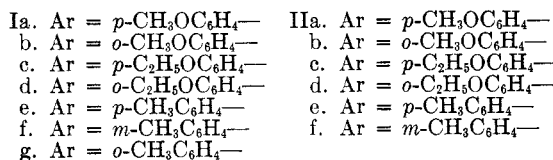
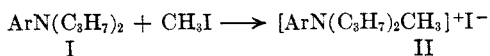


N-Methyl-*N,N*-di-*n*-propylanilinium salts of the tertiary bases (Ia-g) were prepared by the action of methyl iodide on the corresponding *N,N*-di-*n*-propylanilines.



Only in the case of *N,N*-di-*n*-propyl-*o*-toluidine, could the formation of the quaternary ammonium salt not be achieved under normal conditions, when the tertiary base was treated with methyl iodide or methyl sulfate, due probably to steric effect.^{1,2}

The thermal decomposition of the quaternary ammonium iodides was affected by heating above their melting points. The remaining tertiary bases, left after decomposition, were identified as the corresponding picrates. Mixed melting-point determination of the picrates of the starting materials (Ia-f) and the picrates obtained on thermal decomposition, showed depression in each case. This fact, together with the analytical figures obtained from decomposition picrates, indicated that thermal decomposition led to the formation of the mixed dialkylaniline, i.e., *n*-propyl iodide was always eliminated and *N*-methyl-*N*-propyl aromatic base was left. A similar result has been reported previously.¹⁻³

Decomposition of the iodides IIa-f with ethanolic sodium ethoxide followed the same route observed in the thermal decomposition. Mixed melting-point determination of the picrates obtained on thermal decomposition and those from alkaline decomposition showed no depression, indicating that they are identical. The quaternary iodides, the quaternary picrates, the picrates of the starting materials, and the picrates of the products of decomposition are listed in Table II.

EXPERIMENTAL

Preparation of the dipropylanilines (Ia-g). Tri-*n*-propyl phosphate was prepared according to the general procedure described for the synthesis of *n*-alkyl phosphates.⁵

The method used for the preparation of Ia-g was that adopted by Bilman *et al.*⁴ The corresponding picrates were prepared by mixing an ethanolic solution of the freshly distilled tertiary base with saturated ethanolic solution of picric acid. The products were filtered and crystallized.

Preparation of the quaternary ammonium iodides. Equimolecular proportions of the tertiary base Ia-g and methyl iodide were mixed in a sealed tube and left for some days at room temperature (20°) (in case of Ia, Ic, and Ie), or heated at 100° for 5-10 hr. (Ib, Id, and If), (40 hr. in case of

Ig). The solid products were washed with ether and crystallized.

Preparation of the quaternary ammonium picrates. The quaternary ammonium picrates were obtained when an aqueous solution of the corresponding iodide was added to an excess of a saturated aqueous solution of picric acid. The precipitate was collected, dried, and crystallized.

Decomposition of the quaternary ammonium iodides. (a) *By heat.* The thermal decomposition of the iodides IIa-f was effected by heating 0.5 g. of the pure substance in a Pyrex tube above its melting point until bubbles ceased to evolve. The oily residue was extracted with ether, filtered to remove any undecomposed iodide and the ether removed. A few drops of ethanol were added, followed by a saturated ethanolic solution of picric acid. The picrate was filtered off and crystallized.

(b) *By ethanolic sodium ethoxide.* The decomposition of the iodides IIa-f was carried out by heating (1.5 g.) with ethanolic sodium ethoxide [from metallic sodium (0.3 g.) and absolute ethanol (20 ml.)] for 5 hr. on the steam bath. Sodium iodide, formed as a result of decomposition, was filtered, the ethanol was concentrated and a few ml. of water added. The oil that separated was taken up in ether, dried, and the ether removed. The oily residue was converted into the picrate, which was then filtered and crystallized.

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Thiophosgenation of Dimethylammonium Chloride¹

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In continuation of studies³ on the preparation and properties of the thiaziazole ring system a supply of dimethylthiocarbonyl chloride (II) was required. Billiter and Rivier^{4,5} report a convenient procedure using dimethylammonium chloride (I) and thiophosgene in the presence of aqueous sodium hydroxide. The thiophosgene (in alcohol-free chloroform) is added to an aqueous solution of I followed by slow addition of sodium hydroxide, the temperature being maintained at 25° by addition of ice. Yields of 65 to 95% of II were reported. Two moles of alkali are used per mole of I and at the end of the reaction the aqueous phase was reported⁴ to be alkaline. At this point the chloroform layer changes from red to yellow in color. In our hands the repetition of this procedure failed to confirm any of these observations; only a 7%

(1) The authors gratefully acknowledge the support of these studies by the Air Force Office of Scientific Research.

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(3) E. Lieber, J. Ramachandran, C. N. R. Rao, and C. N. Pillai, *Can. J. Chem.*, **37**, 563 (1959).

(4) O. Billiter and H. Rivier, *Ber.*, **37**, 4319 (1904).

(5) Houben-Weyl, *Methoden der Organischen Chemie*, Georg Thieme Verlag, Stuttgart, Germany, volume IX, page 830 (1955).

