{12},\ 69\%}{(\text{CH}_3)_2\text{CHSCH}_2\text{OCOCH}_3} + \underset{\textbf{13},\ 20\%}{(\text{CH}_3)_2\text{CHCH}_2\text{OCH}_3} + \underset{\textbf{14},\ 6\%}{(\text{CH}_3)_2\text{CHSCH}_3} \quad (16)$$

acetic anhydride was examined.[10] In an analysis of the reaction mixture by vpc the only product detected was acetoxymethyl isopropyl sulfide (**12**). Likewise in the reaction of *n*-propyl methyl sulfoxide and *n*-butyl methyl sulfoxide with acetic anhydride we were able to detect only acetoxymethyl sulfides.[11] Thus it appears that the α substitution occurs on the *least* substituted α-carbon.

Discussion

Our experimental observations are best reconciled on the basis that sulfur-stabilized carbonium ions intervene in the rearrangement of alkoxysulfonium salts to thioacetals. The data leading to this suggestion are summarized as follows. (1) In cases when more than one reaction pathway is available, *i.e.*, eq 11 and 12, it has been found that substituents (R) which are predicted to stabilize a carbonium ion favor the production of the Pummerer products. (2) Highly polar solvents which are capable of stabilizing carbonium ions facilitate the reaction. (3) In a double-label experiment, crossover products indicated that the alkoxy group and the sulfur-containing fragment become solvent separated, and hence the reaction is not necessarily intramolecular in nature.

The reaction of alkoxysulfonium salts with acetate ion has been shown to be substantially the same reaction as the reaction of sulfoxides with anhydrides. From the reaction illustrated in eq 16 it is clear that the initial step in the rearrangement reaction must be the formation of an acetoxysulfonium salt. For when salt **11** is treated with nonexchanging base such as sodium hydride, no rearrangement product **13** is obtained. The formation of compound **13** can be accounted for only by the formation of acetoxy salt **15** which subsequently collapses to carbonium ion **16** (Scheme I).

In all examples thus far examined in our laboratory, the migration of a group from a dialkylsulfonium sulfur has always proceeded to the least-substituted α-carbon. (In most cases, this α-carbon is also the site of the least-stable carbonium ion.) This is most logically explained by the intervention of an ylide intermediate prior to the formation of the carbonium ion. If the carbonium ion were formed in a concerted manner as depicted in eq 4 it would appear that in the transition state connecting the salt and the carbonium

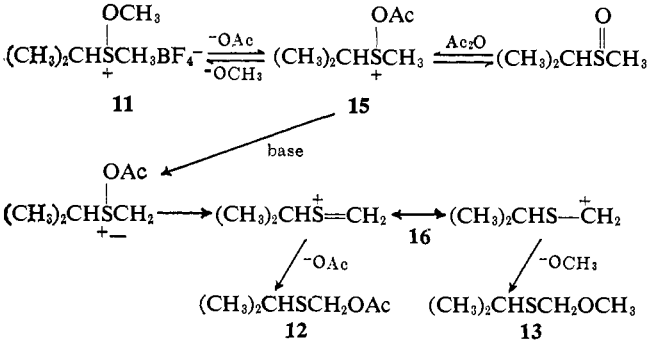
(8) K. Torssell, *Acta Chem. Scand.*, 21, 1 (1967).

(9) J. Albright and L. Goldman, *J. Am. Chem. Soc.*, 89, 2416 (1967).

(10) S. Oae, T. Kitao, and S. Kawamura [*Tetrahedron*, 19, 1783 (1963)] have also treated unsymmetrical sulfoxides with acetic anhydride. They obtained a 9% yield of acetoxymethyl *n*-butyl sulfide along with several unidentified products upon treatment of methyl *n*-butyl sulfoxide with acetic anhydride at reflux. These facts under their conclusion that migration occurs exclusively to the methyl group were questionable. Their results with methionine sulfoxide were also unclear.

