

AN ATTEMPT TO PREPARE  
METHYLDIPHENYLSULFONIUM FLUOROBORATE

by

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This Thesis

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Background

In the past few years there has been growing interest in two types of organic salts, those of sulfonium and oxysulfonium ions.

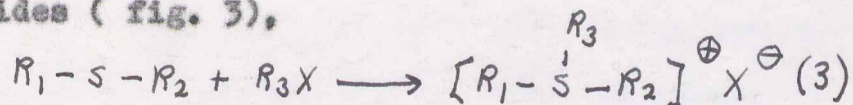
Probably the better known are the sulfonium compounds. In general they are crystalline salts, and they are water soluble giving neutral solutions. The trialkyl sulfonium ion ( fig. 1),



like the quaternary ammonium ion, has the tetrahedral structure except that in the sulfonium ion the fourth group is an unshared pair of electrons rather than a bonded group( fig. 2)

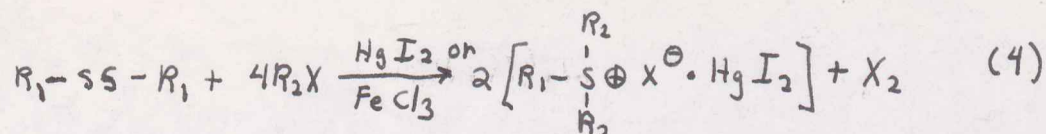


There are generally two methods of production of these salts. They can be formed from the reaction of alkyl sulfides with alkyl halides to give trialkylsulfonium halides ( fig. 3),

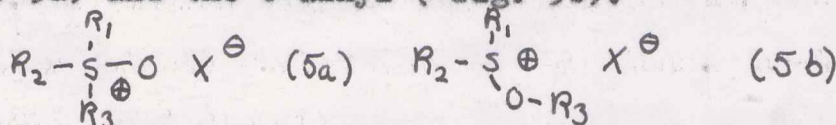


or they can be produced by reacting an alkyl disulfide with an alkyl halide in the presence of either ferric chloride or mercuric iodide to act as a catalyst to give again a trialkylsulfonium halide ( fig. 4).

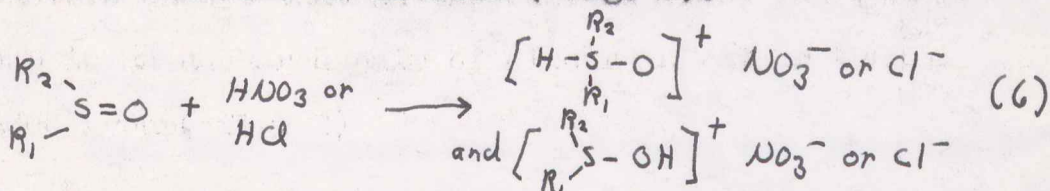
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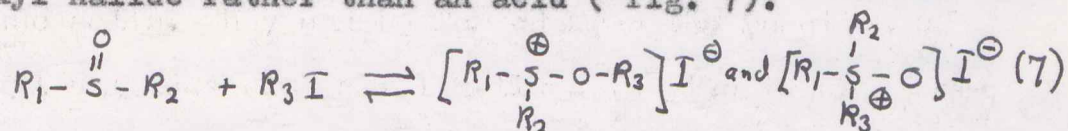
Somewhat less known and until the last ten years less understood are the oxysulfonium compounds. These oxysulfonium ions occur in two isomeric forms, the S- alkyl ( fig. 5a) and the O-alkyl ( fig. 5b).



One way of arriving at oxysulfonium salts is to react alkylsulfoxides with either nitric or hydrochloric acid to get both of the isomeric forms of the ion in solution as a chloride or nitrate ( fig. 6).



This gives us the dialkyl form, and in order to get the trialkyl form we simply react the sulfoxide with an alkyl halide rather than an acid ( fig. 7).

