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The Preparation of Aryl Thioethers by Reaction of Aromatic Halogen Compounds with Cuprous Thiophenolate or Cuprous Thiobutylate

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The reaction of cuprous thiophenolate with an aryl halide in a mixture of quinoline and pyridine appears to be a general method for obtaining high yields of aryl thioethers. Only two halogen compounds were encountered which gave unexpected products. Cuprous thiobutylate will not react with inactivated aryl chlorides but readily with aryl bromides to replace the halogen atom with a butylmercapto group.

Aryl thioethers have been synthesized by several methods each of which has limitations in its application. Sodium thiophenolate, usually in presence of copper as a catalyst, serves as a reagent to replace iodine in aryl iodides,¹ to replace chlorine or bromine in aryl chlorides or bromides when the halogen atoms are activated by other functional groups² and to replace chloro, nitro and sulfonic acid groups in anthraquinones³ or a nitro group in *o*-dinitrobenzenes by arylmercapto groups.⁴ An aromatic bromine atom, when not activated, may be substituted by a phenylmercapto group through the use of lead thiophenolate.⁵ The authors who studied this reaction reported yields of 90–95%. The procedure is not applicable to aryl chlorides nor to aryl bromides which contain certain functional groups.^{1a}

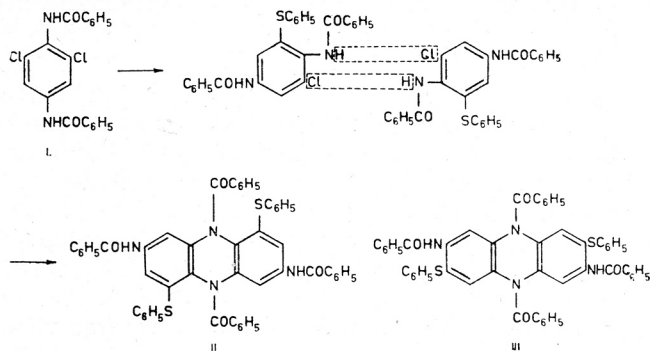
A general synthesis for aryl thioethers consists in treatment of an aryl-diazonium salt with a thiophenol in alkaline solution, usually with copper powder as a catalyst.⁶ This method provides a means of introduction of an aryl- or alkyl-mercapto residue at a position where a similarly placed halogen would be inert and could not be substituted by one of the reactions previously described. Aromatic compounds react with sulfur⁷ or with sulfur mono- or di-chloride⁸ or with aromatic sulfenylchlorides⁹ in presence of aluminum chloride to give thioethers. Still another method which has not been extensively studied is the condensation of phenylmagnesium bromide with an aryl-sulfenyl chloride.¹⁰

In the course of another investigation, the successful replacement of an inert aromatic halogen atom by a phenylmercapto group through the use of cuprous thiophenolate was reported.¹¹ The scope of this reaction has now been explored and the results are described in this communication.

Selected aryl chlorides and bromides have been studied and, with few exceptions, excellent yields of phenylmercapto compounds were obtained. The reaction merely requires heating cuprous thiophenolate with the aryl halide in presence of a mixture of quinoline and pyridine in a ratio that will provide

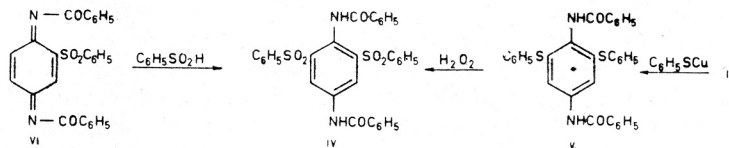
a reaction temperature of approximately 200—210°. The chlorine atoms in 1,4-dichloro-, 1,2,4,5-tetrachloro- and, indeed, in hexachlorobenzene are all easily replaced. Aryl halides with other functional groups present appear to offer no difficulty, as exemplified by the conversion of *p*-chloroaniline, *p*-chlorophenol, *m*-bromobenzoic acid, and *m*-nitrochlorobenzene to the corresponding phenylmercapto derivatives. A glance at the table will reveal the variety of compounds that have been studied. Bromides require less reaction time for replacement than the chlorides.

In the case of 2,6-dichloro-*p*-phenylenedibenzamide (I), two products resulted, one of which was the expected 2,6-diphenylmercapto-*p*-phenylenedibenzamide and the other a compound with three fused rings. Elemental analyses and the infrared spectrum suggested structure II. It was probably formed by replacement of one of the halogens in the dihalide by a phenylmercapto group, followed by condensation of two of the resulting molecules with elimination of hydrogen chloride. 2,5-Dichloro-*p*-phenylenedibenzamide gave a mixture of analogous products (III).



Many of the thioethers were oxidized with hydrogen peroxide in acetic acid to the corresponding sulfones which serve as a further characterization of the products. The dimeric products from 2,6- and 2,5-dichloro-*p*-phenylenedibenzamide were also readily oxidized to the corresponding sulfones.

