Studies on Oxosulfonium Salts. I. Preparation and Physical Properties.[1]

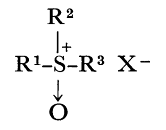
Michio Kobayashi, Kenji Kamiyama, Hiroshi Minato, Yukio Oishi, Yoko Takada,
and Yoshitaka Hattori

Department of Chemistry, Tokyo Metropolitan University, Fukazawa, Setagaya-ku, Tokyo

(Received June, 1 1972)

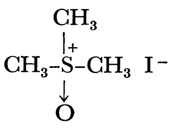
Methods for preparation and physical properties of oxosulfonium salts have been discussed. Optically active ethylmethylphenyloxosulfonium salts have been prepared and their absolute configurations have been determined.

Very little has been reported on the oxosulfonium salts (I) except trimethyloxosulfonium iodide (II), which can easily be prepared by heating dimethyl sulfoxide and methyl iodide[2,3] and are used as a source of dimethyloxosulfonium ylid (III).



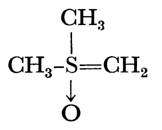
$R^1\text{-}\overset{R^2}{\underset{O}{\overset{|+}{\underset{\downarrow}{S}}}}\text{-}R^3\ X^-$

(I)



$CH_3\text{-}\overset{CH_3}{\underset{O}{\overset{|+}{\underset{\downarrow}{S}}}}\text{-}CH_3\ I^-$

(II)



$CH_3\text{-}\overset{CH_3}{\underset{O}{\overset{|}{\underset{\downarrow}{S}}}}{=}CH_2$

(III)

It seems of interest to investigate the methods for synthesizing oxosulfonium salts containing various substituents, especially the optically active salts containing three different substituents. The results of the investigation carried out in our laboratories will be described in this paper.

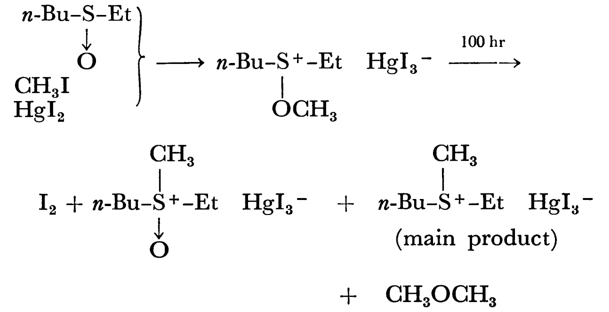
Results and Discussion

(I) Methods for Syntheses of Oxosulfonium Salts. As methods for synthesizing oxosulfonium salts, the following two approaches have been examined.

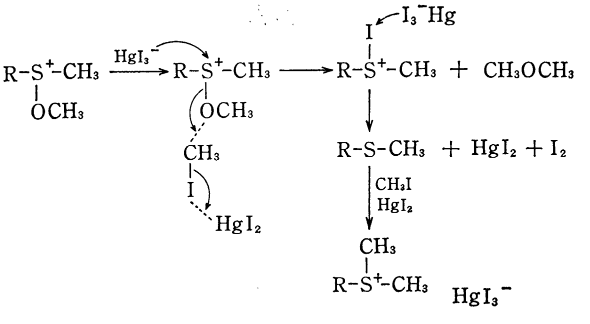
1) Oxidation of Sulfonium Salts: In the literature[4,5] oxidations of sulfonium salts to the corresponding oxosulfonium salts by use of hydrogen peroxide were described, but the products were not isolated as pure substances. In an attempt to examine this route as a possible method for synthesis of oxosulfonium salts, several sulfonium salts were treated with 30% H_2O_2, 87% H_2O_2–CF_3CO_2H, $PhCO_3H$–MeCN, NaOBr, HNO_3, Cl_2–CH_3CO_2H and PhIO under varied conditions, but no oxosulfonium salts were found. These results indicate that oxidation of sulfonium salts is not likely to be a general method for synthesizing oxosulfonium salts.

2) Alkylation or Arylation of Sulfoxides: In contrast with the very easy *S*-methylation of dimethyl sulfoxide, alkylation (alkyl groups larger than methyl) of dimethyl sulfoxide or methylation of dialkyl sulfoxides is very difficult. It was stated in the literature[6] that alkylations did not take place, but the reason why oxosulfonium salts were not formed was not discussed and what happened instead was not described.