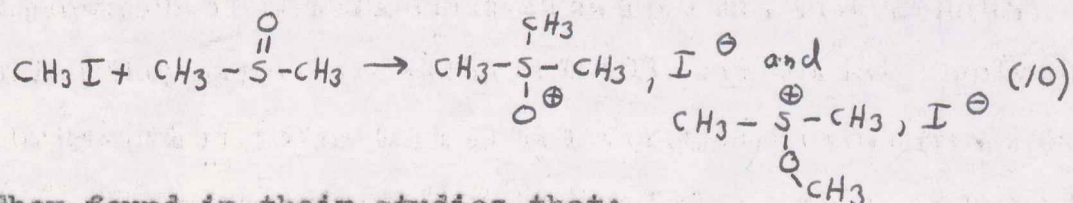


One sulfoxide that has come into common use as a nucleophile is dimethylsulfoxide, often and hereafter abbreviated as DMSO.





In 1958 Randolph T. Major and Hans-Jurgen Hess (1) revealed their work on the reaction of organic halides with DMSO, using mainly methyl iodide ( fig. 10).

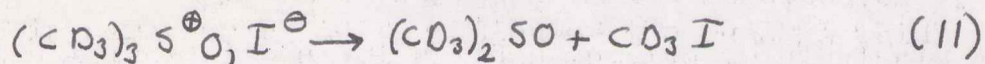


They found in their studies that:

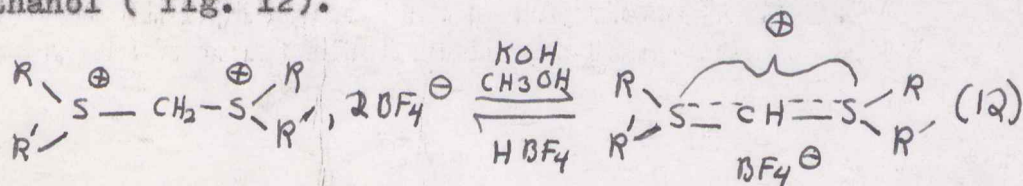
1) Other simple alkyl halides did not react with dimethylsulfoxide under conditions similar to those observed in the reaction with methyl iodide, which reacted at room temperature.

2) Halides in which the halide atom is attached to the alpha carbon of a carbonyl or ester group did react with DMSO at room temperature.

As a result of this work, F.A. Cotton and associates (3) found in 1959 a "rapid, simple and inexpensive preparation of ( $^2\text{H}_3$ ) methyl iodide and ( $^2\text{H}_6$ ) dimethylsulfoxide by pyrolysis of trimethyloxysulfonium iodide ( fig. 11).



This year, 1966, Dr. C. Peter Lillya and Phillip Miller isolated three stable bis ( dialkylsulfonium) methylenes by reacting the methylene bis ( dialkylsulfonium) difluoroborates with potassium hydroxide and methanol ( fig. 12).





The alkyls are methyl or ethyl groups. The most remarkable thing about the sulfonium ylides is their stability which is accounted for by the stabilization of the negative charge on carbon by the sulfonium groups.

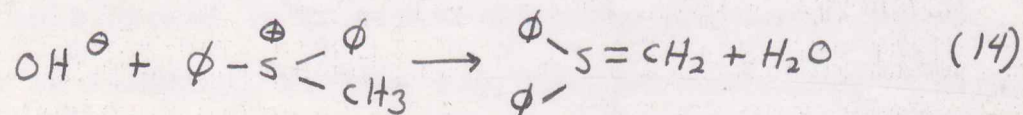
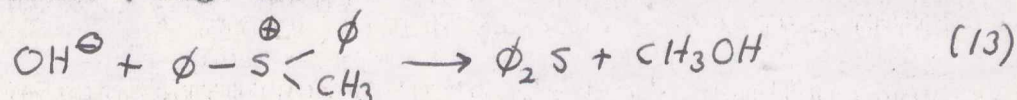
Drs. Lillya and Miller hoped that these ylides would react with carbonyl compounds, thus making them useful reagents for organic synthesis.