(5) G. R. Dutton and C. R. Noller, *Org. Synthesis*, Vol. XVI, p. 9.

yield of II was obtained, the aqueous layer was acidic and the chloroform layer remained red in color. In addition, a nicely crystalline product melting at 104° consistently appeared by fractional recrystallization of the crude II. This was identified as tetramethylthiuram monosulfide (III) and in one experiment (Table I) it became the major product. Tetramethylthiourea was also isolated in this instance. Billiter and Rivier⁴ fail to mention the formation of any by-products in their reaction.

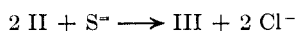
TABLE I
THIOPHOSGENATION OF DIMETHYLAMMONIUM CHLORIDE^a

Temp. °	Ratio NaOH/ + Me ₂ NH ₃ Cl - Cl	% Yield of Dimethylthio- carbonyl Chloride
28	1	2
28	2	7
28	2.5	None ^b
20	2.7	25 ^c
10	2	15
-5 ^d	2	38
-20 ^e	2	46-50

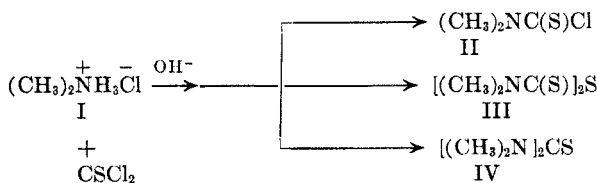
^a In all experiments a one to one molar ratio of thiophosgene to dimethylammonium chloride was maintained.

^b Tetramethylthiuram monosulfide was isolated in 1.6% yield, the major product being an unworkable oil. ^c The major product (47%) was III; 5% of IV was also obtained. ^d The temperature varied from 0° to -5°. ^e The temperature varied from -10° to -20°.

An investigation of this reaction was conducted. The results are summarized in Table I. Increasing the quantity of sodium hydroxide until the aqueous layer became alkaline was without effect, in fact no yield of II was obtained and only 1.6% of III and an intractable oil were the major products. The most important variable was the temperature of the reaction regardless of whether the aqueous phase ended up in an acidic or alkaline condition. The lowest practical temperature with the set of reagents used was found to be -10 to -20° in which case consistent yields of II of 46 to 50% were obtained. At lower temperatures increase in sodium hydroxide reduces the yield of II while favoring the formation of III. This suggests that the formation of III can be accounted for by a nucleophilic displacement of chloride ion by sulfide ion: the sulfide ion arising from the alkaline



hydrolysis of the thiophosgene.



EXPERIMENTAL^{6,7}

Dimethylthiocarbonyl chloride (II). Into a three necked round-bottom flask equipped with a mechanical stirrer, reflux condenser, and dropping funnel and surrounded by acetone-Dry Ice bath was placed 8.3 g. (0.1 mole) of dimethylammonium chloride dissolved in 10 ml. of water. The temperature was adjusted to -10°. Thiophosgene (12 g., 0.1 mole) dissolved in 30 ml. of alcohol-free chloroform was added to the reaction flask with stirring over a period of 30 min. An aqueous solution of sodium hydroxide (100 ml. of a 2*M* solution) was then added over a period of 1 hr., not allowing the temperature to rise above -10°. The mixture was finally stirred for an additional 30 min., the chloroform layer separated and immediately dried over calcium chloride. The chloroform was then removed at reduced pressure at steam bath temperature. The residue (which is semisolid when cooled in an ice bath) was recrystallized from petroleum ether yielding a product melting at 41° in agreement with that reported.⁴ The yield varied from about 5 to 5.5 g. (45 to 50% based on I).

Tetramethylthiuram monosulfide (III). This arises (Table I) from the fraction-crystallization of crude II. It was identified by mixture melting point with an authentic specimen of tetramethylthiuram monosulfide prepared according to the procedure of von Braun and Stechele.⁸ When using anhydrous ether (as solvent for the thiophosgene) II is recovered as the ether soluble fraction, while recrystallization of the ether-insoluble residue yields III.

Tetramethylthiourea (IV). This was found in several instances as a by-product of the fractional crystallization of II. It was identified by its melting point⁹ of 75-76°.

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(6) Melting points are uncorrected.

(7) The thiophosgene was supplied by the Rapter Chemical Company, Chicago, Illinois. Vapor phase chromatography showed this to be 99% plus in thiophosgene content.

(8) J. von Braun and F. Stechele, *Ber.*, **36**, 2274 (1903).

(9) O. Billiter, *Ber.*, **43**, 1856 (1910).

Cyclic Sulfites and the Bissinger Rearrangement

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The "Bissinger rearrangement" is a convenient name for the reaction first described by Bissinger, Kung, and Hamilton,¹ in which a dialkyl sulfite gives an alkyl alkanesulfonate on heating with a tertiary base. Dimethyl sulfite gave a 49-56% yield of methyl methanesulfonate after 24 hr. with 1 mol. per cent of tributylamine; the yield decreased with increasing size of alkyl groups. The rearrangement of dimethyl sulfite gave dimethyl ether as by-product, and a mechanism was suggested which accounted for both the rearrangement and the ether formation. We have found triethylamine is also a

(1) W. E. Bissinger, F. E. Kung, and C. W. Hamilton, *J. Am. Chem. Soc.*, **70**, 3940 (1948).