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Abstract

Full Text

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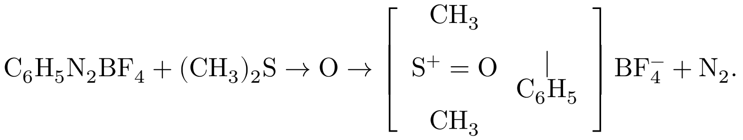
DIMETHYLPHENYLSULFOXONIUM SALTS

In the heterolytic decomposition of aryldiazonium fluoroborates in halobenzenes, diarylhalonium salts are formed. The yields of salts under these conditions are very low (0.5-0.6%) (^{1}).

In order to increase the yield of onium salts, we studied the decomposition reaction of phenyldiazonium fluoroborate in the presence of various solvents—acetone, dimethylformamide, nitromethane, tetrahydrofuran, and dimethyl sulfoxide. The most suitable solvent proved to be acetone, which made it possible to increase the yield of diphenylhalonium salts by a factor of 10-12. In dimethylformamide the yield of salts increases by a factor of 5-6, while in nitromethane and tetrahydrofuran the reaction proceeds in the same way as without solvent. Unexpected results were obtained by us when the reaction was carried out in dimethyl sulfoxide.

When a solution of phenyldiazonium fluoroborate in dimethyl sulfoxide is added to bromobenzene heated to 80-85°, instead of the expected diphenylbromonium salts, dimethylphenylsulfoxonium salts are formed (in a yield of about 3% of theory)



$$C_6H_5N_2BF_4 + (CH_3)_2S \to O \to \left[\begin{array}{cc} CH_3 & \\ S^+ = O & | \\ & C_6H_5 \\ CH_3 & \end{array} \right] BF_4^- + N_2.$$

The reaction proceeds analogously in the presence of chlorobenzene (and also diphenyl ether). In the case of iodobenzene, a mixture of dimethylphenylsulfoxonium and diphenyliodonium salts was obtained.

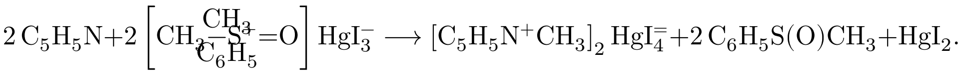
Since sulfoxonium salts with aromatic radicals had not previously been obtained, the description of the properties of the dimethylphenylsulfoxonium salts obtained by us is of definite interest.

It should be noted that aliphatic sulfoxonium salts—trimethylsulfoxonium salts—were obtained by Kuhn and Trischmann in 1957 by alkylating dimethyl sulfoxide by boiling it with an excess of methyl iodide (^{2}). Under milder conditions—cold, under the action of triethyloxonium fluoroborate or methyl iodide in the presence of anhydrous silver fluoroborate—dimethyl sulfoxide is alkylated at oxygen with the formation of dimethylalkoxysulfonium salts (^{3}).

We found that the phenylation reaction of dimethyl sulfoxide discovered by us can also be carried out in the absence of bromobenzene, by adding an acetone solution of phenyldiazonium fluoroborate to dimethyl sulfoxide. By treating aqueous extracts from the reaction mixture with solutions of $NaHgI_3$ and $NaB(C_6H_5)_4$, it is possible to precipitate salts that are sparingly soluble in water —the double salt of dimethylphenylsulfoxonium iodide with mercuric iodide (m.p. 134-135°) and dimethylphenylsulfoxonium tetraphenylborate (m.p. 142-143°). Both of these salts are readily soluble in acetone, acetonitrile, and nitromethane, and insoluble in ether and hydrocarbons.

The structure of the dimethylphenylsulfoxonium salts was proved on the example of the double salt of dimethylphenylsulfoxonium iodide with mercuric iodide, by its reaction with pyridine. As a result of this reaction, double salts of pyridine methyl iodide and mercuric iodide of composition (2 : 1) and (1 : 1) and

methyl phenyl sulfoxide, identified in the form of the sulfone:



$$2\,C_5H_5N+2\left[CH_3-\overset{CH_3}{\underset{C_6H_5}{S^+}}=O\right]HgI_3^- \longrightarrow [C_5H_5N^+CH_3]_2\,HgI_4^{=}+2\,C_6H_5S(O)CH_3+HgI_2.$$

The formation of the latter proves convincingly that the phenyl group in dimethylphenylsulfoxonium salts is bonded to the sulfur atom.

