oxygen and of air were 3.2, 4.4 and 2.8, respectively. The percentage decomposition in the presence of oxygen at the end of five hours was 32.5.

Summary

1. The rates of pyrolysis of the methyl, ethyl, and isopropyl ethers derived from triphenylcarbinol have been determined at several temperatures.

2. The ethyl ether at the lower temperatures and up to about 11% decomposition showed the characteristics of a reaction of the first order and the rate doubled for a rise of 10 degrees. Similar results were obtained with isopropyl ether up to about 28% decomposition.

3. The calculated first order velocity constants in the case of the methyl ether increased rapidly with time. It was shown that triphenylmethane, a product of the decomposition, had a marked accelerating effect on the decomposition.

4. The presence of a small amount of air increased greatly the rate of pyrolysis.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NEW YORK UNIVERSITY]

Basis for the Physiological Activity of Onium Compounds. XV. Sulfonium Compounds[1,2]

BY R. R. RENSHAW AND D. S. SEARLE

In earlier work[3] it was found that one of the derivatives of the sulfur analog of choline (acetylthioformocholine) produced a very marked lowering of the blood pressure (muscarine action) and that this action was not complicated, as is the case with most of the choline derivatives, by the evidence of any stimulating nicotine action. The need of an effective product having this type of action is considerable in therapeutics. The authors, in coöperation with Reid Hunt, have, therefore, undertaken to investigate a number of sulfonium derivatives.

The successful preparation of sulfonium compounds by the direct addition of a halide to a sulfide is in general restricted to the relatively simple compounds. One difficulty, as has been pointed out in an earlier paper,[4] is the tendency of the unsymmetrical sulfonium structures to dissociate in two or more ways and of the products then to recombine to produce a mixture difficult or impossible to separate. Often, too, the dissociation is

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(1) This problem is being carried out in coöperation with Dr. Reid Hunt of the Harvard Medical School. The physiological data are the basis of another series of papers published elsewhere by him.

(2) This is the first paper from a thesis presented by D. S. Searle, June, 1930, for the degree of Doctor of Philosophy at New York University.

(3) Hunt and Renshaw, *J. Pharm. Exptl. Therap.*, **25**, 315 (1925).

(4) Renshaw, Bacon and Roblyer, THIS JOURNAL, **48**, 517 (1926).

rapid and the equilibrium point well over toward the dissociation products which tend to form uncrystallizable oils with the sulfonium compounds present. When heavy groups are involved condensation takes place very slowly and in some cases apparently not at all after considerable time. Salsbury[5] was unable to condense β-bromo-ethyl acetate with ethyl, propyl or butyl sulfides as was evident by the fact that neither a solid nor an oil was precipitated after adding an excess of toluene to the reaction of mixtures which had stood several weeks. We were unable, too, to obtain appreciable condensation of benzyl or phenyl sulfides with β-bromoethyl phenyl ether.

A partial solution of the difficulties was obtained by taking advantage of an observation of Smiles[6] that in the presence of mercuric iodide sulfonium formation takes place rapidly with the production of the sulfonium-mercuric iodide double salt. By using this procedure, it has been possible to prepare the mercuric iodide or bromide double salts of a number of sulfonium compounds the simple onium salt of which could not be formed directly. In a number of cases, however, it was impossible or very difficult to isolate the free sulfonium compound after precipitating the mercury on account of the easy dissociation of the latter. Since the alkyl derivatives of the oxygen acids do not show the ready addition to the onium elements that the halides do it was thought that the oxygen acid salts of the onium compounds would likely be very stable. This was found to be the case and the sulfonium compounds were easily isolated as the stable nitrates or sulfates by first converting the double mercury halide salts into salts of these acids as described in the experimental part.

Experimental Part

The sulfides were condensed with molecular equivalent amounts of halide and mercuric salt using acetone or alcohol as the solvent. The double salts thus formed are soluble in acetone, insoluble in water, alcohol and ether. Details of the procedure for each case will be found in notes to Table I.

