[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON, N. J.]

# SOME PROPERTIES OF THE THIOMETHYLENE RADICAL. BEHAVIOR WITH ALUMINUM CHLORIDE IN BENZENE

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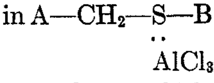
Organic sulfides and mercaptans form addition compounds with anhydrous aluminum chloride in which there is presumably a dative bond between the sulfur and the aluminum atoms, *i.e.*,

$$\mathrm{R}:\underset{\mathrm{AlCl_3}}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{S}}}}:\mathrm{R}.$$

It might be supposed that one effect of the addendum would be to weaken the carbon-sulfur linkage and permit reactions which involve the breaking of this bond to occur. A search of the literature, and our own experiments indicate, however, that, under mild conditions, at room temperature, this is not generally the case. Aryl sulfides, such as diphenyl sulfide, form one-to-one addition complexes with aluminum chloride which remain unchanged in benzene, even in the presence of a substantial excess of aluminum chloride.[1] This is also true of primary alkyl sulfides. Normal primary amyl sulfide was recovered unchanged after heating for two hours at 80° in benzene with more than one equivalent of aluminum chloride. Ethyl mercaptan, and *n*-amyl mercaptan showed little activity at room temperature in similar experiments. At the boiling point of benzene some hydrogen sulfide was evolved, but little or no alkylation of the benzene took place.

It is generally observed that in molecules of the type A—$CH_2$—B, the bond between $CH_2$ and A or B is most easily broken when both A and B are negative in nature. It was thought, therefore, that if A, in  $\mathrm{A—CH_2—}\underset{\mathrm{AlCl_3}}{\underset{\cdot\cdot}{\mathrm{S}}}\mathrm{—B}$, were such a negative atom or group, the activity of the complex would be enhanced. This idea was tested using the easily available and suitable compounds: benzyl mercaptan, benzyl sulfide, and *s*-trithiane. It was found that all three were quite active at room temperature when in contact with benzene and aluminum chloride.

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[1] BOESEKEN, *Rec. trav. chim.*, **24**, 213 (1905).

Benzyl mercaptan with one molecule of aluminum chloride in a large excess of benzene reacted mainly according to the equation:

(1) $C_6H_5CH_2SH + C_6H_6 + AlCl_3 \rightarrow C_6H_5CH_2C_6H_5 + H_2S + AlCl_3$.

In addition to diphenylmethane, some high-boiling (above 360°) material was obtained. This material contained no sulfur, however, so that it is safe to say that the reaction was mainly one of alkylation.

With benzyl sulfide and one molecule of aluminum chloride, under the mild conditions used, the benzene did not enter into the reaction. The principal product, obtained in good yields, was tribenzylsulfonium chloride. Obviously here the primary reaction was a scission of the carbon-sulfur bond, and the whole process may be expressed as follows:

(2) $C_6H_5CH_2SCH_2C_6H_5 \cdot AlCl_3 \rightarrow C_6H_5CH_2Cl + C_6H_5CH_2S{-}AlCl_2$

(3) $C_6H_5CH_2SCH_2C_6H_5 \cdot AlCl_3 + C_6H_5CH_2Cl \rightarrow (C_6H_5CH_2)_3SCl \cdot AlCl_3$.

Benzyl chloride and benzyl sulfide do not ordinarily add to form a sulfonium salt. In the above case it is probable that the aluminum chloride not involved in the splitting reaction accelerated the production of the sulfonium salt and formed with it a one-to-one addition compound. This is in agreement with the observation of Hofmann and Ott,[2] who found that ferric chloride catalyzed the addition of benzyl chloride to benzyl sulfide. They, however, apparently did not obtain a pure tribenzylsulfonium chloride by removal of the ferric chloride with water.

If an excess of aluminum chloride over molecular proportions was used, diphenylmethane became a major product, and the amounts of tribenzylsulfonium chloride and benzyl mercaptan produced were correspondingly less.