For comparison, we also prepared previously unknown salts of isomeric structure —methylphenylmethoxysulfonium salts—by Meerwein' s method, by the action of methyl iodide on methyl phenyl sulfoxide in the presence of anhydrous silver borofluoride. IR spectra of the salts obtained were recorded.* Comparison of the spectra showed that the spectra of the double salts of dimethylphenylsulfoxonium iodide and trimethylsulfoxonium iodide with mercury iodide have a strong absorption band in the region 1234-1246 cm^{-1}, which may be assigned to vibrations of the $S = O$ bond, in agreement with the data of Kuhn (²) and Winstein (⁴). This absorption band, as would be expected, is absent from the IR spectrum of the double salt of methylphenylmethoxysulfonium iodide with mercury iodide, which also proves phenylation of dimethyl sulfoxide by phenyldiazonium borofluoride at sulfur, and not at oxygen.

Experimental Part

1. Decomposition of phenyldiazonium borofluoride in bromobenzene. A solution of 9.6 g (0.05 mole) of phenyldiazonium borofluoride in 15.6 g (0.2 mole) of dimethyl sulfoxide was added over 1.5 h to 31.4 g (0.2 mole) of bromobenzene at 80-85°. After completion of the reaction, the reaction mixture was diluted twofold with chloroform and washed 5 times with water (20 ml each). From the aqueous extracts, washed with ether, addition of a saturated solution of $NaHgI_3$ precipitated the double salt of dimethylphenylsulfoxonium

Fig. 1. IR spectra of double salts with mercury iodide

Figure 1: Fig. 1. IR spectra of double salts with mercury iodide

iodide and mercuric iodide. After reprecipitation from acetone with ether, the weight of the salt was 0.7 g (2% of theory), mp 134-135°.

Found, %:	C 13.23; H 1.75
$C_8H_{11}I_3HgOS$. Calculated, %:	C 13.05; H 1.50

2. Decomposition of phenyldiazonium borofluoride in chlorobenzene. Under the conditions of the preceding experiment, from 9.6 g (0.05 mole) of phenyldiazonium borofluoride and 15.6 g (0.2 mole) of dimethyl sulfoxide in 22.5 g (0.2 mole) of chlorobenzene, 0.7 g (2% of theory) of the double salt of dimethylphenylsulfoxonium iodide with mercuric iodide was obtained. Decomp. temp. of the salt 135° (from CH_3NO_2).

Found, %:	C 13.05; 12.84,	H 1.57; 1.55
$C_8H_{11}I_3HgOS$. Calculated, %:	C 13.05;	H 1.50

3. Decomposition of phenyldiazonium borofluoride in diphenyl ether. On decomposition of 9.6 g (0.05 mole) of phenyldiazonium borofluoride, dissolved in 15.6 g (0.2 mole) of dimethyl sulfoxide, in 34 g (0.2 mole) of diphenyl ether under the conditions of experiment No. 1, 1.04 g (3% of theory) of the same double salt of dimethylphenylsulfoxonium iodide with mercuric iodide was isolated. Decomp. temp. 134-135° (from CH_3NO_2).

Found, %:	C 13.18; 13.20;	H 1.27; 1.46
$C_8H_{11}I_3HgOS$. Calculated, %:	C 13.05;	H 1.50

4. Double salt of dimethylphenylsulfoxonium iodide and mercuric iodide. To 7.8 g (0.1 mole) of dime-

dimethyl sulfoxide at 80-90° (bath temperature), with stirring over 1.5 h, a solution of 9.3 g (0.05 mole) of phenyldiazonium fluoroborate in 300 ml of acetone was added. The reaction mixture was worked up as in experiment No. 1. The yield—

Fig. 1. IR spectra of double salts with mercury iodide: dimethylphenylsulfoxonium iodide (a), trimethylsulfoxonium iodide (b), methylphenylmethoxysulfonium iodide (c) (in Vaseline oil)

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* The spectra were recorded in the optical laboratory of the Institute of Organoelement Compounds, Academy of Sciences of the USSR, on a UR-10 instrument. (Accuracy of determination \$±\$4 cm^{-1}.)

—of the double salt of dimethylphenylsulfoxonium iodide and mercuric iodide was 0.73 g (2% of theoretical). M.p. 134–135°.

