

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF SYRACUSE UNIVERSITY]

**Condensation of Thiophenols and Formaldehyde
with Some Aromatic Amines**

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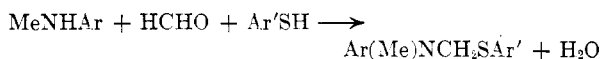
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N-Arylaminoethyl aryl sulfides and 1,3,5-triaryl-1,5-dithia-3-azapentanes have been prepared by condensing primary aromatic amines with formaldehyde and thiophenols. *N*-Methylanilines condense with formaldehyde and thiophenols to form *N*-methyl-*N*-arylaminoethyl aryl sulfides.

Two arylaminoethyl aryl sulfides were prepared by condensing β -chloroethylaniline with the sodium salt of the thiophenol. Basicities of these arylaminoalkyl aryl sulfides have been related to (a) the presence of electrophilic substituents attached to the aryl groups and (b) the number of carbon atoms separating the nitrogen and sulfur atoms.

Recently Grillo *et al.*¹ have demonstrated that the thiophenols condense with secondary aliphatic amines and formaldehyde to form dialkylaminoethyl aryl sulfides similar in structure to the dialkylaminoethyl alkyl sulfides prepared by McLeod and Robinson² by condensing aliphatic mercaptans with aliphatic amines and formaldehyde. The formation of these aminomethyl aryl sulfides was somewhat surprising, since phenols condense with secondary aliphatic amines and formaldehyde to form ortho and para substituted dialkylaminomethylphenols.³

Although aromatic amines generally react with more sluggishness in the Mannich reaction than the corresponding aliphatic amines, *N*-methylaniline, *N*-methyl-*p*-anisidine, and *N*-methyl-*p*-nitroaniline react with thiophenols and formaldehyde according to the following equation:



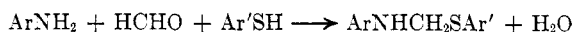
to give moderately stable crystalline *N*-methyl-*N*-arylaminoethyl aryl sulfides.

(1) G. F. Grillo, H. R. Felton, B. R. Garrett, H. Greenberg, R. Green, R. Clementi, and M. Moskowitz, *J. Am. Chem. Soc.*, **76**, 3969 (1954).

(2) C. M. McLeod and G. M. Robinson, *J. Chem. Soc.*, **119**, 1470 (1921).

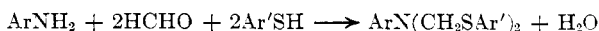
(3) F. F. Blicke, *Organic Reactions*, John Wiley & Sons, Inc., New York, N. Y., (1942), Volume 1, page 311.

Whereas primary aliphatic amines generally give a mixture of secondary and tertiary amines in the Mannich reaction, primary aromatic amines can be condensed with thiophenols and formaldehyde in a 1:1:1 mole ratio to give almost exclusively moderately stable usually crystalline *N*-arylaminoethyl aryl sulfides as follows:



Under similar conditions, benzylamine, a primary aliphatic amine, condenses with *p*-chlorothiophenol and formaldehyde to give a mixture of presumably the mono- and di-(arylmethylaminoethyl)amine from which *N*-benzylaminoethyl *p*-chlorophenyl sulfide is difficult to isolate.

If a mole ratio of thiophenol, primary aromatic amine, and formaldehyde of 2:1:2 is employed in this condensation, 1,3,5-triaryl-1,5-dithia-3-azapentanes are obtained:



There was no evidence for the formation of a 3,4-dihydro-1,3,2H-benzo-*m*-thiazine when the condensation of the thiophenol, aniline and formaldehyde in the mole ratio of 1:1:2 was attempted. Under similar conditions phenols form the corresponding dihydrobenzo-*m*-oxazines.⁴

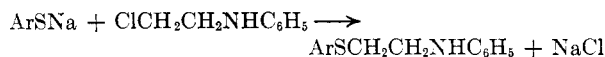
(4) W. J. Burke, *et al.*, *J. Am. Chem. Soc.*, **71**, 609 (1949); **74**, 3601 (1952); **76**, 1677 (1954); **77**, 5637 (1955).

