prepared: 1(9)-methoxy-acridine, 1(9)-hydroxy-acridine, 3(7)-ethoxy-acridine, 3(7)-hydroxy-acridine, 5-methyl-acridine, 5,3(7)-dimethyl-acridine, 5-methyl-3(7)-nitro-acridine, 5-phenyl-1(7)-nitro-acridine, 5-phenyl-3(7)-nitro-acridine, 5-phenyl-3(7)-methyl-acridine, 5-phenyl-3(7)-ethoxy-acridine and 5-phenyl-3(7)-hydroxy-acridine.

It has been shown that the chlorine in 5-nitro-2-chloro-acetophenone is labile enough to react with aniline and with *o*- and *p*-nitro-aniline.

The preparation of the methyl and ethyl esters of acridine-5-carboxylic acid has been described.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE ACTION OF SODIUM TRIPHENYLMETHYL UPON TRIMETHYLMETHOXYAMMONIUM IODIDE AND OF TRIPHENYLMETHYL HALIDES UPON TRIMETHYLAMINE[1]

BY LAUDER W. JONES AND MERRILL W. SEYMOUR

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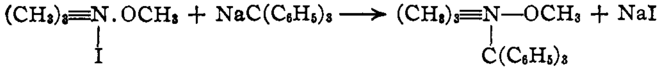
The researches of Schlenk and Holz, which led to the preparation of tetramethylammonium triphenylmethyl, $(CH_3)_4N\cdot C(C_6H_5)_3$, and tetramethylammonium benzyl, suggested the possibility of synthesizing compounds of a new class similar in type to the isomeric alkylated amine oxides, $R_3N(OR)(OR')$, investigated by Meisenheimer,[2] but differing from them by a substitution of the triphenylmethyl radical for an alkoxy group, for example, $R_3NOR\cdot C(C_6H_5)_3$. Isomeric with compounds of this class would be alcoholates of the form $R_3N[C(C_6H_5)_3]\cdot OR$. The experiments described below were undertaken with the hope of obtaining derivatives of these types.

I. **The Action of Sodium Triphenylmethyl upon Trimethylmethoxyammonium Iodide.**—When these two substances were shaken together in very carefully purified ether, the deep red color of the solution changed in time to a pale yellow shade, but no intensely colored compound such as that described by Schlenk as characteristic of tetramethylammonium aryls was noticed; sodium iodide, trimethylamine, triphenylmethane and triphenylethanol were the chief products isolated.

These results suggest that trimethylmethoxyammonium triphenylmethyl was undoubtedly formed in the first stages of the reaction.



$$(CH_3)_3\equiv\underset{\displaystyle I}{\underset{|}{N}}.OCH_3 + NaC(C_6H_5)_3 \longrightarrow (CH_3)_3\equiv\underset{\displaystyle C(C_6H_5)_3}{\underset{|}{N}}-OCH_3 + NaI$$

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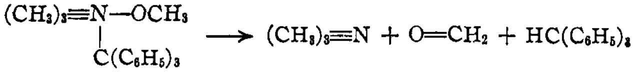
[1] This article is based upon a thesis presented by Merrill W. Seymour to the Faculty of the Graduate School of Princeton University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Meisenheimer, *Ann.*, **397**, 273 (1913).

It decomposed at once in the following manner



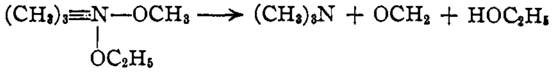
$$(CH_3)_3{\equiv}N{-}OCH_3 \atop \quad | \atop C(C_6H_5)_3 \longrightarrow (CH_3)_3{\equiv}N + O{=}CH_2 + HC(C_6H_5)_3$$

Formaldehyde is known to react with sodium triphenylmethyl to give sodium triphenylethanol[3]

$$CH_2{=}O + NaC(C_6H_5)_3 \longrightarrow NaO{-}CH_2C(C_6H_5)_3$$

These reactions account for the main products actually isolated.