Experimentation

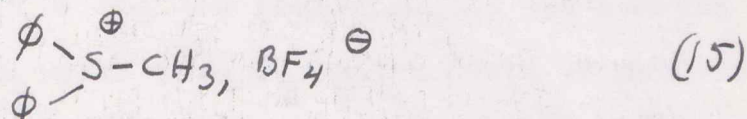
My specific problem was to react the methyldiphenylsulfonium ion with bases and nucleophiles to determine which of two mechanisms the reaction would follow.

One possible reaction mechanism is a simple displacement ( fig. 13).

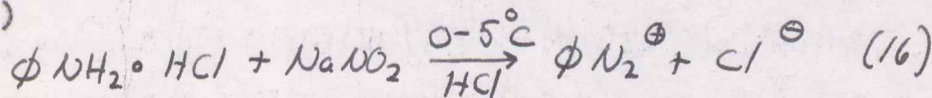


The other possibility is a mechanism resulting in proton transfer and the formation of an ylide ( fig. 14).

The first task was to synthesize the methyldiphenylsulfonium ion in the form of a stable salt. It was decided to use the fluoroborate ion as the anion because of its relative stability.

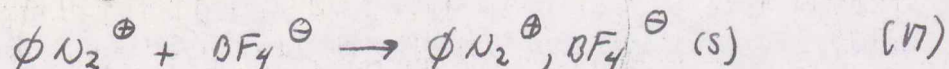


The first step of the synthesis was to prepare phenyldiazonium chloride by a simple diazotization, ( fig. 16) reacting aniline with sodium nitrite in a hydrochloric acid medium at a temperature of zero to five degrees centigrade. (10)

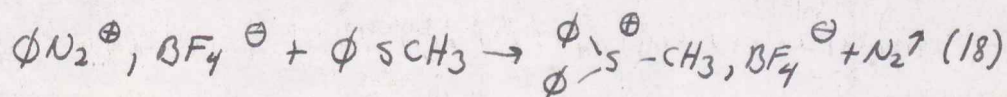


By adding 48% fluoboric acid to the reaction mixture I was able to precipitate phenyldiazonium fluoro-

borate ( fig. 17).



The next problem was to somehow react the diazonium salt with thioanisole to get the sulfonium salt.



My first attempt was to slurry the two materials together and then to heat the mixture. Since the diazonium salt proved to be rather unstable and would decompose on standing, heating only speeded the decomposition into  $BF_3$  and other products.

My next attempt was to slurry the two materials together and allow them to react at room temperature, but in this case no reaction proceeded as evidenced by the lack of evolution of nitrogen.

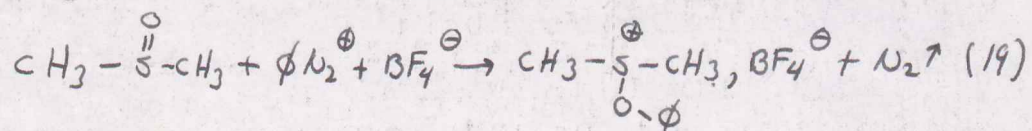
The problem appeared to be that there wasn't a homogeneous mixture of the two reactants. It was decided to use a solvent in which both reactants would be soluble, thus giving the desired homogeneity. The solvent chosen was DMSO.

It was found that the reactants would dissolve in DMSO and would react at room temperature with the evolution of a gas, not  $BF_3$ , and assumed to be nitrogen.

While the reactants were being worked up in an effort to isolate the desired product it was realized that DMSO was not only a good solvent, but it was also



a very good nucleophile. It was proposed at that time that the DMSO was competing with the thioanisole as a nucleophile for the diazonium salt ( fig. 19).



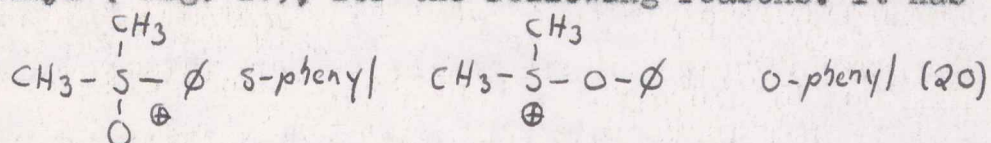
When the diazonium salt was added to the DMSO alone, a reaction proceeded with the evolution of a gas which was not  $\text{BF}_3$  and was assumed to be nitrogen.