(11) In similar reactions conducted in refluxing acetic anhydride small amounts of the more highly substituted α-acetoxy sulfides have been detected [W. E. Parham and L. D. Edwards, *J. Org. Chem.*, 33, 4150 (1968)].

Scheme I



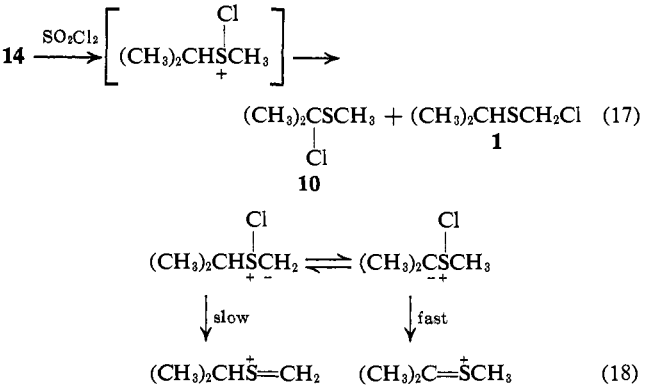
ion the α-carbon would develop carbonium ion character which would direct substitution on the direction of the more highly substituted product.

We conclude that the direction of migration is a reflection of the difference in acidities of the α protons of the alkoxy- or acetoxysulfonium salt. Removal of the α-proton is the product-determining step of the reaction.[12] There is some evidence which suggests that abstraction of the proton may also be the rate-determining step. Ylides of this type are not reprotonated to any significant extent. If the decomposition of the ylide were rate determining the chances that the ylide would be reprotonated would be greater than if the rate-limiting step were the formation of the ylide. Along these lines it is pertinent to note that sulfoxides, such as β-carbonyl sulfoxides, in which the acidity of the α-protons is enhanced, undergo Pummerer reactions with great ease.

The mechanism for the Pummerer reaction suggested by Oae and coworkers[3a,b] and illustrated in eq 9 should be commented on. The carbanionic site of an ylide appears to the present authors as a highly unlikely center for nucleophilic attack. The suggestion that this type of reaction occurs appears to be without precedent elsewhere in the literature. We hesitate to suggest what effects changes in structural or solvent parameters might have if such a mechanism were to be obtained.

It might be anticipated that the mechanism illustrated by example in Scheme I could be generalized to include all represented by eq 1. However this does not appear to be the case. Tuleen and Stephens[13] have recently examined the chlorination of dialkyl sulfides by N-chlorosuccinimide and sulfuryl chloride. For example, it was found that methyl isopropyl sulfide chlorinated predominantly at the more highly substituted α-carbon (eq 17). Those investigators concluded that a sulfur-stabilized carbonium ion intervenes between the halosulfonium salt and the products.

It may be that a concerted elimination of hydrogen chloride (*cf.* eq 4) represents a lower energy pathway for the rearrangement of halosulfonium salts. On the other hand it is possible that ylides derived from halosulfonium do not immediately collapse upon generation and equilibration can occur (eq 18).



It is clear that much additional information such as relative rates of formation and stabilities of ylides, effects of changes in the leaving groups, bases, and solvents, and the possibility of intervention of tetravalent sulfur species must be at hand before generalized statements can be made about the reactions represented by eq 1.

