The second fraction of the chloroform eluate contained the desired product, which was recrystallized from ligroin to give (1.0 g, 2.5 mmoles, 50%) of **37** as colorless crystals, mp 35–36°. An analytical sample was prepared by further recrystallization from ligroin: mp 35–36°; ultraviolet $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 237 mμ (log ε 4.07) and 287 (4.09); nmr singlet τ 6.12, OCH_3) and complex multiplet centered at τ 8.7.

Anal. Calcd for $C_{22}H_{34}O_4S$: C, 66.98; H, 8.69. Found: C, 67.16; H, 8.63.

4-Dodecanethiophthalic acid was prepared by the hydrolysis of dimethyl ester **37** with hot aqueous alkali followed by acidification. Recrystallization from benzene yielded crystals melting at 110–110.5°.

Anal. Calcd for $C_{20}H_{30}O_4S$: C, 65.55; H, 8.25. Found: C, 65.54; H, 8.19.

6-Dodecanethio-2,3-dihydro-1,4-phthalazinedione (38).—A mixture of dimethyl 4-dodecanethiophthalate (0.84 g, 2.1 mmoles) in 0.3 g of 95% hydrazine was heated on a boiling-water bath for 24 hr. The reaction product was washed with water, then recrystallized from acetic acid to give the hydrazide as colorless needles (0.66 g, 1.8 mmoles, 85%), mp 185°. An analytical sample was prepared by two recrystallizations from acetic acid: mp 186–188.5° (sinters at 180°); ultraviolet $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 230 mμ (sh) (log ε 4.08), 240 (sh) (4.00), and 282 (4.31).

Anal. Calcd for $C_{20}H_{30}N_2O_2S$: C, 66.27; H, 8.37; N, 7.73. Found: C, 66.59; H, 8.47; N, 7.84.

Registry No.—**8**, 10351-64-1; **13**, 5566-47-2; **14**, 10351-66-3; **15**, 10351-67-4; **16**, 10351-68-5; **17**, 10378-07-1; **18**, 10351-69-6; **19**, 10351-70-9; **20**, 10351-71-0; **21**, 10351-72-1; **22**, 10351-73-2; **23**, 10351-74-3; **27**, 582-60-5; **28**, 10351-75-4; **29**, 10351-76-5; hydrochloride of **29**, 10351-77-6; **30**, 10351-78-7; **31**, 10351-79-8; **32**, 10351-80-1; **33**, 7153-23-3; **34**, 10351-82-3; **37**, 10351-83-4; **38**, 10351-84-5; 4-dodecanethiophthalic acid, 10351-85-6.

Acknowledgment.—We thank Dr. Giorgio Gaudiano for carrying out some of the reactions in the benzimidazole series and the National Institutes of Health (GM 10849) for its support of this work.

Reactions of Alkoxysulfonium Salts with Alkoxides[1,2a]

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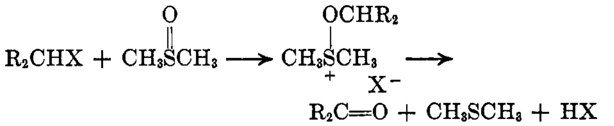
The reaction of representative alkoxysulfonium salts with a variety of alkoxides has been examined. The salts were found to undergo rapid alkoxy exchange followed by (a) base-catalyzed collapse to carbonyl compounds and sulfides or (b) α rearrangements (analogous to the Pummerer reaction) to produce monothioacetals. An ylide appears to be a common intermediate in these reactions. Appropriate deuterium-labeling experiments reveal that the elimination to carbonyl compounds proceeds *via* a cyclic transition state involving the sulfur ylide. The preponderance of the α-rearrangement reaction appears to be a function of the stability of the carbonium ion formed *via* elimination of alkoxide from the ylide intermediate. In all cases the ylide reacts rapidly in the manners stated and is not reprotonated to any significant extent.

A number of synthetically intriguing oxidation reactions that depend on the intervention of alkoxysulfonium salts have now been developed. Halides and tosylates are oxidized by dimethyl sulfoxide (DMSO) at elevated temperatures to the corresponding carbonyl compounds;[3] alcohols are converted to aldehydes or ketones by DMSO and dicyclohexylcarbodiimide under acid–base catalysis;[4] similar reactions can be initiated between alcohols and dimethyl sulfoxide in the presence of acetic anhydride[5] or phosphorus pentoxide[6] or by prior conversion of the alcohol to a chloroformate.[7] These reactions are schematically summarized by eq 1.

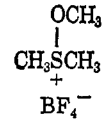


$$R_2CHX + CH_3\overset{\overset{\displaystyle O}{\|}}{S}CH_3 \longrightarrow \underset{+\quad X^-}{CH_3\overset{\overset{\displaystyle OCHR_2}{|}}{S}CH_3} \longrightarrow R_2C{=}O + CH_3SCH_3 + HX \quad (1)$$

The collapse of the intermediate alkoxysulfonium salts to carbonyl compounds and sulfide is promoted by base. The present paper is concerned with the reactions of isolated and characterized alkoxysulfonium salts with alkoxides.[8] The results have a mechanistic bearing on the above-described reactions and are of preparative and interpretive significance.

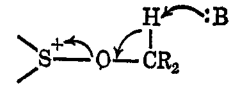
Results and Discussion

Exchange Reactions.—The reaction of simple alkoxysulfonium salts with alkoxides proceeds with rapid exchange of the alkoxy group followed by base-catalyzed elimination to provide carbonyl compounds. When dimethylmethoxysulfonium fluoroborate (I) labeled with carbon-14 in the O-methyl group was treated with sodium hydride in dimethyl sulfoxide, correspondingly labeled formaldehyde was obtained; however, when sodium methoxide in methanol was employed as the base the formaldehyde exhibited less than 1% of the radioactivity of the starting salt. The formaldehyde was characterized and its radioactivity determined as the methone. Exchange was also dictated by the observation that when the reaction was run part-



$$\underset{\displaystyle BF_4^-}{\underset{+}{CH_3\overset{\overset{\displaystyle OCH_3}{|}}{S}CH_3}}$$

I



II

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[1] (a) Part VII in the series Chemistry of Sulfoxides; (b) part VI, C. R. Johnson and M. P. Jones, *J. Org. Chem.*, **32**, 2014 (1967).