When *n*-alkyl bromides or chlorides and sulfoxides were heated at 100°C for several days, no reaction took place. When a mixture of dialkyl sulfoxides or aryl sulfoxides and methyl iodide was refluxed for one day, almost no reaction took place. However, when mercury(II) iodide was added the reaction was greatly accelerated, but an NMR study indicated that the first step is the *O*-alkylation instead of the *S*-alkylation; the oxosulfonium salt must arise by subsequent rearrangement of the *O*-alkylated product or reaction of the unchanged sulfoxide with the *O*-alkylated product. At the same time a great amount of the corresponding sulfonium salt was always formed, and iodine and dimethyl ether were found as by-products. A typical example is shown below.



A plausible mechanism for the formation of the sulfonium salt is expressed as follows.



Since the solubilities of sulfonium salts and oxosulfonium salts are similar, their separation is difficult. However, repeated recrystallizations (more than a dozen times) from tetrahydrofuran–ether or alcohol can separate the two salts. Sulfonium salts are always the main product, and the yields of oxosulfonium salts are very low.

In the reaction between *p*-substituted phenyl methyl sulfoxides and methyl iodide–mercury iodide, considerable substituent effect was observed; the reaction was very slow with the sulfoxides containing electron-withdrawing substituents. With the *p*-bromophenyl

---

[1] Organic Sulfur Compounds. Part XXXVII.

[2] R. Kuhn and H. Trischmann, *Ann*, **611**, 117 (1958).

[3] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1957 (1965).

[4] H. Distler and F. Fucks, *Tenside*, **6**, 65 (1969).

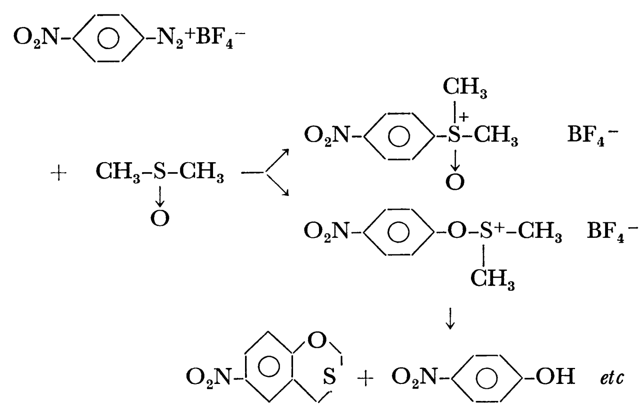
[5] D. R. P. 1258865

[6] R. T. Major and H. -J. Hess, *J. Org. Chem.*, **23**, 1563 (1958).

methyl sulfoxide, formation of the oxosulfonium salt was detected after 100 hr of refluxing. With the *p*-nitrophenyl methyl sulfoxide it was detected after 300 hr of refluxing, and the maximum yield after longer refluxing was below 1%.

When such powerful alkylating agent as trimethyl- or triethyloxonium tetrafluoroborate was used, only *O*-alkylation took place.[7]

Although sulfoxides generally do not react with aryl halides, heating a mixture of dimethyl sulfoxide and an anhydrous aryldiazonium salt results in the formation of an aryldimethyloxosulfonium salt,[8] but the main reaction was *O*-arylation and the maximum yield of oxosulfonium salts was 20%. Since substituted benzenediazonium salts are generally more stable than the non-substituted salt, higher temperature was used for their decomposition and the yields were lower (for the *p*-nitro salt, the yield was about 1%).



In the literature, it was described that the reaction among dimethyl sulfoxide, phenol and dicyclohexylcarbodiimide yields the *O*-phenylated dimethyl sulfoxide, which changes into 1,3-oxathian.[9]

(II) Physical Properties. *1) Solubilities*: Oxosulfonium salts are soluble in acetone, acetonitrile, tetrahydrofuran, trifluoroacetic acid, hot methanol or hot ethanol, and insoluble in benzene, ether, chloroform, or carbon tetrachloride.

2) Infrared Spectra: Oxosulfonium salts show a strong absorption ($\varepsilon \sim 300$) at 1220—1240 cm^{-1} due to their S–O stretching. The wave number of this absorption is approximately equal to the average of the wave numbers of the symmetric and asymmetric stretching of the S–O bond of the sulfones (1220 cm^{-1}) or that of the sulfoximines (1220—1240 cm^{-1}). This suggests that the double bond character of the S–O bond of oxosulfonium salts is similar to those of sulfones and sulfoximines, and much stronger than that of sulfoxides (1050 cm^{-1}).