In many details this decomposition resembles the behavior of the unstable alkylated amine oxides described by Meisenheimer. Thus a solution of trimethylmethoxyammonium ethylate gave trimethylamine, formaldehyde and ethyl alcohol.



$$(CH_3)_3{\equiv}N{-}OCH_3 \atop {\quad | \atop \quad OC_2H_5} \longrightarrow (CH_3)_3N + OCH_2 + HOC_2H_5$$

In our reaction the methoxy group, as it left its position in the molecule, furnished a hydrogen atom (or proton) which ultimately united with the negative ion, triphenylmethyl; thus formaldehyde and triphenylmethane resulted.

II. Attempts to Synthesize Trimethyltriphenylmethyl Ammonium Salts.—Schlubach[4] states that he submitted triethyltriphenylmethyl ammonium iodide, $(C_6H_5)_3C{-}N{\equiv}(C_2H_5)_3.I$, to electrolysis in liquid ammonia solution, but he makes no mention of the properties of this substance or the method of its preparation. This is the only reference that could be found in the literature concerning ammonium salts in which one of the radicals attached to nitrogen by a co-valence is triphenylmethyl, unless addition products of triphenylchloromethane to pyridine and to quinoline[5] may be considered as representatives of this type.

In our efforts to obtain salts of this class two procedures were followed, namely, the addition of methyl iodide to dimethylamino-triphenylmethane, and the action of triphenylmethyl halides upon trimethylamine.

Dimethylaminotriphenylmethane and methyl iodide, with and without solvents, showed little tendency to react with each other at room temperature. Some tetramethylammonium iodide was formed, together with a small amount of a dark red, crystalline material which appeared to be partially triphenylmethyl iodide. To account for such a reaction it seems reasonable to assume that some addition of methyl iodide occurred and that the addition product dissociated as follows

$$(C_6H_5)_3C{-}N = (CH_3)_2 + CH_3I = (C_6H_5)_3C{-}N{\equiv}(CH_3)_3{\cdot}I$$
$$(C_6H_5)_3C{-}N{\equiv}(CH_3)_3.I = (C_6H_5)_3C{\cdot}I + N(CH_3)_3$$
$$N(CH_3)_3 + CH_3I = N(CH_3)_4{\cdot}I$$

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[3] Schlenk and Ochs, *Ber.*, **49**, 610–611 (1916).

[4] Schlubach and Miedel, *Ber.*, **56**, 1895 (1923).

[5] Meyer and Fischer, *J. prakt. Chem.*, [2] **82**, 523 (1910).

When triphenylchloromethane was treated with trimethylamine in solvents or without solvents at various temperatures and pressures, no addition product could be isolated. Triphenylmethyl bromide behaved similarly. The failure to obtain addition products confirms the earlier experiments of Nef.[6]

Experimental Part

I. The Action of Sodium Triphenylmethyl upon Trimethylmethoxyammonium Iodide.—This iodide was obtained by the action of methyl iodide upon trimethylamine oxide in methanol solution.[7]

A solution of sodium triphenylmethyl in about 600 cc. of carefully purified ether was prepared from 8.52 g. of triphenylchloromethane and an amalgam made with 1.8 g. of sodium and 90 g. of mercury.[8] A reaction tube similar in form to that described by Schlenk[9] was used. All operations were carried out in an atmosphere of nitrogen. After the tube had been charged and sealed, it was shaken for twelve hours in a dark room. The tube was then opened in an atmosphere of nitrogen and the sodium chloride was separated by filtration of the liquid through a dried Soxhlet thimble in a stream of nitrogen with an apparatus similar to that of Schlenk.[10] The filtrate, deep red in color, was collected in a second reaction tube.

At this stage, 3.66 g. of finely powdered trimethylmethoxyammonium iodide, previously dried over phosphorus pentoxide, was mixed with the filtered solution. Some small glass beads were also added. The tube was then sealed and placed in a shaking machine.