[2] (a) We gratefully acknowledge support by the National Science Foundation (Grant No. GP-1159 and GP-5944); (b) Alfred P. Sloan Research Fellow; (c) National Aeronautics and Space Administration Trainee, 1965–1966.

[3] N. Kornblum, W. J. Jones, and G. J. Anderson, *J. Am. Chem. Soc.*, **81**, 4113 (1959).

[4] A. H. Fenselau and J. G. Moffatt, *ibid.*, **88**, 1762 (1966), and previous papers.

[5] J. D. Albright and L. Goldman, *ibid.*, **87**, 4214 (1965).

[6] K. Onodera, S. Hirano, and N. Kashimura, *ibid.*, **87**, 4651 (1965).

[7] D. H. R. Barton, B. J. Garner, and R. H. Wightman, *J. Chem. Soc.*, 1855 (1964).

[8] Portions of this work have been presented in preliminary form by C. R. Johnson and W. G. Phillips, *Tetrahedron Letters*, 2101 (1965).

way, recovered salt showed considerable reduction in radioactivity.

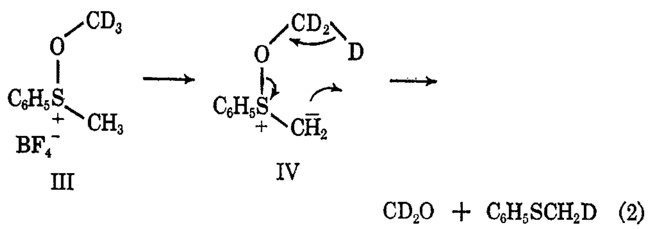
This type of exchange can also be readily observed by titrating I with an alkoxide other than methoxide. Treatment of dimethylmethoxysulfonium fluoroborate (I) with sodium ethoxide in ethanol produced acetaldehyde; sodium isopropoxide in isopropyl alcohol yields acetone; benzaldehyde is produced from benzoxide. Such reactions are of limited synthetic utility, because a large excess of alcohol is required to produce high yields of the carbonyl compound. Use of *t*-butoxide in *t*-butyl provides an intermediate *t*-butoxysulfonium salt which cannot eliminate to a carbonyl compound but which yields isobutylene and dimethyl sulfoxide by carbon–oxygen cleavage.

Fast alkoxy exchange is observed even with bulky groups on the sulfur; *t*-butylmethylmethoxysulfonium fluoroborate was found to produce acetaldehyde in 58% yield when titrated with sodium ethoxide in ethanol. The *t*-butyl methyl sulfide was isolated as its mercuric chloride complex and the acetaldehyde as its 2,4-dinitrophenylhydrazone.

These O-alkyl salts of sulfoxides undergo alkoxy exchange in alcohol solution in the absence of alkoxides or other catalysts although the exchange is considerably slower.[9] For example, when dibenzylethoxysulfonium fluoroborate is dissolved in radioactive ethanol after 1 hr at 70°, recovered salt shows only 4.2% exchange of the ethoxy group with solvent. By employing optically active benzyl *p*-tolylethoxysulfonium fluoroborate in ethanol the exchange could be followed polarimetrically, but the situation is complicated by the formation of ethyl ether and sulfoxide.[10]

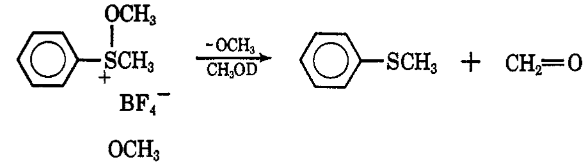
Elimination to Carbonyl Compounds.—Our first indication that the collapse of alkoxysulfonium salts to carbonyl compounds does not proceed by straightforward elimination pathway depicted in II was provided by the observation that treatment of diphenylmethoxysulfonium fluoroborate with sodium methoxide (or other bases[11]) does not produce formaldehyde. Instead, diphenyl sulfoxide and dimethyl ether are produced. On the other hand, base readily initiated the production of formaldehyde and methyl phenyl sulfide from methylphenylmethoxysulfonium fluoroborate. The labeling experiments described below clearly delineate the role of protons α to sulfur in these reactions.

When methylphenyltrideuteriomethoxysulfonium fluoroborate (III) was treated with sodium hydride in tetrahydrofuran (THF), phenyl monodeuteriomethyl sulfide was formed in high yield (eq 2).



The mass spectrum showed the molecular ion of the product to be at *m/e* 125 (C_7H_7DS). The peak at *m/e* 124 (M − 1 peak or nondeuterated sulfide) had a relative intensity of 9.35% compared with the molecular ion. Since nondeuterated thioanisole gave a M − 1 peak with an intensity of 8.1% of the molecular ion, one can conclude very little, or no nondeuterated phenyl methyl sulfide was formed.