TABLE I
 N-ARYLAMINOMETHYL ARYL SULFIDES, Ar¹NHCH₂SAr²

Compound	Ar ¹	Ar ²	M.P., °C.	Formula	Yield, %	Carbon, %		Hydrogen, %	
						Calcd.	Found	Calcd.	Found
I	C ₆ H ₅	C ₆ H ₅ ^a	52-54.5	C ₁₂ H ₁₃ NS	56	72.52	72.66	6.09	5.89
II	C ₆ H ₅	<i>p</i> -ClC ₆ H ₄ ^b	62-63.5	C ₁₃ H ₁₂ NSCl	16 ^c	62.51	62.64	4.84	4.58
III	<i>p</i> -ClC ₆ H ₄	<i>p</i> -ClC ₆ H ₄	66.2-67	C ₁₃ H ₁₁ NSCl ₂	33	54.94	54.89	3.90	3.63
IV	<i>o</i> -ClC ₆ H ₄	C ₆ H ₅ ^c	^h	C ₁₃ H ₁₂ NSCl	28	62.51	62.28	4.84	4.60
V	<i>o</i> -ClC ₆ H ₄	<i>p</i> -ClC ₆ H ₄	64-65	C ₁₃ H ₁₁ NSCl ₂	86	54.94	54.80	3.90	3.84
VI	<i>m</i> -ClC ₆ H ₄	<i>p</i> -ClC ₆ H ₄	62.5-64.5 ⁱ	C ₁₃ H ₁₁ NSCl ₂	23	54.94	55.04	3.90	3.46
VII	C ₆ H ₅	2,4,6-(CH ₃) ₃ C ₆ H ₂	68-70.8	C ₁₆ H ₁₉ NS	19	75.06	75.19	7.44	7.46
VIII	2,4,6-(CH ₃) ₃ C ₆ H ₂	2,4,6-(CH ₃) ₃ C ₆ H ₂	157-159.2	C ₁₉ H ₂₅ NS	67	76.20	75.31	8.42	7.82
IX	<i>p</i> -CH ₃ OC ₆ H ₄	<i>p</i> -ClC ₆ H ₄	73.6-75.6	C ₁₄ H ₁₄ NSClO	21	60.08	60.18	5.04	5.30
X	<i>p</i> -CH ₃ C ₆ H ₄	<i>p</i> -ClC ₆ H ₄ ^d	113-115	C ₁₄ H ₁₄ NSCl	^j	63.72	64.63	5.35	4.52
XI	<i>p</i> -NO ₂ C ₆ H ₄	<i>p</i> -ClC ₆ H ₄ ^e	139-141.5	C ₁₃ H ₁₁ N ₂ O ₂ SCl	74	52.97	53.18	3.76	3.18
XII	C ₆ H ₅	C ₆ Cl ₅ ^{f,g}	125-135	C ₁₃ H ₉ NSCl ₅	^k	40.29	38.07	2.08	1.75

^a S. Calcd.: 14.89. Found: 14.71. ^b S. Calcd.: 13.84. Found: 12.45. Cl. Calcd.: 14.20. Found: 13.72. ^c d_{25}^{20} 1.2348; n_D^{20} 1.6412. ^d A small amount of what presumably was the corresponding triarylazathiapentane was obtained. ^e Recrystallized from toluene-petroleum ether. ^f S. Calcd.: 8.28. Found: 8.09; 9.69. Cl. Calcd.: 45.75. Found: 45.28. ^g Recrystallized from toluene. ^h B.P. 120-122/1 mm. ⁱ B.P. 120-123/1 mm. ^j Very probably contaminated with the triarylazapentane and attempts to achieve a separation were unsuccessful. ^k A 46% yield of crude product was obtained. Although repeated recrystallization of this product from chloroform gave a product of m.p. 154-156°, analysis of this product was inferior to that of the crude product. The nature of the impurities are unknown.

In order to compare the properties of the arylaminomethyl aryl sulfides and the arylaminoethyl aryl sulfides, that is the effect of adding a second methylene group between the nitrogen and sulfur atoms, phenylaminoethyl phenyl sulfide and phenylaminoethyl *p*-chlorophenyl sulfide were prepared by the reaction of the sodium salt of the thiophenol with β -chloroethylaniline, thus:



EXPERIMENTAL⁵

Materials. The pentachlorothiophenol, which was kindly furnished by E. I. Du Pont de Nemours, Inc., Wilmington, Del., was recrystallized from toluene. The commercially available benzylamine was redistilled before use.