TABLE I

SULFONIUM COMPOUNDS

	M. p., °C.	Analyses, N		
		Calcd.	Found	
$(C_6H_5CH_2)_2S(NO_3)CH_3$[a]	79	4.81	4.83	4.89
$(C_6H_5CH_2)_2S(NO_3)CH_2COOC_2H_5$[b]	120	3.86	3.85	3.81
$(C_6H_5)_2S(NO_3)CH_3$[c]	108	5.32	5.22	5.33
$(CH_3)_2S(NO_3)CH_2CH_2OC_6H_5$[d]	62–65	5.71	5.60	6.10
		Analyses for Br		
$(C_2H_5)_2S(Br)CH_2CH_2OC_6H_5 \cdot HgBr_2$[e]	78	36.81	36.88	36.75
$(C_3H_7)_2S(Br)CH_2COOC_2H_5$[f]	70	28.02	28.00	27.95
$(C_6H_5CH_2)_2S(Br)CH_2COOC_2H_5 \cdot HgBr_2$	127	32.34	32.39	...

[a] Prepared from $(C_7H_7)_2S(I)CH_3 \cdot HgI_2$, m. p. 155°, which was obtained in nearly quantitative yield by condensing $(C_7H_7)_2S$ with CH_3I and HgI_2 in acetone as described

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(5) Salsbury, Master's Thesis, New York University, 1927.

(6) Smiles, *J. Chem. Soc.*, **77**, 160 (1900).

by Smiles and Rossignol. The nitrate first formed as an oil which solidified on stirring with absolute ether.

[b] From $(C_7H_7)_2S(Br)CH_2COOC_2H_5 \cdot HgI_2$, m. p. 120°, or from $(C_7H_7)_2S(Br)CH_2COOC_2H_5 \cdot HgBr_2$. The dibenzyl sulfide, ethyl bromoacetate, and mercuric halide were condensed in acetone solution by heating the solution in a steam-bath for about half an hour, then after standing several days precipitating the double salt by the addition of alcohol. The free nitrate formed as a white crystalline solid on the addition of ether to the final filtrate, no oil forming at any time.

[c] From $(C_6H_5)_2S(I)CH_3 \cdot HgI_2$, m. p. 95°, which was obtained by condensing $(C_6H_5)_2S$, CH_3I and HgI_2, in acetone solution as described under *b* above.

[d] From $(CH_3)_2S(Br)CH_2CH_2OC_6H_5 \cdot HgBr_2$, obtained by condensing $(CH_3)_2S$, $BrCH_2CH_2OC_6H_5$ and $HgBr_2$ in alcohol solution. It was found that acetone was not suitable for this condensation since insoluble $(CH_3)_2S \cdot HgBr_2$ formed instead of the sulfonium salt. This sulfide complex was soluble in alcohol, however, and the best results were obtained when the alcohol was added to the reactants in quantity sufficient to dissolve them. The solution was then heated in a pressure bottle immersed in a steam-bath for several hours. A viscous oil formed and was separated and solidified by stirring with alcohol or ether. The substance was insoluble in alcohol, ether and water, but soluble in acetone, m. p. 70–71°. It did not decompose when heated to its melting point as the sulfide complex did. The yield was 81%. This double salt yielded the free nitrate first as an oil, which solidified on standing with absolute ether for a few hours. The nitrate was somewhat more hygroscopic than the other nitrates, which is due in part, perhaps, to its low m. p.

[e] This double salt was prepared in a manner analogous to that described above in *d*. The free nitrate could be obtained only as a gummy semi-solid. As noted above the corresponding dimethyl compound was somewhat hygroscopic and of low melting point (70°). It would be expected therefore that the diethyl compound would have an even lower melting point and be more hygroscopic.

[f] Prepared by Salsbury by direct condensation.

The double salts were in each case dissolved in acetone and an excess of solid silver nitrate was added and stirred until no more silver bromide or iodide formed. The filtered solution was then treated with hydrogen sulfide until precipitation of mercuric sulfide and silver sulfide was complete. The solution was filtered and ether was added to precipitate the sulfonium nitrate. The nitrates were white crystalline solids soluble in water, alcohol and acetone, and insoluble in ether. These nitrates appear to be very stable, and on long standing are free of odor or other evidence of dissociation so characteristic of sulfonium halides. Once obtained in dry form they exhibit little or no tendency, for the most part, to be very hygroscopic.

Summary

1. A method has been described for the preparation of crystalline, stable sulfonium compounds.

2. Several new sulfonium compounds have been prepared as mercuric halide double salts and as nitrates. The halogen salts of many of the sulfonium compounds undergo onium dissociation so readily that they cannot be isolated in a crystalline form. The nitrates are much more stable, showing little or no tendency to undergo this dissociation under ordinary conditions. They are also much less hygroscopic.

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