When phenylmethylmethoxysulfonium fluoroborate was treated with sodium methoxide in deuteriomethanol, phenyl methyl sulfide was produced with little or no deuterium incorporation (eq 3 and 4).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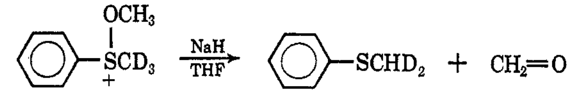
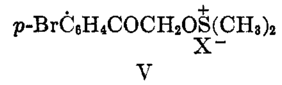

(4)

The M − 1 peak in the mass spectrum of the product was 8.55% of the height of the molecular ion (*m/e* 124) while the M + 1 peak of authenic thioanisole was 8.26% of the height of the molecular ion (calcd 8.46%). Consistent with this result was the observation that phenyltrideuteriomethylmethoxysulfonium fluoroborate (IV) treated with sodium hydride in tetrahydrofuran yielded only phenyl dideuteriomethyl sulfide.

These results can best be explained by invoking an ylide intermediate, which can then form the carbonyl compound *via* a five-membered transition state as shown in eq 2. The ylide is apparently very efficient in acting as an internal base and is not reprotonated to form the starting alkoxysulfonium salt.

Two other laboratories have reported similar evidence for the role of the ylide in reactions of this sort. Fenselau and Moffatt[4] have found that, in the oxidation of 1,1-dideuteriobutanol with DMSO–dicyclocarbodiimide reagent, monodeuteriodimethyl sulfide is produced; in a similar reaction utilizing butanol and hexadeuteriodimethyl sulfoxide, pentadeuteriodimethyl sulfide is formed. The isotopic species were measured by mass spectroscopy. More recently, Torssell[12] has described the thermal and base (triethylamine) induced decomposition of isolated alkoxysulfonium salts, including appropriate deuterium-labeled compounds; for analysis of the deuterium-labeled species the less sensitive nmr method was employed. Furthermore, the latter worker has cited evidence that mechanism of type II is operative in cases where the protons α to the oxygen are activated, *e.g.*, salt V.


$p\text{-BrC}_6\text{H}_4\text{COCH}_2\text{O}\overset{+}{\underset{X^-}{\text{S}}}(\text{CH}_3)_2$

V

α Rearrangements.—The course of the reaction of alkoxides with alkoxysulfonium salts is subject to variation with the alkyl groups attached to sulfur. In one

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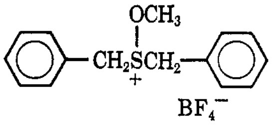
[9] Alkoxy exchange on alkoxysulfonium salts in alcohol solution has also been suggested by P. Skell and M. F. Epstein, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April, 1964, p 26N. We wish to thank Professor Skell and Dr. Epstein for valuable discussions on this matter.

[10] C. R. Johnson and J. B. Sapp, Jr., 145th National Meeting of the American Chemical Society, New York, N. Y., Sept 1963, p 23Q.

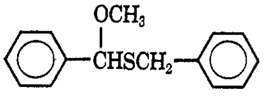
[11] A number of bases were examined including other alkoxides, amines, sodium hydride, and organolithium compounds. In the reaction with phenyllithium a small amount of diphenyl sulfide was formed along with a heavy oil believed to be triphenylsulfonium fluoroborate. Recently, the synthesis of triarylsulfonium salts *via* a reaction of diarylethoxysulfonium salts with arylmagnesium halides has been described [K. K. Anderson and N. E. Papanikolaou, *Tetrahedron Letters*, 5445 (1966)].

[12] K. Torssell, *ibid.*, 4445 (1966).

example dibenzylmethoxysulfonium fluoroborate (VI) was titrated with methoxide in methanol. When the reaction mixture was worked up in the absence of acid α-methoxydibenzyl sulfide (VII) was obtained in 71% yield. When the reaction mixture was directly treated with 2,4-dinitrophenylhydrazine reagent the benzaldehyde derivative was obtained.



VI



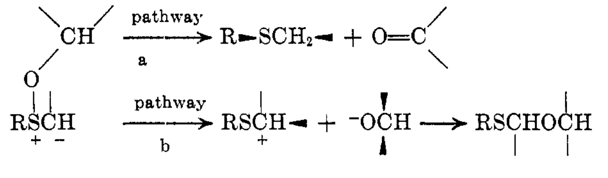
VII

We suggest that the initial step in this rearrangement is again the formation of an ylide. The ylide once formed may collapse by the cyclic pathway discussed above to form a carbonyl compound and the sulfide (pathway a), or may expel alkoxide to form a carbonium ion which readds alkoxide (pathway b). The stability of the carbonium ion formed seems to be an important factor in determining which path will predominate. Table I provides comparative data on the production of thioacetals (pathway b) and sulfides (pathway a) from reactions of representative alkoxysulfonium salts with sodium methoxide. When unsubstituted benzylalkoxysulfonium salts are employed, the stable benzyl carbonium ion can be formed and pathway b predominates. However, in the cases of *p*-nitrobenzyl or methyl salts a relatively unstable carbonium ion would be formed *via* pathway b; in the main, the reaction then proceeds by pathway a.

TABLE I

PRODUCT DISTRIBUTION. REACTION OF ALKOXYSULFONIUM SALTS WITH METHOXIDE

Salt (fluoroborate)	% acetal	% sulfide
Dibenzylmethoxysulfonium	91	9
Benzylphenylmethoxysulfonium	72	28
Benzylmethylmethoxysulfonium	72	28
Ethylphenylmethoxysulfonium	71	29
p-Nitrobenzylphenylmethoxysulfonium	19	81
Methylphenylmethoxysulfonium	<1	>99

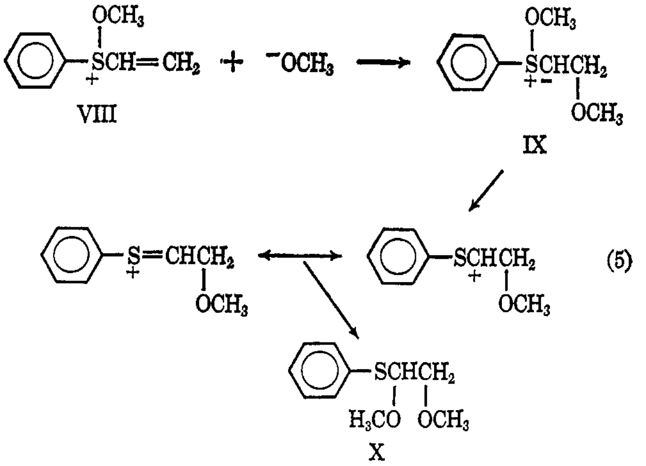


Those reactions that proceed by pathway b are unique in that the loss of alkoxide from the ylide converts a carbon with carbanion character to one with carbonium ion character.