2,4,6-Trimethylbenzenesulfonyl chloride was prepared essentially by the method employed by Morgan and Cretcher in their synthesis of *p*-methoxybenzenesulfonyl chloride.⁶ The former was then reduced with zinc and sulfuric acid to 2,4,6-trimethylbenzenethiol(thiomesitol) using the method of Adams and Marvel.⁷

2,4,6-Trimethylaniline (mesidine) was prepared by nitrating mesitylene⁸ and reducing the nitro compound to give a yellow oil (yield 77%) boiling at 230-234°.

N-Methyl-*p*-anisidine was prepared by converting *p*-anisidine to *N*-methyl-*p*-methoxyacetanilide by the method of Hepp.⁹ The latter was then converted by treatment with sodium nitrite and hydrochloric acid to *N*-nitroso-*N*-

methyl-*p*-anisidine. The nitroso group was removed by the method of Reilly and Hickinbottom.¹⁰

β -Chloroethylaniline hydrochloride was prepared by treating β -hydroxyethylaniline (Matheson) with concentrated hydrochloric acid and thionyl chloride in the presence of chloroform according to the method of G. D. Jones.¹¹ A product melting at 155-160° was obtained. (Literature,¹¹ m.p. 155-157°.)

***N*-Arylaminoethyl aryl sulfides.** Generally 0.1 mole of the thiophenol, 0.1 mole of the primary aromatic amine, and 0.1 mole of 35-40% formaldehyde and 20 ml. of 95% alcohol were added to the reaction flask which was then heated with stirring for 2 hr. at 80°. During this heating period the solution became cloudy and an immiscible liquid separated. The reaction mixture was then placed in the refrigerator until crystallization occurred. If crystallization did not occur on standing, the immiscible oil was extracted with ether and was then vacuum distilled. These compounds with the exception of those listed in the footnotes of Table I were purified by crystallization from ligroin. In the synthesis employing pentachlorothiophenol, benzene or toluene was used as the solvent and paraformaldehyde replaced formalin. For melting points, boiling points, yields, and analyses see Table I.

***N*-Methyl-*N*-arylaminoethyl aryl sulfides.** These were prepared by the same general method as the *N*-arylaminoethyl aryl sulfides by condensing 0.1 mole of the thiophenol and 0.1 mole of the *N*-methylaniline with 0.1-0.17 mole of 35-40% formaldehyde in 20 ml. of 95% ethyl alcohol. The resulting solid products, with the exceptions noted in the footnotes of Table II, were purified by recrystallization from ligroin. Like the *N*-arylaminoethyl aryl sulfides, these compounds would form neither picrates nor *p*-nitrobenzoates. For data concerning these compounds see Table II.

1,3,5-Triaryl-1,5-dithia-3-azapentanes. In the reaction flask were placed 0.1 mole of the thiophenol, 0.05 mole of aniline, 0.1 mole of 35-40% formaldehyde, and 20 ml. of 95% alcohol. Upon heating for 2 hr. at 80° with stirring, immiscible oils separated that crystallized upon cooling and standing. The resulting solids were recrystallized from ligroin. Data for these compounds appear in Table III.

(5) Carbon, hydrogen, and nitrogen analyses were performed by Drs. Weiler and Strauss, Oxford, England, and Mr. Richard Downing of Bristol Labs., Inc., Syracuse, N. Y. The sulfur and chlorine analyses were performed by R. E. S.

(6) M. S. Morgan and L. H. Cretcher, *J. Am. Chem. Soc.*, **70**, 375 (1948).

(7) R. Adams and C. S. Marvel, *Org. Syntheses*, **Coll. Vol. 1**, Second Edition, p. 504.

(8) G. Powell and F. R. Johnson, *Org. Syntheses*, **14**, 68 (1934).

(9) P. Hepp, *Ber.*, **10**, 327 (1877).

(10) J. Reilly and W. J. Hickinbottom, *J. Chem. Soc.*, **115**, 180 (1919).

(11) G. D. Jones *et al.*, *J. Org. Chem.*, **9**, 125 (1944).