$C_8H_{11}J_3HgOS$. Found, %: C 12.91; 12.79; H 1.64; 1.45; S 4.35; 4.40
Calculated, %: C 13.05; H 1.50; S 4.34

5. **Tetraphenylborodimethylphenylsulfoxonium.** In another analogous experiment, from the last three aqueous extracts tetraphenylborodimethylphenylsulfoxonium was precipitated in an amount of 0.2 g. M.p. 142–143° (after threefold reprecipitation from nitromethane with ether).

$C_{32}H_{31}BOS$. Found, %: C 80.38; 80.64; H 6.70; 6.75; B 2.51; 2.37
Calculated, %: C 80.99; H 6.57; B 2.28

6. **Decomposition of the double salt of dimethylphenylsulfoxonium iodide and mercuric iodide in pyridine.** A solution of 5.18 g (0.007 mole) of the double salt of dimethylphenylsulfoxonium iodide and mercuric iodide in 10 ml of pyridine was boiled for 1.5 h. After cooling, the reaction mixture was diluted with abs. ether. The precipitate that separated (4.05 g) was a mixture of two double salts of pyridinium methylate with mercuric iodide of compositions (2 : 1) and (1 : 1). The salts were separated by fractional crystallization from alcohol.

The double salt of composition (2 : 1) was a colorless crystalline substance with m.p. 159.5–161° (with decomposition).

$C_{12}H_{16}J_4HgN_2$. Found, %: C 16.28; 16.23; H 1.86; 1.87; N 3.41; 3.12
Calculated, %: C 16.07; H 1.80; N 3.12

The double salt of composition (1 : 1) consisted of bright-yellow crystals with m.p. 85° (from alcohol).

$C_6H_8J_3HgN$. Found, %: C 10.83; 10.66; H 1.36; 1.17
Calculated, %: C 10.67; H 1.20

The ether-pyridine filtrate was distilled to remove ether, and the residue was boiled for 3.5 h with 1.13 g of Cr_2O_3 in 12 ml of glacial acetic acid. The reaction mixture was poured into water. The precipitate that separated was filtered off and washed with water. The filtrate was extracted with chloroform. The chloroform solution was washed twice with conc.

HCl and dried over $MgSO_4$. The yield of methyl phenyl sulfone, crystallized after distilling off the chloroform, was 0.65 g (66% of theory). M.p. 84.5–86.5°

(from water). A mixed sample with an authentic specimen gives no depression of the melting point. Literature data: m.p. of methyl phenyl sulfone 86.5-86.8° (^{5}).

7. Methylphenylmethoxysulfonium borofluoride. To a mixture of 7 g (0.05 mole) of methyl phenyl sulfoxide and 1 g (0.5 mole) of methyl iodide, 9.7 g (0.05 mole) of anhydrous $AgBF_4$ (^{3}) was added in small portions. The reaction mixture was stirred at room temperature for 3-4 hours and left overnight. The precipitate that formed was filtered off and washed repeatedly on the filter with acetonitrile. On addition of absolute ether to the resulting solution, 6 g (50% of theory) of methylphenylmethoxysulfonium borofluoride precipitated. M.p. 88.5-90° (after reprecipitation from CH_3CN with ether).

$C_8H_{11}BF_4OS$. Found, %: C 39.53; 39.71; H 4.59; 4.47
Calculated, %: C 39.71; H 4.58

8. Double salt of methylphenylmethoxysulfonium iodide and mercuric iodide. Obtained by mixing aqueous solutions of methylphenylmethoxysulfonium borofluoride and $NaHgJ_3$. Decomp. temp. 74-75° (after reprecipitation with ether from CH_3NO_2).

$C_8H_{11}J_3HgOS$. Found, %: C 12.93; 12.94; H 1.58; 1.58; S 4.71; 4.95
Calculated, %: C 13.03; H 1.50; S 4.34

9. Trimethylsulfoxonium salts. From 0.38 g of trimethylsulfoxonium iodide, prepared by the method of Kuhn and Trischmann (^{2}), and $NaHgJ_3$ in aqueous solution, 0.77 g (63% of theory) of the double salt of trimethylsulfoxonium iodide with mercuric iodide was obtained. M.p. 133-134° (after reprecipitation from CH_3NO_2 with ether).

$C_3H_9J_3HgOS$. Found, %: C 5.61; H 1.48
Calculated, %: C 5.35; H 1.34

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Note: Figure translations are in progress. See original paper for figures.