Dibenzylmethoxysulfonium fluoroborate (VI) was treated with sodium methoxide in deuteriomethanol and the reaction mixture treated with 2,4-dinitrophenylhydrazine reagent. The derivative of benzaldehyde which formed was analyzed by mass spectroscopy for deuterium content. It was found that 2.53% deuterium had been incorporated into the derivative. Since α-methoxydibenzyl sulfide was found not to exchange under the reaction condition, one can conclude that the ylide is formed from the salt and that it is reprotonated to the extent of *ca.* 5% (only one of the two benzyl groups is carried through to the dinitrophenylhydrazone).

In order to test the possibility of transfer of assymmetry from sulfur to carbon during such a rearrangement, R-benzyl-*p*-tolylmethoxysulfonium fluoroborate ([α]D +189°) was treated with sodium hydride in the nonexchanging solvent, tetrahydrofuran. A mixture of benzyl *p*-tolyl sulfide and racemic α-methoxybenzyl *p*-tolyl sulfide was formed providing additional evidence for the formation of a free carbonium ion as depicted in pathway b.

A similar reaction can also be initiated by the Michael-type addition of methoxide to vinylphenylmethoxysulfonium fluoroborate (VIII) (eq 5). The product obtained was 1,2-dimethoxy-1-phenylthioethane (X).



Authentic 1,2-dimethoxy-1-phenylthioethane was prepared by the action of *t*-butyl hypochlorite on phenyl vinyl sulfide in the presence of methanol and silver fluoroborate.

A concerted mechanism involving simultaneous attack of methoxide ion and formation of a carbonium ion was ruled out on the basis that 8.3% deuterium was incorporated into the final product when phenylvinylmethoxysulfonium fluoroborate was treated with sodium methoxide in deuteriomethanol. Again, we suggest that an ylide intermediate (IX) is involved.

The similarity of these reactions to the familiar Pummerer reaction is noteworthy. Furthermore, we have observed that dimethylmethoxysulfonium fluoroborate treated with sodium acetate in dimethyl sulfoxide yields α-acetoxymethyl sulfide. The acetate ion apparently displaces the methoxide ion to form an acetoxysulfonium salt as an intermediate which can rearrange to the product. We shall elaborate upon such reactions in a future paper.

Experimental Section

General.—The mass spectra were determined with an Atlas CH4 mass spectrometer[13] 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 (nmr) were obtained on either a Varian DP-60 or a A-60 spectrometer. The carbon-14 was counted with a Tri-Carb liquid scintillation counting system, Model 314EX. The liquid scintillator for the

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(13) The mass spectrometer was purchased from funds provided by a National Science Foundation Research Equipment Grant.

TABLE II

ALKOXYSULFONIUM FLUOROBORATES

Salt (fluoroborate)	% yield	Mode of prepn	Mp, °C	Formula	Calcd, %			Found, %		
					C	H	Neut equiv	C	H	Neut equiv
Dibenzylethoxysulfonium	..	B	117–118	$C_{16}H_{19}BF_4OS$	55.49	5.49	346	55.32	5.48	345
Dibenzylmethoxysulfonium	69	C	113–114	...	...	...	332	...	...	333
Benzylphenylethoxysulfonium	69	B	104–105	$C_{15}H_{17}BF_4OS$	54.22	5.12	...	54.38	5.28	...
Benzylphenylmethoxysulfonium	..	A	111–113	$C_{14}H_{15}BF_4OS$	52.83	4.72	...	53.03	4.90	...
Dimethylmethoxysulfonium	40	C[a]	110–112 (lit.[b] mp 106–108)	...	...	...	...	...	...	...
Phenylvinylmethoxysulfonium	64	A	67–69	...	...	...	254	...	...	255
t-Butylmethylmethoxysulfonium	72	A	128–129	...	...	...	222	...	...	228
Diphenylmethoxysulfonium	67	A	73–74	$C_{13}H_{13}BF_4OS$	51.31	4.28	...	51.43	4.34	...
Methylphenylmethoxysulfonium	71	A	92–94	...	...	...	242	...	...	245
Ethylphenylmethoxysulfonium	65	C	88–91	...	...	...	256	...	...	256
Benzylmethylmethoxysulfonium	..	A	37–39	...	...	...	256	...	...	263
4-Nitrobenzylphenylmethoxysulfonium	58	A	127–129	...	...	...	363	...	...	366
Trideuteriomethylphenylmethoxysulfonium	70	C	96–97.5	...	...	...	...	...	...	...
Methylphenyltrideuteriomethoxysulfonium	71	A	97–98	...	...	...	...	...	...	...
(+)-Benzyl-*p*-tolylmethoxysulfonium	50	A	118.5–119.5	$C_{15}H_{17}BF_4OS$	54.22	5.12	...	54.19	5.25	...

[a] This salt is insoluble in ethylene chloride and the silver iodide must be washed with acetonitrile. [b] H. Meerwein, V. Hederich, and K. Wunderlich, *Arch. Pharm.*, **291**, 541 (1958).