The ν_{S-O} of *p*-substituted dimethyl phenyl oxosulfonium salts changes with the substituents, and a Hammett relationship was found to hold between $\Delta\nu$ and σ^+ values, as shown in Table 1.

TABLE 1. ν_{S-O} OF $p\text{-X-C}_6\text{H}_4\text{-}\underset{\underset{\text{O}}{\downarrow}}{\overset{+}{\text{S}}}(\text{Me})_2\ \text{HgI}_3^-$

X	ν_{S-O} (in MeCN)
CH_3O	1238
CH_3	1240
H	1242
Br	1243
NO_2	1245

3) NMR Spectra: Oxosulfonium salts show the $\underset{\underset{\text{O}}{\downarrow}}{\text{S}^+}\text{—CH}_3$ signals at δ 4—4.5 and the $\underset{\underset{\text{O}}{\downarrow}}{\text{S}^+}\text{—CH}_2\text{—}$signals at δ 5. Since the corresponding methyl and methylene signals of sulfonium salts are observed at higher magnetic fields (by 0.5 ppm), these signals can be used for detection and quantitative determination of oxosulfonium and sulfonium salts. Changes of the methyl signals of *p*-substituted dimethylphenyloxosulfonium salts are shown in Table 2. A Hammett relationship was found to hold between $\Delta\nu$ and σ^+ values.

TABLE 2. NMR METHYL SIGNALS OF $p\text{-X-C}_6\text{H}_4\underset{\underset{\text{O}}{\downarrow}}{\overset{+}{\text{S}}}(\text{Me})_2\ \text{HgI}_3^-$ AND $p\text{-X-C}_6\text{H}_4\overset{+}{\text{S}}(\text{Me})_3\ \text{HgI}_3^-$

(in acetone-d_6)

X	Oxosulfonium Salts	Sulfonium Salts
CH_3O	δ 4.35	δ 3.50
CH_3	4.40	3.51
H	4.43	3.57
Br	4.47	3.59

(III) Reactions. *1) Alkylation by Use of Oxosulfonium Salts*: Oxosulfonium salts can alkylate reactive anions. The reaction of dimethylphenyloxosulfonium ion with sodium *p*-toluenesulfinate gave methyl *p*-tolyl sulfone exclusively, and no methyl *p*-toluenesulfinate was found. When dimethylphenyloxosulfonium ion was heated with sodium iodide in acetone, the oxosulfonium ion was readily demethylated and converted to methyl phenyl sulfoxide.

The results of a detailed investigation on these S_N2 type reactions with nucleophiles will be described in a separate paper.

2) Oxidation by Use of Oxosulfonium Salts: Since an oxosulfonium ion contains an extra oxygen compared with a sulfonium ion, it may be expected to act as an oxidizing agent under some conditions. However, when a mixture of an oxosulfonium salt and benzyl alcohol, cyclohexanol, or *sec*-butyl alcohol was heated at 120—140°C, no oxidation to carbonyl compounds was observed. Neither hydroiodic acid nor zinc and hydrochloric acid reacted with oxosulfonium salts at room temperature. These findings indicate again that the S–O bond of an oxosulfonium salt is as strong as that of sulfones.

---

[7] C. R. Johnson and W. G. Phillips, *J, Amer. Chem. Soc.*, **91**, 682 (1967).

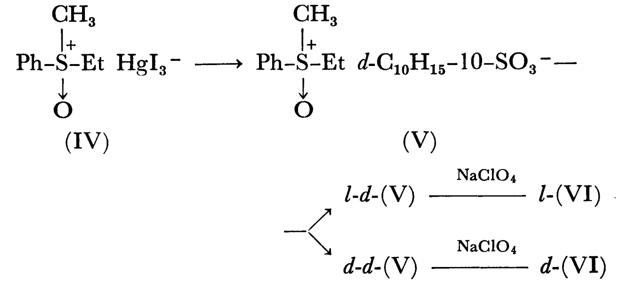
[8] M. Kobayashi, H. Minato, E. Yamada, and N. Kobori, This Bulletin, **43**, 215 (1970).

[9] M. G. Burdon and G. Moffatt, *J. Amer. Chem. Soc.*, **88**, 5855 (1966).

