Tetrahedron Letters No. 6, pp 497 - 500, 1972. Pergamon Press. Printed in Great Britain.

# THE SYNTHESIS, THERMOLYSIS AND BASE-CATALYZED REARRANGEMENT OF AZASULFONIUM SALTS[1]

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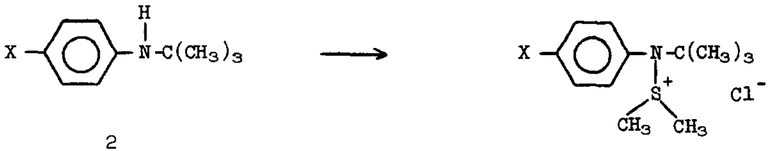
(Received in USA 30 November 1971; received in UK for publication 5 January 1972)

The lack of thermal stability of N-chlorinated aromatic amines has been well established.[2-4] In view of the utility of N-chloroanilines as nitrenium ion[5] precursors in the synthesis of substituted anilines[6] and of derivatives of 2,5-cyclohexadienones,[7] we sought to prepare storable derivatives of N-chloroanilines which might serve as useful intermediates in organic synthesis. We now wish to report that N-chloroanilines react readily with dialkyl sulfides to produce azasulfonium salts (**1**).[8-10] In addition we wish to report on the thermolysis and base-catalyzed rearrangement of these interesting intermediates.

Treatment of anilines (**2**) with calcium hypochlorite, followed by dimethyl sulfide resulted in the formation of salts of general formula **1**. When X was methyl, hydrogen, or



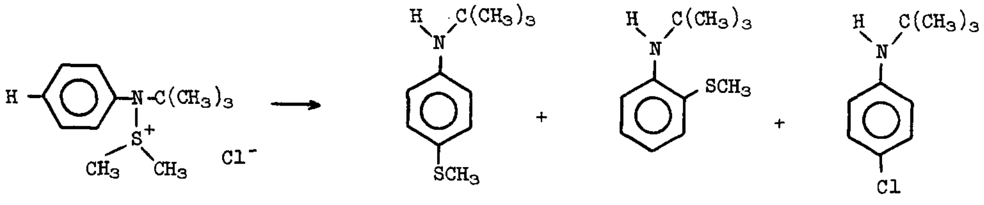
**2**

a) X = $CH_3$
b) X = H
c) X = Cl

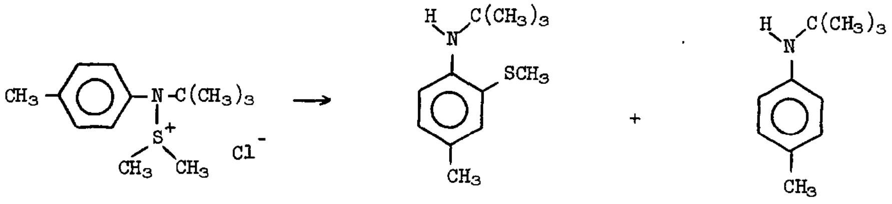
**1**

chlorine the yields were 76, 80, and 59%, respectively. After thermolysis at 100° in dimethylformamide for 2 hr, the azasulfonium salt, **1b**, was completely reacted and a mixture of

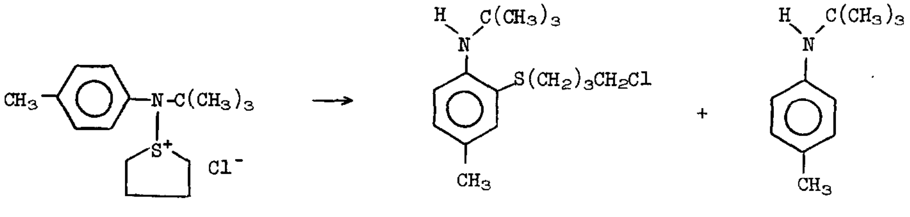
3 (36%), 4 (8%), 2c (3%), and 2b (36%) was formed. Similar thermolysis of 1a gave 58% of 5 and 32% of 2a,[11] while thermolysis of 6 gave 35% of 7[12] and 47% of 2a.[11,13]