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 various companies and used without further purification: diphenyl sulfide (Eastman), phenyl methyl sulfide (Aldrich), phenyl benzyl sulfide (Columbia), and benzyl methyl sulfide (Aldrich). Other sulfides were made by routine alkylation of sodium thiolates with the appropriate alkyl halide. Sulfides were oxidized to sulfoxides by commercial 30% hydrogen peroxide employing acetone as a cosolvent or by 0.5 *M* aqueous sodium metaperiodate.[14]

General Methods of Preparation of Alkoxysulfonium Salts. A. Trimethyloxonium Fluoroborate.—To a solution of the sulfoxide in methylene chloride was added 1 equiv of trimethyloxonium fluoroborate. After about 1 hr of stirring the insoluble trimethyloxonium fluoroborate would usually disappear. In cases when it did not, it was removed by filtration. Ether then was added to precipitate the sulfonium salt; the salt was purified by redissolving it in methylene chloride and adding ether to the cloud point and cooling to crystallize.

B. Triethyloxonium Fluoroborate.—The procedure employed was the same as that for the alkylation with trimethyloxonium fluoroborate; the triethyl salt is soluble in methylene chloride.

C. Methyl Iodide and Silver Fluoroborate.—To a solution of the sulfoxide in ethylene chloride or methylene chloride was added 1 equiv of silver fluoroborate. A twofold excess of methyl iodide was then added to this mixture. After about 1 hr of stirring, the precipitated silver iodide was removed by filtration and ether was added to the filtrate to precipitate the alkoxysulfonium salt. The product was purified by crystallization from methylene chloride–ether mixtures.

Reactions of Dimethylmethoxysulfonium Fluoroborate with Sodium Alkoxides. A. Sodium Methoxide.—To 0.69 g (3.8 mmoles) of dimethylmethoxysulfonium fluoroborate was added 20 ml of 0.221 *M* sodium methoxide in methanol. Immediately 2,4-dinitrophenylhydrazine reagent was added; formaldehyde 2,4-dinitrophenylhydrazone (68%) was isolated; recrystallization from ethanol–ethyl acetate gave a product with mp 163–164°, lit.[15] mp 166°.

B. Dimethylmethoxysulfonium-O-C^{14} Fluoroborate with Sodium Methoxide.—To 0.104 g (0.555 mmole) of dimethylmethoxysulfonium fluoroborate (4340 cpm/μmole) was added 0.61 mmole of sodium methoxide in methanol. Immediately 0.20 g of 5,5-dimethyl-1,3-cyclohexanedione in 5 ml of ethanol was added. After 1 hr of standing the solution was cooled and formaldehyde methone (85 mg) crystallized. After recrystallization from ethanol the product had mp 188–190° (lit.[15] mp 189°), and an activity of 35 cpm/μmole. When the same reaction was run using 0.5 equiv of sodium methoxide, some of the starting salt could be recovered by adding ether to the reaction mixture. It was purified by dissolving it in N,N-dimethylacetamide and by adding ether to the cloud point. The activity of recovered salt was found to be 51% of that of the starting salt.

C. Sodium Ethoxide.—A solution of 2.1 mmoles of sodium ethoxide in ethanol was added to 2.1 mmoles of salt. The acetaldehyde dimethone was prepared in 23% over-all yield by the standard procedure, mp 139–140°, lit.[15] mp 140°. From a similar reaction the 2,4-dinitrophenylhydrazone was prepared in 72% yield, mp 143–145°, lit.[15] mp 147°.

D. Sodium Isopropoxide.—The reaction was run in the same manner as for sodium ethoxide. Acetone was obtained in 50% yield as its 2,4-dinitrophenylhydrazone, mp 122–125°, lit.[15] mp 126°.

E. Sodium *t*-Butoxide.—To 2.9 mmoles of sodium *t*-butoxide in *t*-butyl alcohol was added 0.5 g (2.2 mmoles) of dimethylmethoxysulfonium fluoroborate. Nitrogen was passed through the reaction mixture and into a bromine–carbon tetrachloride solution. The carbon tetrachloride solution was analyzed by vapor phase chromatography (vpc) (0.25 in. × 8 ft, 10% Carbowax, 100°) which showed a solvent peak and one other. The second peak was collected; its infrared spectrum was identical with that of 1,2-dibromo-2-methylpropane and its vpc retention time was the same as that of authentic material.

F. Sodium Benzoxide.—This was prepared in the same manner as sodium ethoxide. Benzaldehyde was isolated in 20% yield as the 2,4-dinitrophenylhydrazone, mp 236–237°, lit.[15] mp 237°.

Reaction of Dimethylmethoxysulfonium-O-C^{14} Fluoroborate with Sodium Hydride in Dimethyl Sulfoxide.—A solution of 0.090 g (0.50 mmole) of labeled salt (1483 cpm/μmole) in dimethyl sulfoxide was treated with 0.023 g of sodium hydride. Immediately the methone derivative was prepared by the standard procedure, mp 188–189°, lit.[15] mp 189°. A mixture melting point with the authentic derivative prepared from formaldehyde was undepressed. The derivative had an average activity of 1527 cpm/μmole.

Reaction of Diphenylmethoxysulfonium Fluoroborate with Sodium Methoxide in Methanol.—To 0.320 g (1.05 mmoles) of diphenylmethoxysulfonium fluoroborate was added 1.2 mmoles of sodium methoxide in 25 ml of methanol. After 10 min the methanol was evaporated, the residue was extracted with ether, and the solvent was removed to yield 0.15 g, 0.74 mmole, of diphenyl sulfoxide (70%), mp 69–70°, lit.[15] mp 70°.

Reaction of Methylphenylmethoxysulfonium Fluoroborate with Sodium Methoxide in Methanol.—To 1.4 mmoles of sodium methoxide in dry methanol was added 0.35 g (1.4 mmoles) of methylphenylmethoxysulfonium fluoroborate. The methanol was immediately removed under reduced pressure and ether was added to the resulting slurry. Filtration, followed by removal of

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[14] N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, **27**, 282 (1962).