[10] M. Kobayashi, K. Kamiyama, H. Minato, Y. Oishi, Y. Takada, and Y. Hattori, *Chem. Commun.*, **1971**, 1577.

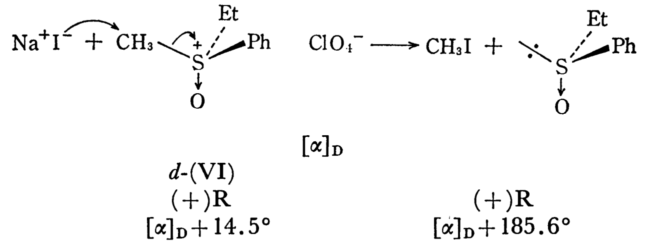
(IV) Optical Resolution.[10] Trimethyloxosulfonium ion was shown to possess a tetrahedral structure,[11] and the oxosulfonium ions containing three different substituents must be resolvable to a pair of enantiomers.

Ethylmethylphenyloxosulfonium mercuritriiodide (IV) was converted to its *d*-camphor-10-sulfonate (V), which was separated to *d-d* crystals (mp 142—143.5°C) and *l-d* crystals (mp 125—126°C) by repeated recrystallizations from acetone.



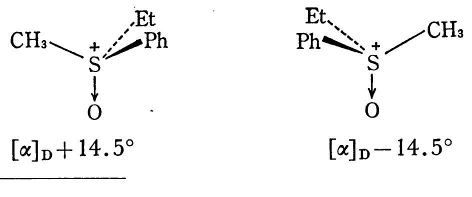
A solution of the *d-d*(V) or *l-d*(V) in acetone–water (1 : 1) was then passed through an anion-exchange resin which had been treated with aqueous sodium perchlorate solution. Recrystallization from ethanol yielded the *d*-perchlorate (VI)(mp 79.0—79.5°C, $[\alpha]^{32}_{\mathrm{D}}+14.5°$, *c* 5.52, acetone) and the *l*-perchlorate (mp 79.0—79.5°C, $[\alpha]^{30}_{\mathrm{D}}-14.3°$, *c* 4.61, acetone).

The absolute configuration of the *d*- and *l*-perchlorate (VI) were determined by conversion into the corresponding sulfoxides. From the *d*-perchlorate, the *d*-sulfoxide was obtained. Since Mislow and his co-workers have established that *d*-alkyl aryl sulfoxides possess the R-configuration,[12] the *d*-sulfoxide obtained here must also possess the R-configuration.



Since demethylation of the ethylmethylphenyloxosulfonium ion proceeds by S_N2 attack of iodide ion on the methyl group, not the sulfur atom, the stereochemistry of the sulfur atom must be retained during this demethylation. Therefore, the *d*-ethylmethylphenyloxosulfonium ion must also have the R-configuration.

These findings establish the following assignments for absolute configuration of the oxosulfonium ions.



Experimental

Materials. Ethyl phenyl sulfoxide was synthesized by oxidation of the corresponding sulfide with 30% H_2O_2 in acetone at 25—30°C for one week.[13] Bp 102—110°C/5 mmHg, IR, ν_{S-O} 1040 cm⁻¹.

Synthesis of Ethylmethylphenyloxosulfonium Mercuritriiodide (IV). After a mixture of mercury(II) iodide (11.0 g, 24.2 mmol) and methyl iodide (15 m*l*) was stirred in a 50 m*l* flask for 0.5 hr, ethyl phenyl sulfoxide (10.0 g, 64.6 mmol) was added. After nitrogen was bubbled through the mixture for 45 min, the mixture was refluxed under nitrogen for 65 hr. Then the excess methyl iodide was evaporated and the unchanged sulfoxide was removed with ether. When the reddish brown oil obtained was washed with ether several times, crude crystals were obtained, which gave yellow plates upon recrystallizations from methanol. Yield, 8.7 g (17.7%); mp 94—95°C; IR, 1240, 1210, 750 cm⁻¹; NMR, δ 1.54 (t, 3H), 4.37 (s, 3H), 4.58 (q, 2H), 8.10 (m, 5H).

In this reaction, a considerable amount of ethylmethylphenylsulfonium mercuritriiodide is formed. When the amount of methyl iodide relative to the amount of the sulfoxide is smaller, the yield of the sulfonium salt is greater. The reaction conditions described above are the optimum ones on the basis of the results of many experiments. When mercury(II) iodide was not added, no reaction takes place.