(4) $C_6H_5CH_2SCH_2C_6H_5 \cdot AlCl_3 \rightarrow C_6H_5CH_2Cl + C_6H_5CH_2S{-}AlCl_2$

(5) $C_6H_5CH_2Cl + C_6H_6 + AlCl_3 \rightarrow C_6H_5CH_2C_6H_5 + HCl + AlCl_3$

(6) $C_6H_5CH_2S{-}AlCl_2 + C_6H_6 + AlCl_3 \rightarrow C_6H_5CH_2C_6H_5 + HS{-}AlCl_2 + AlCl_3$.

*s*-Trithiane contains the structural unit A—$CH_2$—B, in which both A and B are sulfur atoms. This compound varied remarkably in its behavior with aluminum chloride in benzene at room temperature, the products obtained depending on the relative quantity of the aluminum chloride present. The following molecular ratios of *s*-trithiane to aluminum chloride were studied: *a*, 4:3; *b*, 1:1; *c*, 2:3; *d*, 1:2; and *e*, 1:3. In the cases of the ratios *a*, *b*, and *c*, the benzene entered into the reaction

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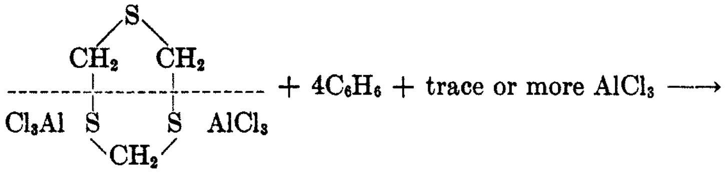
[2] HOFMANN AND OTT, *Ber.*, **40**, 4933 (1907).

only to a slight extent. The products formed on decomposition of the reaction mixture with water were sulfur and the sulfonium salt, *s*-trithiane methyl chloride, $(CH_2S)_3 \cdot CH_3Cl$. With the ratios *d* and *e*, on the other hand, the main products were diphenylmethane and benzyl sulfide. The results may be explained by assuming that the normal addition compound of *s*-trithiane and aluminum chloride, under the conditions of the reaction, has the composition $(CH_2S)_3 \cdot 2AlCl_3$. It is not until this ratio is exceeded and there is at least a slight excess of aluminum chloride, that the benzene can become active and take part in the reaction.

(7)



$$+ 4C_6H_6 + \text{trace or more } AlCl_3 \longrightarrow$$

$$C_6H_5CH_2SCH_2C_6H_5 \cdot AlCl_3$$

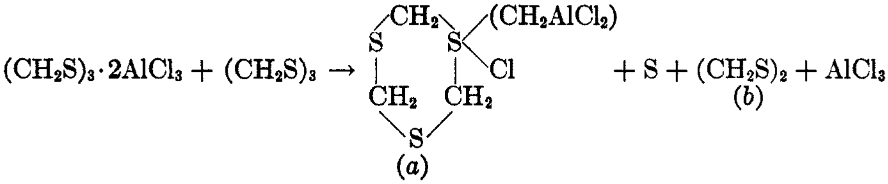
and

$$C_6H_5CH_2C_6H_5 + 2H_2S + AlCl_3$$

The trithiane molecule breaks, and there is an addition of two moles of benzene. Dimercaptomethane, which is formed, reacts immediately with benzene to give diphenylmethane and hydrogen sulfide. No tribenzylsulfonium chloride was isolated, although it might be expected from a consideration of the results of the benzyl sulfide-aluminum chloride reaction. It is probable that this was due to the fact that hydrogen sulfide forms a complex with aluminum chloride, somewhat diminishing the activity of the latter.