TABLE II
 N-ARYL-N-METHYLAMINOMETHYL ARYL SULFIDES, Ar¹N(CH₃)CH₂SAr²

Compound	Ar ¹	Ar ²	M.P., °C.	Formula	Yield, %	Carbon, %		Hydrogen, %	
						Calcd.	Found	Calcd.	Found
XIII	C ₆ H ₅	C ₆ H ₅ ^a	36.4–38	C ₁₄ H ₁₅ NS	71	73.32	73.70	6.59	6.59
XIV	C ₆ H ₅	<i>p</i> -ClC ₆ H ₄	44.6–46.7	C ₁₄ H ₁₄ NSCl	72	63.72	64.36	5.35	5.34
XV	C ₆ H ₅	2,4,6-(CH ₃) ₃ C ₆ H ₂ ^b	51.8–52.8	C ₁₇ H ₂₁ NS	89	75.60	75.32	7.80	8.01
XVI	C ₆ H ₅	C ₆ Cl ₆ ^c	118–121.4	C ₁₄ H ₁₀ NSCl ₆	91	41.87	42.09	2.51	2.50
XVII	<i>p</i> -NO ₂ C ₆ H ₄	<i>p</i> -ClC ₆ H ₄ ^d	91.8–93.6	C ₁₄ H ₁₃ N ₂ O ₂ SCl	66	54.45	54.56	4.24	4.28
XVIII	<i>p</i> -CH ₃ OC ₆ H ₄	<i>p</i> -ClC ₆ H ₄	56.6–58.2	C ₁₅ H ₁₆ NOSCl	93	61.26	61.61	5.49	5.61

^a S. Calcd.: 13.98. Found: 13.98. ^b Recrystallized from alcohol. ^c Recrystallized from toluene. ^d Recrystallized from toluene-petroleum ether.

 TABLE III
 1,3,5-TRIARYL-1,5-DITHIA-3-AZAPENTANES, Ar¹SCH₂NCH₂SAr¹

Compound	Ar ¹	Ar ²	M.P., °C.	Formula	Yield, %	Carbon, %		Hydrogen, %	
						Calcd.	Found	Calcd.	Found
XIX	C ₆ H ₅	C ₆ H ₅	50.2–52.2	C ₂₀ H ₁₉ NS ₂	56	71.18	71.58	5.68	5.69
XX	<i>p</i> -ClC ₆ H ₄	C ₆ H ₅	60.6–61.4	C ₂₀ H ₁₇ NS ₂ Cl ₂	74	59.11	59.31	4.22	4.08
XXI	<i>p</i> -ClC ₆ H ₄	<i>p</i> -CH ₃ C ₆ H ₄	71–74	C ₂₁ H ₁₉ NS ₂ Cl	^a	60.01	61.02	4.56	4.81

^a Obtained as a by-product in the preparation of the corresponding arylaminomethyl aryl sulfide and is probably contaminated with the latter compound.

N-Benzylaminomethyl *p*-chlorophenyl sulfide (Compound XXII). This compound was prepared in the same general manner as the *N*-arylaminoethyl aryl sulfides by condensing 0.1 mole of benzylamine, 0.1 mole of *p*-chlorobenzenethiol and 0.1 mole of 35–40% formaldehyde in 20 ml. of 95% alcohol. A white solid formed when the thiol and amine were mixed, but this dissolved upon the addition of the alcohol. When the formaldehyde solution was added, an immiscible liquid formed which soon crystallized. Eight grams (30% yield) of fine white needles, m.p. 54–55.6° was obtained. This, however, appeared to be a mixture as it formed a picrate that melted in the range 81–145°. A small quantity of material as fine needles was obtained from the alcoholic mother liquor. This substance melted at 71–73° and the following analyses indicated that it was the substance sought.

Anal. Calcd. for C₁₄H₁₄NSCl: C, 63.72; H, 5.35; neut. equiv., 264. Found: C, 64.11; H, 4.63; neut. equiv., 263.

N-Phenylaminoethyl *p*-chlorophenyl sulfide (Compound XXIII). In a beaker was placed 10 g. (0.06 mole) of *β*-chloroethylaniline hydrochloride and sufficient water to bring the solid into solution. To this was added 4.1 g. (0.03 mole) of anhydrous potassium carbonate, whereupon a dark colored oil separated. This solution was extracted with ether and the extracts were dried over anhydrous magnesium sulfate.

In a 500 ml. round bottom flask fitted with a mercury sealed stirrer, dropping funnel, condenser, and drying tube filled with calcium chloride were placed 100 ml. of absolute alcohol and 3 g. (0.13 mole) of sodium. When the sodium had dissolved, 0.06 mole of *p*-chlorothiophenol in 20 ml. of absolute alcohol was added. Then the filtered ethereal solution of *β*-chloroethylaniline, equivalent to 7.9 g. (0.06 mole) of the free base was slowly added and the resulting reaction mixture was refluxed for 2 hr.