Experimental Section

General. The mass spectra were determined with an Atlas CH_4 mass spectrometer at an ionizing potential of 70 eV and an ionizing current of 10 or 18 μA. Melting points were determined with a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were measured with a Perkin-Elmer 137B Infracord. Nuclear magnetic resonance spectra were obtained on either a Varian DP-60 or an A-60 spectrometer. The carbon-14 was counted with a Tri-Carb liquid scintillation counting system, Model 314EX. The liquid scintillator for the sulfonium salts consisted of a mixture of naphthalene, 2,5-diphenyloxazole (PPO), ethanol, toluene, and hexane. For the organic derivatives, a mixture of toluene, PPO, and 1,4-bis[2-(5-phenyloxazolyl)]benzene (POPOP) was employed. Microanalyses were performed by Midwest Microlab, Inc., Indianapolis, Ind. The following sulfides were purchased from Aldrich and used without further purification: isopropyl methyl sulfide, *n*-propyl methyl sulfide, and *n*-butyl methyl sulfide. Other sulfides were prepared by routine alkylation of sodium thiolates with the appropriate alkyl halide. Sulfides were oxidized to sulfoxides by 0.5 *M* aqueous sodium metaperiodate.[14]

Alkoxysulfonium fluoroborates were prepared by the general methods previously recorded.[6] New salts prepared for this study were isopropylmethylmethoxysulfonium fluoroborate, mp 79–81° (calcd neut equiv, 206; found 191) and ethyl-*p*-tolylmethoxysulfonium fluoroborate, mp 51–54°, (calcd neut equiv, 270; found 271). Phenylethylmethoxysulfonium-*O*-^{14}C fluoroborate was prepared employing methyl-^{14}C iodide.

Treatment of Phenylethylmethoxysulfonium-*O*-^{14}C Fluoroborate and Ethyl-*p*-tolylmethoxysulfonium Fluoroborate with 2,6-Lutidine in Acetone. To 2.14 g (0.02 mol) of 2,6-lutidine in dried acetone (distilled from phosphorus pentoxide) was added 2.56 g (0.01 mol) of phenylethylmethoxysulfonium-*O*-^{14}C fluoroborate (1389 cpm/μmol) and 2.70 g (0.01 mol) of ethyl-*p*-tolylmethoxysulfonium fluoroborate. After stirring a few minutes, the acetone was removed under vacuum and the resulting oil washed with ether. Filtration and evaporation of the ether gave 3 g of a liquid. Vapor phase analysis (0.25 in. × 6 ft, silicone gum rubber, 150°) of the product showed four peaks. The first had the same retention time as 2,6-lutidine. The second was collected, and its ir was identical with that of phenyl ethyl sulfide. The third had the same retention time as *p*-tolyl ethyl sulfide and α-methoxyethyl phenyl sulfide. The nmr of the collected mixture was consistent with a 70:30 mixture of these compounds with the thioacetal predominating. Correcting for the sulfide present the thioacetal had an activity of 999 cpm/μmol. Before the mixture was counted, it was reinjected into the vpc and collected again to ensure complete separation from the other peaks. The fourth peak was also collected, and its ir was identical with that of authentic α-methoxyethyl *p*-tolyl sulfide.[6]

(12) Oae and coworkers[3b] have reached a similar conclusion based on kinetic studies and deuterium isotope effects.

(13) D. L. Tuleen and T. B. Stephens, *J. Org. Chem.*, in press. We wish to thank Professor Tuleen for communicating his results to us prior to publication.

(14) N. J. Leonard and C. R. Johnson, *ibid.*, 27, 282 (1968).

Table I. Reaction of Acetic Anhydride and Sulfoxides

Sulfoxide	Product structure	% yield	Bp, °C (mm)	$n^{25}D$	Nmr spectra, chemical shift, δ[a]
Methyl isopropyl	$(CH_3)_2CHSCH_2OCOCH_3$	69	35–37 (0.5)	1.4533	5.1 (s), 3.1 (h), 2.0 (s), 1.3 (d)
Methyl *n*-propyl	$CH_3(CH_2)_2SCH_2OCOCH_3$	73	...	....	5.1 (s), 2.6 (t), 2.0 (s), 1.7 (h), 1.0 (t)
Methyl *n*-butyl	$CH_3(CH_2)_3SCH_2OCOCH_3$	64	...	....	5.1 (s), 2.6 (t), 2.0 (s), 1.5 (m), 0.9 (m)

[a] The multiplicity of the signal is given by s = singlet, d = doublet, h = hextet, h′ = heptet, t = triplet, m = unresolved multiplet.