[15] "Tables for Identification of Organic Compounds," Chemical Rubber Publishing Co., Cleveland, Ohio.

the ether yielded 95 mg of a liquid whose infrared spectrum was identical with that of phenyl methyl sulfide. The vpc of the product (0.25 in. × 6 ft silicone gum rubber, 145°) showed a peak which had the same retention time as authentic thioanisole and only very minor (1%) other peaks.

Reaction of Methylphenyltrideuteriomethoxysulfonium Fluoroborate with Sodium Hydride.—To 0.10 g (4 mmoles) of sodium hydride in dried THF was added 0.85 g (3.8 mmoles) of methylphenyltrideuteriomethoxysulfonium fluoroborate. After stirring overnight, the solvent was removed under reduced pressure and ether was added to the residue. Upon filtration and removal of the ether, 0.44 g of liquid remained. After distillation, a mass spectrum showed a molecular ion of 125, corresponding to monodeuteriomethyl phenyl sulfide. Very little or no nondeuterated thiolanisole was found.

Reaction of Trideuteriomethylphenylmethoxysulfonium Fluoroborate with Sodium Hydride in Tetrahydrofuran.—The same procedure as that for methylphenyltrideuteriomethoxysulfonium fluoroborate was followed. Dideuteriomethylphenyl sulfide was isolated in nearly quantitative yield. The mass spectrum indicated that the molecular ion was at *m/e* 126. Very little or no trideuteriomethyl or monodeuteriomethyl phenyl sulfide could be detected. The $M - 1$ peak was 4.8% that of the molecular ion (126) and the $M - 2$ peak was 3.6%.

Reaction of Benzylmethylmethoxysulfonium Fluoroborate with Sodium Methoxide in Methanol.—To 1.4 g (0.005 mole) of benzylmethylmethoxysulfonium fluoroborate was added 1 equiv of sodium methoxide in dry methanol. Immediately the methanol was removed under reduced pressure and ether was added to the remaining slurry. After filtration and removal of the ether, a liquid remained. Vapor phase analysis (0.25 in. × 6 ft silicone gum rubber, 140°) showed two peaks only. The first was collected and shown to be benzyl methyl sulfide by comparing its infrared spectrum with that of an authentic sample. The second peak was also collected and shown to be α-methoxybenzyl methyl sulfide by infrared and nmr analysis. The ratio of the area of the second peak to that of the first was 2.8:1. The α-methoxybenzyl methyl sulfide gave benzaldehyde 2,4-dinitrophenylhydrazone upon addition of the reagent, mp 233–236°, lit.[15] mp 237°.

Reaction of Dibenzylmethoxysulfonium Fluoroborate with Sodium Methoxide in Methanol.—This salt was treated in the same manner as benzylmethylmethoxysulfonium fluoroborate except that the crude product was dissolved in benzene and passed through an alumina column which served to remove the small amount of dibenzyl sulfoxide which was formed in the reaction. Evaporation of the benzene and distillation of the product gave a 73% yield of α-methoxybenzyl sulfide. The infrared spectrum gave major peaks at 3050, 2930, 1610, 1500, 1450, 1240, 1190, 1100–1060, 1030, and 960 cm^{-1}. The nmr gave an aromatic complex centered at τ 2.9 (10 H), a singlet at 4.7 (1 H), a quartet at 6.4 (2 H), and a singlet at 6.7 (3 H). The mass spectrum gave a molecular ion at *m/e* 244 (calcd 244) along with major peaks at 45, 51, 65, 77, 91, 105, 121, 122, 123, 135, 152, and 214. The reaction was repeated and an nmr was run of the crude product. Two additional peaks were present in the nmr at 4.2 and 4.5. These were shown to be due to dibenzyl sulfide and dibenzyl sulfoxide by comparison with authentic spectra. Integration of the peaks showed 79% α-methoxybenzyl sulfide, 14% dibenzyl sulfoxide, and 7% dibenzyl sulfide.

Reaction of Benzylphenylmethoxysulfonium Fluoroborate with Sodium Methoxide in Methanol.—This salt was treated in the same manner as benzylmethylmethoxysulfonium fluoroborate. A nmr of the crude material showed an aromatic complex centered at τ 2.8, a singlet at 4.3 and a singlet at 6.5 which is consistent with α-methoxybenzyl phenyl sulfide. Also a singlet was present at 6.0 which is due to phenyl benzyl sulfide. Integration showed the ratio of acetal to sulfide to be 2.6:1. No other peaks were present in the spectrum.

Reaction of Ethylphenylmethoxysulfonium Fluoroborate with Sodium Methoxide in Methanol.—This salt was treated in the same manner as benzylmethylmethoxysulfonium fluoroborate. Vapor phase analysis (0.25 in. × 6 ft silicone gum rubber, 140°) showed only two peaks. The first was collected and shown to be ethyl phenyl sulfide by comparing its infrared spectrum with that of an authentic sample. The second peak was also collected and shown to be α-methoxyethyl phenyl sulfide: infrared selected bands at 2900, 1600, 1480, 1350, 1200, 1120, 1080, 860, 750, and 690 cm^{-1}; nmr (an aromatic complex) τ 2.7, a quartet 5.2, a singlet at 6.5, and a doublet at 8.6. The ratio of the second peak to the first in the chromatograph was 2.5:1. Acetaldehyde 2,4-dinitrophenylhydrazone was formed upon addition of that reagent to the crude product, mp 165–167°, lit.[15] mp 168°.