After cooling, the precipitated sodium chloride was removed by filtration and the alcohol and ether were evaporated under reduced pressure. The solid residue that remained was dissolved in ether and this solution was then extracted with 200 ml. of 10% hydrochloric acid. The white solid that floated between the ether and water layer was collected on a filter and was washed with ether. It was then placed in a beaker and water was added to make a slurry. Sodium hydroxide (10%) was added until the solution was

distinctly alkaline. Ether extraction of this solution followed.

Meanwhile 10% sodium hydroxide was added to the acid wash water. The white solid that separated was extracted with ether and this extract was combined with the other ether extracts. After drying the combined ether extracts over anhydrous magnesium sulfate, the ether was removed under reduced pressure. The resulting residue was dissolved in methanol and cooled, whereupon an amorphous pink powder formed. Most of the color was removed by recrystallizing from methanol using Nuchar. A second recrystallization employed petroleum ether as the solvent. Melting point 45.2–46.6°. Yield 38%.

Anal. Calcd. for C₁₄H₁₄NSCl: C, 63.72; H, 5.35. Found: C, 63.18; H, 5.16.

Picrate. Melting point 126.8–127.6°.

Anal. Calcd. for C₂₀H₁₇N₄O₇SCl: N, 11.37. Found: N, 11.35.

N-Phenylaminoethyl phenyl sulfide (Compound XXIV). This compound was prepared in the same manner as the corresponding *p*-chlorophenyl compound described above, employing thiophenol in place of the *p*-chlorothiophenol. Following the neutralization of the hydrochloric acid extract with 10% sodium hydroxide, a yellow oil was obtained. This oil was dissolved in ether and the resulting solution was dried over anhydrous magnesium sulfate. Upon removal of the ether, 12.1 g. of an oil remained.

After removal under reduced pressure of a few drops of low boiling material, this liquid was dissolved in acetone. Nuchar removed part of the color and water was added, causing an oily liquid to separate. Removal of the water and acetone by evaporation produced a violet color residue that was then recrystallized from ligroin. It was then recrystallized from alcohol using Nuchar as a decolorizing agent. This was followed by a recrystallization from ligroin. Melting point 35–41°. Yield 21%.

Anal. Calcd. for C₁₄H₁₅NS: C, 73.32; N, 6.59. Found: C, 73.29; H, 6.56.

Infrared Spectra. Infrared spectrograms of compounds I, II, V, VII, VIII, XII, XIII, XIV, XV, XVI, and XIX were prepared by Samuel P. Sadtler and Sons, Inc., 1517 Vine St., Philadelphia, Pa.

The following observations have been made from the infrared spectra:

1. In support of the sulfide structure assigned to these compounds, the absorption peak in the 3.7–3.9 micron region, characteristic of the SH group¹² is absent in these spectra.

2. In the *N*-arylaminoethyl aryl sulfides a sharp spike occurs at 2.9 microns characteristic of the NH stretching in secondary amines.¹³

3. An absorption band in the 8-micron region characteristic of aromatic amines¹³ is found in the spectra of all the *N*-arylaminoethyl aryl sulfides.

4. An absorption band in the range of 7.4–7.6 microns and another (a triplet) in the 8.1–8.5 micron region, characteristic of tertiary amines¹³ are present in the spectra of the *N*-methyl-*N*-arylaminoethyl aryl sulfides.

5. A new absorption band characteristic of these latter tertiary amines is found as a "triplet" with a sharp absorption in the 10-micron region. The ortho substituted secondary amines, having a "triplet" in the 8-micron region, may be differentiated by the lack of this triplet in the 10-micron region.

6. The infrared spectra of 2,4,6-trimethylphenylaminoethyl 2,4,6-trimethylphenyl sulfide (compound VIII) indicates a definite existence of steric hindrance which must be due to the interaction of the many methyl groups attached to the ortho positions in the aromatic nuclei.

Potentiometric titrations and the basicities of the arylaminoethyl and ethyl aryl sulfides. Of the *N*-arylaminoethyl aryl sulfides, compounds I, II, VII, and XII, when titrated with perchloric acid in glacial acetic acid, gave end points at acid volumes that represent neutral equivalents that are approximately double the formula weight. This was true whether an indicator was used to determine the end point or when a potentiometric titration was performed.