Table II. Results of the Treatment of Dimethylmethoxysulfonium Fluoroborate with Sodium Carboxylates

Sodium carboxylate	Product formula	Bp (mp), °C (mm)	% yield	n_D (*t*, °C)	Nmr spectra, chemical shift, δ[a]
Sodium acetate	$CH_3SCH_2OCOCH_3$	46–47 (13)[b]	45	1.4512[d] (31)	....
Sodium benzoate	$CH_3SCH_2OCOC_6H_5$	82 (0.5)[c]	50	1.54462[e] (27)	3.1 (m), 7.5 (m), 5.4 (s), 2.3 (s)
Sodium propionate	$CH_3SCH_2OCOCH_2CH_3$	....	51	1.4539 (26)	5.0 (s), 2.3 (q), 2.1 (s), 1.1 (t)
Sodium *p*-nitrobenzoate	$CH_3SCH_2OCOC_6H_4NO_2$	(51–52)	22	....	8.2 (s), 5.4 (s), 2.3 (s)

[a] See footnote *a*, Table I. [b] Lit.[4] bp 48.5° (12 mm). [c] Lit.[4] bp 97.5° (0.5 mm). [d] Lit.[4] $n^{22}D$ 1.4540. [e] Lit.[4] $n^{22}D$ 1.5500.

The collected peak was reinjected and collected again before it was counted to ensure that it was pure. It had an activity of 423 cpm/μmol.

In order to establish if any scrambling of the label occurred in the vpc, a mixture of α-methoxyethyl-*O*-^{14}C phenyl sulfide (279 cpm/μmol), α-methoxyethyl *p*-tolyl sulfide, and phenyl ethyl sulfide was injected into the vpc. The third peak (α-methoxyethyl *p*-tolyl sulfide) was collected, reinjected, and collected again. It had an activity of 3 cpm/μmol indicating insignificant exchange.

Treatment of α-Methoxyethyl Phenyl Sulfide and Phenyl Ethyl Sulfide with Methanol-^{14}C and 2,6-Lutidinium Fluoroborate in Acetone. To 0.300 g of a mixture of 79% α-methoxyethyl phenyl sulfide (1.41 mmol) and 21% phenyl ethyl sulfide in acetone was added 45 mg (1.4 mmol, 328 cpm/μmol) of labeled methanol and 0.275 g (1.41 mmol) of 2,6-lutidinium fluoroborate. After a few minutes, the solvent was removed and an oil remained which was washed with ether. Filtration of the ether followed by evaporation yielded 0.230 g of product. Vapor phase analysis (0.25 × 6 ft, silicone gum rubber, 150°) indicated two products. The second peak was collected and its ir was identical with that of α-methoxyethyl phenyl sulfide. The thioacetal contained no carbon-14.

Reaction of Phenylethylmethoxysulfonium Fluoroborate with 2,6-Lutidine in Acetone. To an excess of 2,6-lutidine in acetone was added 1.5 g (0.006 mmol) of phenylethylmethoxysulfonium fluoroborate. After stirring a few minutes, the acetone was removed under vacuum and an oil remained to which ether was added. The 2,6-lutidinium fluoroborate precipitated and was filtered from the ether solution. Evaporation of the ether gave 0.73 g of a liquid. Analysis by vpc (0.25 in. × 6 ft, silicone gum rubber, 140°) indicated two products were formed; each was collected. The ir of the first was identical with that of phenyl ethyl sulfide and the ir of the second was identical with that of α-methoxyethyl phenyl sulfide.[6] The ratio of the area of the first peak to that of the second was 1:3.6.