After the mixture had been shaken for eighteen hours, the tube contained a pale yellow solution and a fine, flesh-colored precipitate. The solid was collected on a plate in a specially constructed filtering apparatus through which a stream of nitrogen could be passed. The filter flask was connected with two gas wash bottles containing dilute hydrochloric acid and these in turn were connected with a pump. This precaution was necessary to absorb any trimethylamine which might be carried over in the stream of gas. After filtration the ether filtrate was shaken with the hydrochloric acid solution from the two wash bottles and then washed with water.

In this way the products of reaction were distributed into three parts: (1) a solid, (2) a hydrochloric acid solution, (3) an ether solution.

1. The Solid

The solid was washed with ether. Benzene dissolved only 0.01 g. The residue weighed 3.21 g. It was dissolved in 250 cc. of water and 10cc. portions were analyzed for sodium, for iodine ion, sodium as sodium sulfate and iodine as silver iodide. The amount of hydroxyl ion was determined by titrating 20 cc. of the water solution over 0.1 N HCl; 3.63 cc. of acid was required. These results showed sodium ion, 0.0252 g.; iodine ion, 0.0182 g.; hydroxyl ion, 0.0045 g. This corresponds to 2.73 g. of sodium iodide; calculated amount, 2.53 g.

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[6] Nef, *Ann.*, **309**, 168 (1899).

[7] (a) Dunstan and Goulding, *J. Chem. Soc.*, **75**, 797 (1899); (b) Meisenheimer, *Ann.*, **397**, 288 (1913).

[8] Schlenk and Ochs, *Ber.*, **49**, 609 (1916).

[9] Schlenk, *Ber.*, **46**, 2843 (1913), Fig. 1.

[10] Schlenk, *Ber.*, **46**, 2844–2845 (1913), Figs. 2 and 3.

2. The Hydrochloric Acid Solution

The acid solution was evaporated to dryness. The residue, 1.49 g., was recrystallized by dissolving it in warm chloroform and precipitating it with ether. The purified crystals, identified as trimethylammonium chloride, weighed 1.28 g.; calculated amount, 1.49 g.

3. The Ether Solution

After complete evaporation of the ether, a white solid together with a yellow oil was obtained; weight, 7.2 g. The residue was treated carefully with small amounts of dry ether which dissolved the oil and a portion of the crystals. The remaining crystals, collected and dried, weighed 0.95 g.; m. p. 202°.

The ether solution was evaporated and, by a laborious process of crystallization, the semi-solid residue was resolved into two main fractions consisting of triphenylmethane and triphenylethanol. It was observed that triphenylmethane separated from alcoholic solutions of mixtures containing triphenylethanol, and that triphenylethanol could be freed from small amounts of triphenylmethane by crystallization from ligroin. By combining the crops of crystals of similar melting points and working up the mother liquors, it was possible finally to obtain 2.26 g. of triphenylmethane, m. p. 91–92°; calculated amount, 4.12 g. These crystals mixed with pure triphenylmethane showed a melting point of 92–93°.

The second fraction consisted of 0.49 g. of impure triphenylethanol melting at 96°; calculated amount, 3.75 g. Mixed with pure triphenylethanol the melting point was 100–105°. Recrystallization of the solid from ligroin caused the melting point to rise to 104–105°. Triphenylethanol melts at 106–107°.

In addition to these two compounds, about 0.18 g. of colorless material melting at 183–185°, and 0.038 g. melting at 180–185° were obtained. These crystals and the crystals (0.95 g.) melting at 202° probably consisted chiefly of polymers of triphenylmethyl or their peroxides. They were not positively identified.

Since the difficult separation of triphenylmethane from triphenylethanol was accompanied by loss of material at each step, the low values found for triphenylmethane and triphenylethanol are not surprising. Residual oils which could not be solidified undoubtedly contained both of these substances; only the solid crystals of practically pure substances were weighed.