Attempts to separate the product from the reaction mixture met with limited success. The salt seemed to oil out of solution rather than precipitate, which suggested a low melting salt even though there were undoubtedly freezing point depression effects involved due to the impurities of side products and unreacted salt in the solution.

Conclusions

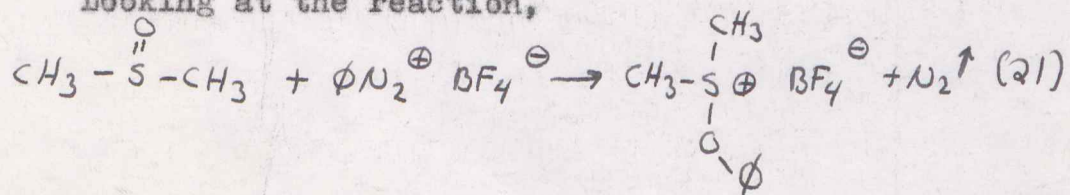
I am fairly certain that the salt in question must be phenyldimethyloxysulfonium fluoroborate because examination of the structure of the reactant materials reveals no other feasible possibility for a reaction mechanism that would yield among other products, a colorless gas which was n't  $\text{BF}_3$ .

Preliminary indications are, assuming it to be phenyldimethyloxysulfonium fluoroborate, that the oxysulfonium ion is of the O-phenyl type as opposed to the S-phenyl (fig. 20), for the following reasons. It has



been shown that during a reaction of this type, the reaction proceeds rapidly toward the formation of the O-phenyl isomer, while, although it forms, the S-phenyl isomer forms at a much slower rate. In order for the O-phenyl to revert to the S-phenyl either the reaction would have to be reversible or the oxysulfonium ion would have to convert itself intramolecularly. If no conversion takes place then the bulk of the salt will be of the O-phenyl isomer, formed by the initial reaction.

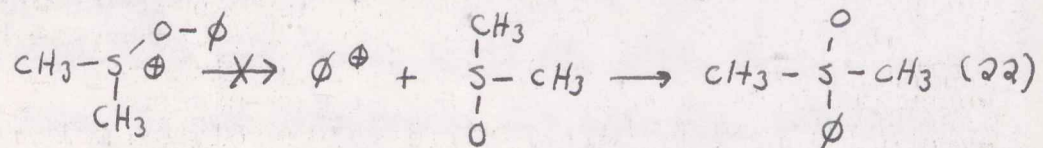
Looking at the reaction,



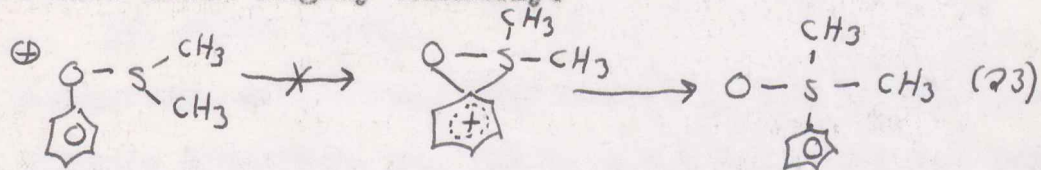


we see that nitrogen is given off, so that the reaction essentially goes to completion and can't be reversible to any extent; the O-phenyl can't possibly revert to the S-phenyl in this manner.

Also it would be highly unlikely that the ion could convert intermolecularly ( fig. 22), because the formation of a  $\phi^{\oplus}$  ion would be unlikely.



In order for the ion to convert intramolecularly ( fig. 23) it would have to undergo an internal strain that also seems highly unlikely.



It is thus difficult to see how this reaction could lead to an S-phenyl product unless if it were formed directly.

One possible method of separating this salt from the solvent, DMSO, might be to freeze dry the salt by freezing the solution ( DMSO normally freezes at six degrees centigrade) and putting it under a vacuum to dry it.

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