Treatment of Ethyl-*p*-tolylmethoxysulfonium Fluoroborate with Sodium Methoxide in Methanol. To 2.0 g (0.0074 mol) of *p*-tolylethylmethoxysulfonium fluoroborate was added an excess of sodium methoxide in methyl alcohol. After a few minutes, the methyl alcohol was removed under vacuum and ether added to the resultant mixture. Filtration and evaporation of the ether yielded 0.9 g of a liquid. Vapor phase analysis (0.25 in. × 6 ft, silicone gum rubber, 165°) showed only two peaks (1.4:1). The first was collected and shown to be ethyl *p*-tolyl sulfide by comparing its ir spectrum with that of an authentic sample. The second peak was also collected and shown to be α-methoxyethyl *p*-tolyl sulfide; ir (selected peaks): 2900, 1480, 1420, 1360, 1260, 1190, 1110, 1090, 850, and 805 cm^{-1}; nmr: δ 7.4 (aromatic H, AB quartet), 4.6 (q, CH), 3.4 (s, OCH_3), 2.3 (s, $ArCH_3$), and 1.4 (d, CH_3).

Figure 1. Influence of methyl alcohol–THF composition on the products from the reaction of phenylethylmethoxysulfonium fluoroborate with sodium methoxide. When 100% THF was used, sodium hydride was employed as the base.

Reaction of Phenylethylmethoxysulfonium Fluoroborate with Sodium Methoxide in Various Methanol–Tetrahydrofuran Mixtures. To 0.6 g of phenylethylmethoxysulfonium fluoroborate was added an excess of sodium methoxide in varying methanol–tetrahydrofuran mixtures. Next, this was worked up in the same manner as with sodium methoxide in methanol alone (above). In each case vapor phase chromatography (0.25 in. × 6 ft, silicone gum rubber, 140°) showed two products formed, phenyl ethyl sulfide and α-methoxyethyl phenyl sulfide, in varying amounts as shown in Figure 1. The products were identified by comparing the ir spectra with that of authentic samples.

Treatment of Phenylmethylmethoxysulfonium Fluoroborate with Sodium Acetate in DMSO. To 9.85 g (0.041 mol) of phenylmethylmethoxysulfonium fluoroborate in *ca.* 100 ml of DMSO was added 11.0 g (0.14 mol) of sodium acetate. After stirring overnight, water was added to the mixture and the resulting solution extracted with pentane. Evaporation of the pentane gave 5.0 g of a liquid. When this liquid was injected into the vpc (silicone gum rubber, 0.25 in. × 6 ft, 145°), three peaks were found which were collected. The ir spectrum of the first was identical with that of thioanisole. The ir spectrum of the second peak gave major bands at 2900, 1580, 1480, 1430, 1300, 1080, 1020, 950, and 890 cm^{-1}; nmr: δ 7.2 (aromatic complex, 5 H), 4.9 (s, 2 H), and

3.3 (s, 3 H). These data suggest the structure of the substance to be α-methoxythioanisole. The ir spectrum of the third peak gave major bands at 3050, 1745, 1580, 1480, 1360, 1310, 1210, 1010, 980, 820, and 740 cm^{-1}; nmr: δ 7.2 (aromatic complex), 5.3 (s, CH_2), and 2.0 (s, CH_3). These data suggest the structure to be α-acetoxythioanisole. The relative areas of the peaks on the vpc were 12.1:1.0:1.6.

General Procedure for Treatment of Sulfoxides with Acetic Anhydride. To a solution of the sulfoxide in benzene was added 1 equiv of acetic anhydride. After refluxing *ca.* 4 hr, the solvent and acetic acid were distilled off at atmospheric pressure. The α-acyloxy sulfide was purified by distillation or vapor phase chromatography. In each case the vpc of the crude product showed only one peak (see Table I).

General Procedure for Treatment of Dimethylmethoxysulfonium Fluoroborate with Sodium Carboxylates. The alkoxysulfonium salt was added to a saturated solution of the sodium carboxylate in DMSO. After stirring for about 1 hr, a liberal amount of water was added followed by extraction of the resulting mixture with pentane. Evaporation of the pentane gave the crude product which was purified by distillation or recrystallization (see Table II).