1b 3 4 2c

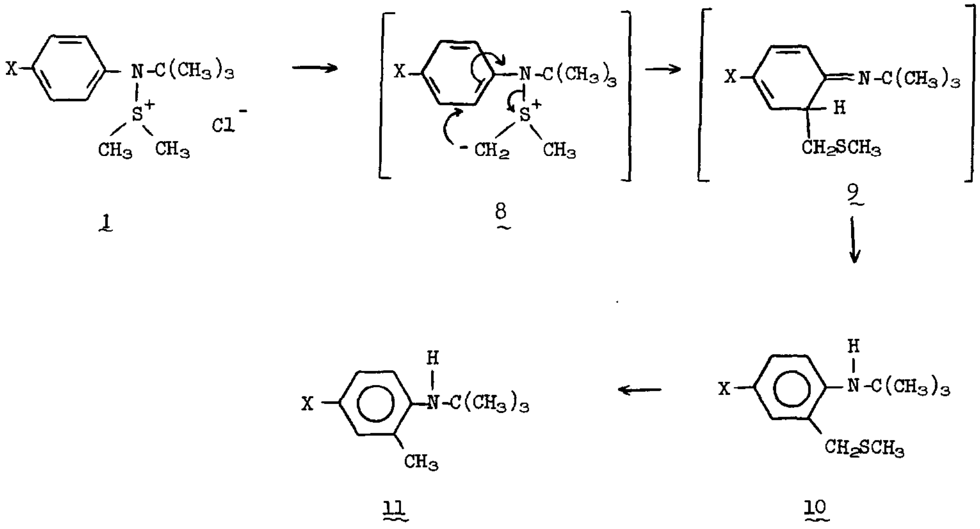


1a 5. 2a



6 7 2a

Treatment of the azasulfonium salts with base at room temperature results in the virtually instantaneous conversion of 1a, 1b, and 1c into 10a, 10b, and 10c in 95, 95, and 83% yields, respectively. Both methanolic sodium hydroxide and diethylamine facilitate this transformation. We presume that base removes one of the protons from the methyl group to give the ylid,[14] 8, which rearranges to give 9 in a Sommelet-Hauser type rearrangement.[15] Proton shift and accompanying rearomatization would transform 9 into 10. In addition to making comcompounds such as 10 readily available, this process provides a simple route to specifically *o*-alkylated aromatic amines, since **10a**, **10b**, and **10c** are readily converted to **11a**, **11b**, and



**11c** in high yield by catalytic reduction over W-2 Raney nickel. Since these results indicate the potential of azasulfonium salts in the synthesis of specifically substituted aromatic amines, we plan to continue to investigate their many possible synthetic applications.

*Acknowledgment.* We are indebted to the National Cancer Institute of the Public Health Service for Grant CA-07110 which supported this investigation.

## References

(1) Paper XIX in a series on The Chemistry of Nitrenium Ions. For the previous paper in this series see P. G. Gassman and G. A. Campbell, *Chem. Commun.*, in press.

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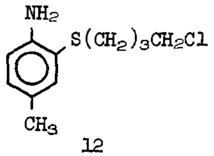
(8) Although such "anilinio" sulfonium salts have not been previously characterized, a few isolated examples of closely related salts have been reported. For these examples see a) C. R. Johnson, J. J. Rigau, M. Haake, D. McCants, Jr., J. E. Keiser and A. Gertsema, *Tetrahedron Lett.*, 3719 (1968); b) R. Appel and W. Büchner, *Chem. Ber.*, **95**, 849, 855 (1962); c) R. E. Cook, M. D. Glick, J. J. Rigau, and C. R. Johnson, *J. Amer. Chem. Soc.*, **93**, 924 (1971). Recently, we have learned that compounds very similar to ours have been prepared in the laboratories of Prof. C. R. Johnson. We wish to thank Professor Johnson for informing us of his unpublished results and for agreeing to simultaneous publication.

(9) Related salts have been referred to as sulfilimine salts (derived from their preparation *via* alkylation of sulfilimines),[8a] sulfiminium salts,[8b] and aminosulfonium salts.[8c]

(10) Satisfactory elemental analyses have been obtained on all new compounds or their derivatives.

(11) Since **2a** is the precursor of both **1a** and **6**, the corrected yields of **5** and **7** based on unrecovered **2a** would be 76% and 52%, respectively. These yields indicate that the procedure described is of preparative value for the synthesis of thioanisoles.

(12) The structure of **7** was established *via* comparison of spectral data with an independently synthesized sample and by comparison of its thermal elimination (215°) product, **12**, with an independently synthesized sample.



**12**

(13) We are currently carrying out a detailed investigation of the mechanism of these thermal rearrangements.

(14) For an alternate synthesis of these ylids and a discussion of their behavior see P. Claus and W. Vycudilik, *Monatsh. Chem.*, **101**, 396 (1970).

(15) For analogous Sommelet-Hauser type rearrangements see M. G. Burdon and J. G. Moffatt, *J. Amer. Chem. Soc.*, **89**, 4725 (1967); P. Claus, *Monatsh. Chem.*, **102**, 913 (1971).