Optical Resolution. After *d*-10-camphorsulfonic acid (14.0 g, 60.0 mmol) and silver oxide (16.8 g) were let to react in acetonitrile (50 m*l*) for 7 hr, the excess silver oxide was filtered. To this acetonitrile solution of silver 10-camphorsulfonate, a solution of (IV) (45 g) in acetonitrile (60 m*l*) was added drop by drop at room temperature, and the AgI and HgI_2 were filtered. After the acetonitrile was removed under reduced pressure, water (100 m*l*) was added to the residue and the insoluble materials were filtered off. Complete removal of water from the aqueous layer by use of a vacuum pump gave colorless crystals of (V); Yield, 18.6 g (80.8%); $[\alpha]^{33}_{\mathrm{D}}+25.6°$ (c 8.32, EtOH); IR, 1730, 1210, 1190, 1170 cm⁻¹; Anal. Calcd. for $C_{19}H_{28}O_5S_2$: C, 56.97; H, 7.05; Found: C, 56.64; H, 6.80%.

When fractional recrystallization of (V) (18.6 g) from acetone was repeated for 7 times, crystals of *d-d*-(V) were obtained; 3.1 g (33%); mp. 142—143.5°C; $[\alpha]^{33}_{\mathrm{D}}+39.7°$ (c 2.90, EtOH). After the mother liquor was concentrated and the crystals initially formed were removed, the filtrate was further concentrated. When the crystals thus obtained were fractionally recrystallized six times, crystals of *l-d*-(V) were obtained; 1.07 g (12%); mp. 125—126°C; $[\alpha]^{32}_{\mathrm{D}}+11.6°$ (c 4.66, EtOH).

Preparation of Ethylmethylphenyloxosulfonium Perchlorate (VI). After about 2 *l* of an aqueous sodium perchlorate solution was passed through a column of ion-exchange resin (Amberlite IRA 400), *d-d*-(V) (2.7 g) dissolved in a small amount of aqueous acetone was added to the column. Then a 1 : 1 mixture (by volume) of water and acetone was passed through the column. Evaporation of the eluate (about 1 *l*) under reduced pressure gave crystals, which were recrystallized from EtOH-ether; 1.52 g (84%); $[\alpha]^{32}_{\mathrm{D}}+14.5°$ (*c* 5.52, acetone); mp. 79.0—79.5°C; IR, 1240, 1210, 1100 cm⁻¹; Anal. Calcd. for $C_9H_{13}O_5SCl$; C, 40.23; H, 4.88; Found: C, 40.21; H, 4.75%.

From *l-d*-(V) (1.07 g), *l*-(VI) was obtained in a similar manner; 0.63 g (87.2%); $[\alpha]^{30}_{\mathrm{D}}-14.3°$ (c 4.61, acetone); mp. 79.0—79.5°C.

---

[11] I. C. Zimmermann, M. Barlow, and J. D. McCullough, *Acta Crystallogr.*, **16**, 883 (1963).

[12] K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simmons, and A. L. Ternary, *J. Amer. Chem. Soc.*, **87**, 1958 (1965).

[13] R. L. Shriner, H. C. Struck and J. Jorison, *ibid.*, **52**, 2066 (1930).

Reaction between Optically Active (VI) and Sodium Iodide. A mixture of *d*-(VI) (0.276 g, 1.09 mmol) and NaI (0.327 g, 2.18 mmol) in 5 m*l* of acetone was refluxed for 1 hr. Water was added to the mixture, and the sulfoxide was extracted with ether. When the ethereal extracts were dried over anhydrous magnesium sulfate and the ether was removed under reduced pressure, ethyl phenyl sulfoxide was obtained; 86.7 mg (51.3%); $[\alpha]_D^{33}+164.9°$ (*c* 1.7, acetone). When this sulfoxide was purified by column chromatography (Florisil), pure sulfoxide was obtained; $[\alpha]_D^{26}+185.6°$ (c 0.71, acetone); NMR, δ 1.14 (t, 3H), 2.70 (q, 2H), 7.49 (m, 5H). In a similar manner, *l*-(VI) (0.230 g, 0.86 mmol) gave *l*-sulfoxide; $[\alpha]_D^{85}-173.4°$ (c 0.89, acetone).