When the neutral equivalent of compound II was determined by a conductometric titration, using the same perchloric acid in acetic acid and when this compound was titrated potentiometrically with a solution of acetylum perchlorate, $\text{CH}_3\text{CO}^+\text{ClO}_4^-$, in acetic acid, the neutral equivalent was equal to the formula weight.

The failure of the true equivalence point to appear in a potentiometric titration may be analogous to the failure to detect the third equivalence point in the titration of H_3PO_4 vs. NaOH, the fact that the acidity of HPO_4^- is close to that of water and the acidity of $\text{Ar}-\text{S}-\text{CH}_2-\overset{+}{\text{N}}\text{H}_2-\text{Ph}$ may be close to acetic acid (Leveling Effect).

Placing a methoxyl or methyl group para or methyl groups in the 2, 4, and 6 positions to the amine in the *N*-arylaminoethyl aryl sulfides apparently increases the basicity of these compounds. These groups are known to be nucleophilic and this property seems to make up the deficit of electrons on the amine group. The NE/FW is no longer equal to two but is shifted toward a value of one, indicating that electrons are becoming more available at the site of the amine nitrogen atom.

(12) F. Bell, *Ber.*, **61**, 1918 (1928).

(13) F. A. Miller, *Organic Chemistry, An Advanced Treatise*, H. Gilman, Ed., John Wiley & Sons, Inc., New York, 1953, Vol. III, p. 140.

It was noted that when a chlorine atom is located ortho, meta, or para to the amine group in these compounds, the condensation product is neutral towards HClO_4 in glacial acetic acid. A para nitro group, another electrophilic group, as expected also produces a neutral compound. Chlorine, when attached to an aromatic nucleus is not only ortho-para directing but also deactivates the ring. It is felt that the *N*-(chlorophenyl)aminoethyl aryl sulfides are examples of the dominance of the inductive effect of the halogens over the mesomeric effect.

It is now felt that steric effects, the existence of which is supported by infrared evidence, play an important role in the case of the compound prepared from thioresitol and mesidine. Here the NE/FW was approximately 1.5 (in the case of the *p*- CH_3 and *p*- CH_3O compound the value was 1.2). The ortho methyl groups on the amine and thiol nucleus make it more difficult for the protonating agent to attack the nitrogen atom.

One may presume that when the sulfide linkage is on an alpha carbon of an alkyl group in an arylaminoalkyl aryl sulfide, the combined electron withdrawal of the sulfur atom and the aromatic nucleus so reduce the availability of the electrons on the nitrogen atom that the typical aromatic amine properties of moderate basicity and ready salt formation are partially destroyed. Note that these compounds do not form stable picrates.

Replacing the aromatic amine with diethylamine, piperidine, or morpholine removes one of the electron withdrawing groups, the aromatic ring. The electron withdrawal of the sulfur atom must be much less than the aromatic ring, for compounds of these latter types give neutral equivalents equal to the formula weights and usually form stable picrates.¹

Except for the sulfide obtained from *N*-methyl-*p*-nitroaniline, the presence of a methyl group on the nitrogen atom in addition to the phenyl group as in *N*-methyl-*N*-phenylaminoethyl phenyl sulfide increases the electron density on the nitrogen atom sufficiently to permit a NE/FW equal to unity, but not sufficient to form stable salts. However, further proof of the powerful electrophilic character of the nitro group is found when this group is placed para to the amine group in these *N*-methyl compounds. The resulting compound is neutral in the HClO_4/HAc titration.

The 1,3,5-triaryl-1,5-dithia-3-azapentanes were neutral when titrated with perchloric acid in glacial acetic acid. Thus the electron withdrawal of the two thiomethyl and an aryl group reduces the basicity of the nitrogen atom so that the resulting tertiary amine is neutral.

If the sulfur and nitrogen atoms are separated by two methylene groups, as in the arylaminoethyl aryl sulfides, neutral equivalents equal to the formula weight are obtained. The arylaminoethyl aryl sulfides also form stable picrates. This "insulating effect" is a well documented phenomenon.¹⁴

SYRACUSE 10, N. Y.

(14) E. R. Alexander, *Principles of Ionic Organic Reactions*, John Wiley and Sons, Inc., New York, 1950, p. 8.