Reaction of Phenyl-4-nitrobenzylmethoxysulfonium Fluoroborate with Sodium Methoxide in Methanol.—This salt was treated in the same manner as benzylmethylmethoxysulfonium fluoroborate. A nmr of the crude product showed two aromatic complexes centered at τ 1.9 and 2.7 and a singlet at 5.8 due to the presence of *p*-nitrobenzyl phenyl sulfide. Also present was a singlet at 4.2 and a singlet at 6.3 due to α-methoxy-*p*-nitrobenzyl sulfide. Integration showed that the ratio of sulfide to acetal was 4.2:1. Formaldehyde 2,4-dinitrophenylhydrazone, mp 164–166° (lit.[15] mp 166°), was formed in 64% yield upon addition of that reagent to the reaction mixture from sodium methoxide and phenyl-4-nitrobenzylmethoxysulfonium fluoroborate.

Reaction of (+)-Benzyl-*p*-tolylmethoxysulfonium Fluoroborate with Sodium Methoxide in Methanol.—To a slurry of 0.095 g (0.00029 mole) of (+)-benzyl-*p*-tolylmethoxysulfonium fluoroborate [$[\alpha]^{27}_D$ 189° (*c* 1.0, CH_2Cl_2)] in dried THF was added 0.020 g (0.0009 mole) of sodium hydride. After 1 hr of stirring, the THF was removed under vacuum and ether was added to the resultant slurry. After filtration the ether was removed under reduced pressure and an oil (0.040 g) remained. In order to remove any sulfoxide which might have been formed, the oil was dissolved in benzene and passed through an alumina column. The optical rotation of the mixture was taken, $[\alpha]^{27}_D$ −0.1 ± 0.1 (*c* 1.9, $CHCl_3$). An nmr spectrum run on a sample prepared identically as above from racemic salt showed that α-methoxybenzyl *p*-tolyl sulfide and benzyl *p*-tolyl sulfide were present in a ratio of 1:5.

Reactions of Alkoxysulfonium Salts with Sodium Methoxide Followed by Addition of 2,4-Dinitrophenylhydrazone Reagent. A. Dibenzylethoxysulfonium Fluoroborate.—To 0.95 g (0.0027 mole) of dibenzylethoxysulfonium fluoroborate was added 1 equiv of 0.035 *M* sodium methoxide in dry methanol. Immediately 2,4-dinitrophenylhydrazine reagent was added and 0.60 g of a precipitate formed which was recrystallized from a mixture of ethanol and ethyl acetate. The yield was 77% based on the 2,4-dinitrophenylhydrazone derivative of benzaldehyde, mp 234–235° (lit.[15] mp 237°); the mixture melting point with an authentic sample was undepressed.

B. Dibenzylmethoxysulfonium Fluoroborate.—This salt was treated in the same manner as dibenzylethoxysulfonium fluoroborate. Benzaldehyde 2,4-dinitrophenylhydrazone was formed in 82% yield, mp 237–238°.

C. Benzylphenylethoxysulfonium Fluoroborate.—This salt was treated in the same manner as dibenzylethoxysulfonium fluoroborate. Benzaldehyde 2,4-dinitrophenylhydrazone (mp 237–238°) was formed in 69% yield, mixture melting point undepressed.

D. Phenyl-4-nitrobenzylmethoxysulfonium Fluoroborate.—This salt was treated in the same manner as dibenzylethoxysulfonium fluoroborate. Formaldehyde 2,4-dinitrophenylhydrazone was formed in 69% yield, mp 164–166° (lit.[15] mp 166°); the mixture melting point with authentic material was undepressed.

Reaction of Dibenzylmethoxysulfonium Fluoroborate with Sodium Methoxide in Deuteriomethanol.—To 2 ml of deuteriomethanol was added 0.01 g of sodium. After the reaction was over, 0.100 g (0.0003 mole) of dibenzylmethoxysulfonium fluoroborate was added followed 1 min later by 2,4-dinitrophenylhydrazine reagent. The precipitate which formed was recrystallized from a mixture of ethanol and ethyl acetate, mp 233–234°, lit.[15] for benzaldehyde, mp 237°. The mass spectrum was taken of the derivative and it was found that the height of the $M + 1$ peak was 18.5% of that of the molecular ion. Also the mass spectrum was taken of nondeuterated benzaldehyde 2,4-dinitrophenylhydrazone and the height of the $M + 1$ peak was 15.9% of that of the molecular ion (calcd 15.9%). These data indicate 2.53% deuterium was incorporated.

Treatment of α-Methoxybenzyl Sulfide with Sodium Methoxide in Deuteriomethanol.—To 2 ml of deuteriomethanol was added 0.01 g of sodium. When the reaction was over, 0.10 g of the acetal was added. After a few minutes, the methanol was removed under reduced pressure and benzene was added to the resulting slurry. After filtration the benzene was removed and a mass spectrum was taken which indicated that the height of the $M + 1$ peak was 17.4% of that of the molecular ion [compared with starting material, 17.4% (calcd 17.3%)], indicating no deuterium incorporation.

Reaction of Phenylvinylmethoxysulfonium Fluoroborate with Sodium Methoxide in Methanol.—To 3.1 g (12.2 mmoles) of phenylvinylmethoxysulfonium fluoroborate was added 1 equiv of sodium methoxide in methanol. The solvent was removed under vacuum and ether was added to the resultant slurry. After filtration and removal of the ether, an oil remained (2.0 g). The infrared spectrum was very similar to that of authentic phenyl 1,2-dimethoxyethyl sulfide. The mercuric chloride complex was prepared and recrystallized five times from a methanol–water mixture, mp 151–152°, melting point of authentic complex 151–152°, mixture melting point undepressed. The reaction was repeated employing deuteriomethanol. A mass spectrum of the distilled compound gave an M + 1 peak of 21.7% of the height of M, whereas product from the reaction with nondeuterated methanol gave an M + 1 peak of 12.6% (calcd 11.9%) indicating 8.3% deuterium incorporation in the former.