Preparation of Triphenylethanol.—The method of Schlenk and Ochs[3] was modified; solid para-formaldehyde was used in place of formaldehyde gas. A solution of sodium triphenylmethyl in ether was prepared from 2.95 g. of triphenylchloromethane and an amalgam made from 4.52 g. of sodium and 6.8 g. of mercury. The solution was filtered into a second reaction tube in a stream of dry nitrogen.

Paraformaldehyde, 0.35 g., previously dried over phosphorus pentoxide, was added, the tube was sealed and placed in a shaking machine. After forty-two hours the color of the solution was pale yellow. The tube was opened and the ether washed with water. After drying the ether, it was distilled. A pale yellow oil remained which gradually deposited crystals. The solid, purified by slow crystallization from ligroin (70–80°), gave large, transparent crystals; m. p. 106–107°. In all 1.44 g., about 50% of the calculated amount, was obtained.

II. Attempts to Prepare Trimethyltriphenylmethylammonium Salts. Preparation of Dimethylaminotriphenylmethane.—Hemilian and Silberstein[11] prepared this substance by passing dimethylamine gas through a solution of triphenylbromomethane in benzene. The method employed by us makes use of triphenylchloromethane and is more saving of dimethylamine.

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[11] Hemilian and Silberstein, *Ber.*, **17**, 746 (1884).

A solution of 15.7 g., of triphenylchloromethane in 60 cc. of benzene was placed in a large glass tube cooled by ice. Then 8 g. of liquid dimethylamine, previously cooled by ice and calcium chloride, was poured into the tube. The tube was sealed and shaken in a shaking machine.

After a few days the benzene solution was filled with crystals. The tube was opened and the contents shaken with water. The benzene layer was dried and the benzene distilled. The residue gradually gave crystals which increased in amount when a little ethyl alcohol was added. After purification of the substance by recrystallization from absolute alcohol, it melted between 95 and 97°; yield, 10.3 g. or 65% of the calculated amount.

Action of Methyl Iodide upon Dimethylaminotriphenylmethane.—No reaction occurred when dimethylaminotriphenylmethyl and methyl iodide were brought together at room temperature.

In one experiment, 2.88 g. of dimethylaminotriphenylmethane was dissolved in 20 cc. of methyl iodide and this solution was heated for two hours in a sealed tube placed in a bath of boiling water. The tube was opened and the contents treated with ether and chloroform. A dark reddish solid weighing 1.52 g. remained. This solid was washed with chloroform and dried. The dry crystals had a brownish color. Hot ethyl alcohol removed the color. They did not melt at 280° but appeared to sublime below that temperature.

Anal. Subs., 0.1226: AgI, 0.1417. Calcd. for $(CH_3)_4NI$: I, 63.13. Found: 62.50.

The chloroform extracts evaporated to dryness gave a dark red solid which was recrystallized from alcohol. This yielded impure red crystals soluble in boiling ligroin. They probably contained triphenylmethyl iodide. This was not definitely established.

All attempts to add triphenylmethyl chloride or bromide to trimethylamine failed. Reactions were tried with and without solvents and at various temperatures. Invariably the triphenylmethyl halide was recovered, practically quantitatively. Usually a very small amount of a trimethylammonium salt was formed but this undoubtedly was produced by slight hydrolysis of the triphenylmethyl halide.

Summary

1. When sodium triphenylmethyl reacted with trimethylmethoxyammonium iodide, the chief products formed were trimethylamine, triphenylmethane, triphenylethanol (by secondary reaction from formaldehyde) and sodium iodide. It is assumed that the primary product of the reaction was trimethylmethoxyammonium triphenylmethyl which decomposed.

2. All attempts to add triphenylmethyl halides to trimethylamine or methyl iodide to dimethylaminotriphenylmethane were unsuccessful.

PRINCETON, NEW JERSEY