Treatment of Isopropylmethylmethoxysulfonium Fluoroborate with Sodium Acetate in DMSO. The same procedure as that for dimethylmethoxysulfonium fluoroborate was employed. Vapor phase chromatography (silicone gum rubber, 0.25 in. × 6 ft, 100°) indicated four compounds were present. The first had the same retention time as isopropyl methyl sulfide. The second was not identified. The third was collected and its mass spectrum was determined. The molecular ion was found to be *m/e* 120 (calcd for $C_5H_{12}OS$: 120). Other major peaks were 28, 39, 41, 43, 45, 78, and 88; ir (selected bands): 3050, 1475, 1380, 1360, 1300, 1250, 1200, 1175, 1090, 940, and 900 cm^{-1}. These data are consistent with methoxymethyl isopropyl sulfide. The fourth peak was also collected and found to be acetoxymethyl isopropyl sulfide; ir (selected bands): 3000, 1735, 1480, 1420, 1360, 1310, 1220, 1170, 1025, 970, 135, and 810 cm^{-1}; nrm: see Table I. The relative areas of the peaks in the chromatogram (in order of elution) were 1.0:1.0:3.5:12.0.

When this salt was treated with sodium methoxide in methyl alcohol, only isopropyl methyl sulfide was formed as evidenced by vpc analysis under the same conditions as stated above.

The Synthesis of *cis*- and *trans*-N-Amino- and N-Nitroso-2,5-diphenylpyrrolidines. Their Abnormal Oxidation and Reduction with Mercuric Oxide and Sodium Hydrosulfite[1]

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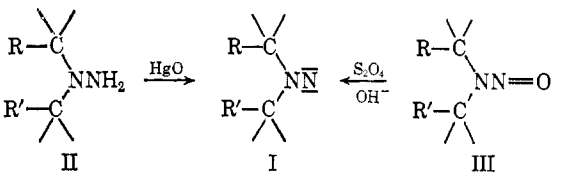
Abstract: The synthesis of *cis*- and *trans*-2,5-diphenylpyrrolidines as well as that of their N-nitroso and N-amino derivatives is reported. The assignment of the structures of each isomer pair is also described. The "abnormal" oxidation of the hydrazines and the "abnormal" reduction of the N-nitrosamines give 1,2-diphenylcyclobutane of retained configuration in fair to high yield; styrene is a by-product in these reactions in an apparently fixed yield. The possible mechanisms of these reactions are discussed.

N-Nitrene intermediates (I) have been used as a convenient rallying point for a number of reactions.[3] Experimental support for this type of intermediate came from the work of McBride and Kruse[4] and Urry, *et al.*,[5] and the recent successful trapping of α-carbonyl N-nitrenes.[6]

Although the evidence for the intermediacy of N-nitrenes is still tenuous, the mechanism by which these presumed intermediates are converted to the observed products is a subject of deep controversy and wide speculation. Our previous contributions dealt mainly with the fragmentation of α-cyano- and of α-aryl-substituted N-nitrenes, which were presumably generated by the mercuric oxide oxidation of the corresponding 1,1-hydrazines (II) or the reduction of the N-nitrosamines (III) with sodium hydrosulfite in basic solution.



II I III

R and/or R' = aryl, CN

In principle, N-nitrenes (I) are valence tautomers of the corresponding azo compounds (IV). The decomposition, with loss of nitrogen, of suitably substituted N-nitrenes results in the formation of products which very often are similar to those obtained from the decomposition of azo compounds. The study of the two series of compounds, particularly those with α-aryl substituents and those where the N–N systems are incorporated in a

(1) This is the 45th in a series of papers concerned with the preparation and decomposition of azo compounds. For the previous paper in this series, see C. G. Overberger and S. Altscher, *J. Org. Chem.*, **31**, 1728 (1966).

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