Phenyl 1,2-Dimethoxyethyl Sulfide.—To 4 ml of methanol at −70° were added 0.216 g (2 mmoles) of *t*-butyl hypochlorite, 0.272 g (2 mmoles) of phenyl vinyl sulfide, and 0.390 g (2 mmoles) of silver fluoroborate. The mixture was allowed to warm to room temperature and stirred for 3 hr after which ether was added. The ether solution was then extracted with sodium bicarbonate and dried with sodium sulfate. Removal of the solvent yielded 0.170 g of a liquid: bp 78–82° (0.1 mm); n^{27}_{D} 1.5404; nmr spectra aromatic complex at τ 2.75, quartet centered at 5.35 (proton α to oxygen and sulfur), two singlets at 6.54 and 6.76 (methoxy protons), and a multiplet between 6.5 and 6.7, partially obscured by the methoxy protons, representing the methylene group; infrared spectra (selected peaks) 2950, 1600, 1480, 1440, 1190, and a broad absorption at 1090–1130 cm^{-1}. A mass spectrum was taken and the molecular ion was found to be 198 (calcd 198). Other major peaks were at *m/e* 45, 51, 59, 65, 88, 89, 109, 110, 123, 135, 136, 153, and 168.

Reaction of *t*-Butylmethylmethoxysulfonium Fluoroborate with Sodium Ethoxide in Ethanol.—To 0.150 g (0.7 mmole) of *t*-butylmethylmethoxysulfonium fluoroborate was added 1 equiv of sodium ethoxide in dry ethanol. The acetaldehyde dimethone was prepared in 40% yield by the standard procedure, mp 138–139°, lit.[15] mp 140°. From a similar reaction the 2,4-dinitrophenylhydrazone was prepared in 58% yield, mp 147–149°, lit.[15] mp 147°. When mercuric chloride was added to the crude reaction mixture, a precipitate formed which was recrystallized twice from aqueous ethanol, mp 128–131°. The melting point of the authentic complex prepared from *t*-butyl methyl sulfide and mercuric chloride was found to melt at 128–131°. A mixture melting point with the complex was undepressed.

Registry No.—α-Methoxybenzyl sulfide, 5873-86-9; α-methoxyethyl phenyl sulfide, 10429-09-1; phenyl 1,2-dimethoxyethyl sulfide, 10429-08-0.

Quantitative Solubility–Structure Relationships for Some *meta*- and *para*-Substituted Benzoic Acids in *p*-Dioxane and in Tetrahydrofuran[1]

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The solubilities at 30° of benzoic acid and 14 *meta*- or *para*-substituted benzoic acids have been determined in *p*-dioxane and in tetrahydrofuran. The solubility values are reported in terms of grams of solute per 100 g of saturated solution, mole fraction of solute, and mole ratio of solute for each acid in each of the solvents. Analyses of the linear regression of log solubility ratio terms on Hammett's σ values are reported. Deviations are discussed and rationalized in terms of various factors which affect solubility. When the present data are compared with those reported previously for benzene and cyclohexane, correlations of the resulting log solubility ratio terms with Hammett's σ values produce V-shaped relationships.

In the first paper[2] of this series, values of log (X_B/X_C) at 30° for 20 *meta*- and *para*-substituted benzoic acids were reported. X_B and X_C are the mole fraction solubilities in benzene and in cyclohexane and, in general, are in the Henry's law range (X_B or X_C exceeded 0.05 in only two cases of the 40 values reported). For 16 of these acids, the correlation[3a] of log (X_B/X_C) with Hammett[4] σ values was highly significant at the 100.0% confidence level.[3b] Large deviations from this correlation were observed for the other four acids which are included among the five weakest of the 20 acids.

The purpose of the present study was to measure the solubilities of a similar series of benzoic acids in other solvents in which solute–solute interactions are minimized.

Coassociation of solute with solvent occurs[5] when intermolecular hydrogen bonds can be formed and association of the solute is thereby reduced. Consequently, *p*-dioxane and tetrahydrofuran were chosen as solvents because they are capable of dissociating dimeric carboxylic acids into single molecules by forming hydrogen bonds[6] and of minimizing solute–solute interactions which involve the substituent groups. If these solute–solute interactions can be minimized or cancelled, the solvent–solute interactions will predominate, and thus a good correlation of solubility with Hammett σ values may result.

Results and Discussion

The solubility in tetrahydrofuran and in *p*-dioxane at 30° of 15 benzoic acids, expressed as grams of acid per 100 g of saturated solution, as mole fraction solubility, and as mole ratio solubility, are given in Table I. From these data, values of log (X_T/X_D) and log (R_T/R_D) were calculated and are recorded in Table II. X_T and X_D are the mole fraction solubilities in tetrahydrofuran and in *p*-dioxane while R_T and R_D are the mole ratio solubilities in these two solvents. In contrast to the previously reported[2] X_B and X_C values, the values of X_T and X_D reported herein are, in general, much larger than 0.05 and are not in the Henry's law range. The solubilities of the benzoic acids were found to be greater in tetrahydrofuran than in *p*-dioxane.

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[1] Abstracted in part from the M.S. thesis of J. P. I., Texas A & M University, Jan 1965.

[2] C. K. Hancock, J. N. Pawloski, and J. P. Idoux, *J. Org. Chem.*, **31**, 3801 (1966).

[3] G. W. Snedecor, "Statistical Methods," 5th ed, The Iowa State College Press, Ames, Iowa, 1956: (a) Chapters VI, VII; (b) pp 46, 418, 441.

[4] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p 184.

[5] E. N. Lassettre, *Chem. Rev.*, **20**, 301 (1937).

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