The course of the reaction obtained between one molecule of *s*-trithiane and less than two molecules of aluminum chloride, may be described by the equation:

(8)



$$(CH_2S)_3 \cdot 2AlCl_3 + (CH_2S)_3 \rightarrow (a) + S + \underset{(b)}{(CH_2S)_2} + AlCl_3$$

Compound (*a*), on hydrolysis, yields trithiane methyl chloride; (*b*) rearranges to $(CH_2S)_3$. The momentary existence of $ClCH_2—AlCl_2$ is assumed in the equation. There is no evidence for such a compound in the literature, but the corresponding ethylene derivative has been postulated in some types of the Friedel-Crafts reaction.

## EXPERIMENTAL

*Normal primary amyl sulfide.*—One-tenth mole of the sulfide and 0.12 mole of aluminum chloride in 60 cc. of benzene were heated at 80° for two hours. The mixture was cooled, and poured into ice water; the benzene layer was separated and fractionated. The sulfide was entirely recovered, except for a small experimental loss. No other substance was found in the benzene layer. The water layer contained no sulfonium compound. A mixture similar to the above was allowed to stand at room temperature for a long period, and the result was the same.

*Ethyl and* n*-amyl mercaptans.*—One-half mole of the mercaptan and 0.6 mole of aluminum chloride in 300 cc. of benzene were heated at 80° for thirty hours. After decomposition of the mixture with water, the benzene layer was distilled, and found to contain no alkylated benzene derivatives.

*Benzyl mercaptan.*—Fifty grams of the mercaptan was added slowly with stirring to 0.5 mole of aluminum chloride in 1.0 mole of benzene. There was immediate reaction, the mixture became warm and it was necessary to cool the reaction flask with ice water during most of the addition. There was a copious evolution of hydrogen sulfide. The reaction mass was poured into ice water, and the benzene layer was separated. It gave on fractionation 15 g. of diphenylmethane, and complex hydrocarbons of boiling point higher than 360°.

*Benzyl sulfide.*—Eleven grams of the sulfide and 6.2 g. of aluminum chloride in 50 cc. of benzene stood at room temperature (protected from moisture in the air) for five days. The mixture was then poured into an open dish, the excess benzene was allowed to evaporate, and the aluminum chloride complex was decomposed by moisture in the air. The white solid mass remaining was washed free of very soluble aluminum compounds with a minimum of cold water. The residue was a white crystalline solid (I) of m. p. 82-84° (corr.). It was soluble in water, alcohol, chloroform, and acetone-water with decomposition. It contained ionizable chlorine. It formed an addition compound with chloroplatinic acid in aqueous solution; m. p. 189°, which is the same as that reported for the complex between tribenzylsulfonium chloride and chloroplatinic acid. It formed a trinitrophenoxide ("picrate") of m. p. 142° and the m. p. was not depressed when it was mixed with a trinitrophenoxide prepared from known tribenzylsulfonium sulfate and picric acid.

*Anal.* Calc'd for $C_{27}H_{35}N_3O_7S$: S, 6.0. Found: S, 6.3.

Compound I in aqueous solution with silver oxide gave tribenzylsulfonium hydroxide; m. p. 133°.

*Anal.* Calc'd for $C_{21}H_{22}OS$: S, 9.94. Found: S, 9.84.

When tribenzylsulfonium chloride (I) was heated in acetone-water solution it decomposed, and benzyl sulfide was isolated. The yield of the sulfonium compound was 80% of the theoretical, based on equations (2) and (3). In another experiment the reaction mixture was poured into water after one day, and the benzene layer was separated and concentrated to a b. p. of 130°. Benzyl mercaptan was present in this residue and was identified by formation of its 2,4-dinitrophenyl thioether, m. p. 130°, and oxidation of this derivative to the sulfone.

s-*Trithiane with two or more moles of aluminum chloride.*—In a typical experiment 23 g. of trithiane and 44 g. of aluminum chloride were mixed in the dry state, and to these reactants 100 cc. of benzene was added. Almost immediately the solution became clear and orange-colored; the evolution of much hydrogen sulfide followed. The reaction appeared to be complete within 15–20 minutes, and the mixture was decomposed by pouring on crushed ice. The benzene layer was distilled until it had a b. p. of 135°. The remaining oil was mainly a mixture of diphenylmethane and benzyl sulfide; it was not easily separated into these constituents. A fractional distillation yielded 10 g. of diphenylmethane, higher hydrocarbons, and decomposition products of benzyl sulfide. If the original concentrated oil was allowed to partition itself between the layers of alcohol-water and petroleum ether, the alcohol-water layer yielded crystalline benzyl sulfide on concentrating and cooling. The benzyl sulfide was identified by its m. p., 49°; oxidation to the sulfone, m. p. 149°; and pyrolysis to stilbene, m. p. 125°. A separation of the benzyl sulfide also resulted from precipitating it as the mercuric chloride complex, formed by mixing hot alcohol solutions of the components. A mixture with the compound made from benzyl sulfide showed no depression in melting point. The complex can be easily recrystallized from alcohol, and may be separated into its parts by warming it in a water solution of ammonium chloride. The purified sulfide solidifies on cooling. This method may be recommended for use in purifying benzyl sulfide prepared in other ways. About 10–11 g. of benzyl sulfide, or about one molecule for each molecule of diphenylmethane, was obtained.

s-*Trithiane with less than two moles of aluminum chloride.*—In a typical experiment 23 g. of trithiane and 22 g. of aluminum chloride were mixed in the dry state, and 100 cc. of benzene was added. The solution soon became clear, and after it stood for a day or two, crystals of sulfur began to appear in the lower, benzene-insoluble layer. When the sulfur stopped precipitating (after three to four days), the reaction was considered complete, and the mixture was decomposed as usual. The benzene layer contained practically no high-boiling material other than sulfur and small amounts of unchanged trithiane. The amount of sulfur formed corresponded roughly to that required in equation (8), or about one atom for each molecule of the sulfonium compound formed. On addition of potassium iodide solution to the water layer, a 50–60% yield of the sulfonium salt, trithiane methyl iodide was precipitated. This compound was identical with the one prepared as follows.

*Preparation of trithiane methyl iodide.*—A mixture of trithiane (one mole) and dimethyl sulfate (two moles) was warmed on a boiling water bath until solution was complete, or for about 2–3 hours. The clear, viscous mass was dissolved in about 10 volumes of warm water, and a slight excess of potassium iodide was added to the diluted sulfonium reaction mixture. Long, flat plates of trithiane methyl iodide crystallized from the solution as it cooled. Yields were about 70%. Trithiane methyl iodide may be recrystallized from methanol with difficulty.

*Anal.* Calc'd for $C_4H_9IS_3$: S, 34.3; I, 45.3; mol. wt. 280.
Found: S, 34.2; I, 44.7; mol. wt. (Rast), 288, 300.

It is stable over long periods of time only if it is pure. It is slightly soluble in cold water, ethyl and methyl alcohols, easily soluble in hot water. It forms molecular compounds with heavy-metal salts. Its trinitrophenoxide melts at 135–137°. Under similar conditions, diethyl sulfate gave a much smaller yield of trithiane ethyl iodide.

## SUMMARY

The behavior of six compounds, containing the thiomethylene group, in benzene in the presence of anhydrous aluminum chloride, at ordinary temperature, has been studied. Normal primary amyl sulfide, *n*-primary amyl mercaptan and ethyl mercaptan underwent little or no change under the conditions. Benzyl mercaptan gave diphenylmethane as the principal product. Benzyl sulfide, depending on the quantity of aluminum chloride

present, reacted to form either the sulfonium salt, tribenzylsulfonium chloride, or diphenylmethane. *s*-Trithiane behaved similarly: with less than two moles of aluminum chloride the principal products were the sulfonium salt, *s*-trithiane methyl chloride, and sulfur; with more than two moles of aluminum chloride, diphenylmethane and benzyl sulfide were the major products. An explanation has been offered for the course of the reaction in the cases of *s*-trithiane and benzyl sulfide.