The sulfone obtained by oxidation of 2-benzamidodiphenylsulfide was synthesized by another route; 2-nitrodiphenylsulfide, 2-nitrodiphenylsulfone, 2-aminodiphenylsulfone, 2-benzamidodiphenylsulfone. The disulfone (IV) from oxidation of the 2,6-diphenylmercapto-*p*-phenylenedibenzamide (V), in turn derived from the 2,6-dichloro compound was identified as the product made previously by addition of benzenesulfinic acid to 2-benzenesulfonyl-*p*-benzoquinonedibenzimide (VI).¹² This establishes in an unequivocal fashion the orientation of groups in the product of the diimide addition.



Among the aliphatic mercaptans only the cuprous thiobutylate was studied. Attempts were made to condense it with *p*-bromoanisole, *p*-dibromobenzene, *p*-dichlorobenzene, and 4-chlorobiphenyl. Good yields of the *p*-butylmercaptanisole and *p*-dibutylmercaptobenzene, respectively, resulted from the first two but the *p*-dichlorobenzene and 4-chlorobiphenyl did not react. It appears therefore that to form aryl alkyl sulfides from inactivated aryl halides by this general procedure, aryl bromides must be used.

The cuprous thiophenolate was usually prepared from freshly precipitated cuprous oxide and thiophenol by heating under reflux in ethanol solution. However, technical cuprous oxide was not much inferior. The cuprous thiobutylate required a much longer time for formation.

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EXPERIMENTAL

Cuprous Thiophenolate

A mixture of 28.6 g. of freshly prepared cuprous oxide,¹³ 44 g. of thiophenol and 500 ml. of ethanol was heated under reflux with mechanical stirring in presence of nitrogen for 3 hours, by which time the color had changed from red to light yellow. The substance was collected by filtration, washed several times with ethanol and dried *in vacuo*. The yield was 69 g.

Calcd. for C_6H_5SCu : C 41.73; H 2.92.

Found: C 41.85; H 3.05.

Cuprous Thiobutylate

The method used for preparing cuprous thiophenolate was employed; however, 10 hours were necessary to complete the reaction. The white substance was obtained in quantitative yield.

Calcd. for C_4H_9SCu : C 31.46; H 5.94.

Found: C 30.80; H 5.91.

Reaction of Aromatic Halogen Compounds with Cuprous Thiophenolate

General Procedure: A mixture of 0.1 mole of an aromatic monobromo or chloro compound (or halogen equivalent thereof of a polyhalogen compound), 18.5 g. cuprous thiophenolate, 60–90 ml. of quinoline and 6–9 ml. of pyridine was heated in a Woods-metal bath to about 200–210° (inside temp.) for one to five hours longer than was necessary to obtain a completely homogeneous solution. With aromatic bromo compounds a homogeneous solution was obtained in about 10–20 minutes, with aromatic chloro compounds in 1–20 hours. The hot solution was then poured into cracked ice and excess conc. hydrochloric acid, the flask washed a few times with pyridine and the washings added to the hydrochloric acid.

After standing for about 2 hours, the gum or tarry solid was collected by filtration or decantation and dried. Five extractions with ether usually served to separate the diaryl sulfides from the copper complexes. The extracts were washed twice with 1 *N* hydrochloric acid and once with water, then dried and the ether evaporated. The residue if solid was crystallized from methanol or ethanol (activated carbon); if liquid it was distilled *in vacuo*. If the diaryl sulfide is only slightly soluble in ether, e. g. hexaphenylmercaptobenzene, the product, after the treatment with hydrochloric acid, was extracted twice with ether to remove some of the colored material. Extraction was made next with chloroform. After washing with hydrochloric acid, then with water and drying, the chloroform was evaporated. The product was now washed with a very little cold acetone to eliminate most of the dark colored material and recrystallized from chloroform-ethanol, from carbon tetrachloride, or from acetic acid. 2-Phenyl-mercapto-6-methyl-*p*-phenylenedibenzamide, 2-phenylmercapto-*p*-phenylenedibenzamide, 2-phenylmercapto-*p*-phenylene-

dibzenesulfonamide and 4-phenylmercaptoacetamide are also quite insoluble in ether.

The yields designated in Table I were the maximum obtained. Since submission of this article, attempts by another experimenter to repeat some of these preparations resulted in lower yields than those reported. The difference is attributed to unidentified changes in reagents and/or experimental conditions.

The preparation of *p*-phenylmercaptoaniline required some modification of the general procedure so is described in detail below.

p-Phenylmercaptoaniline

A mixture of 6.38 g. of *p*-chloroaniline, 9.0 g. of cuprous thiophenolate, 40 ml. of quinoline and 4 ml. of pyridine was heated in a Woods-metal bath to 200—210° (inside temp.) for 30 hours. The hot solution was poured into ice and excess conc. hydrochloric acid. After standing for about 2 hours the solid residue was removed by filtration. The filtrate was made alkaline by adding aqueous sodium hydroxide. The oil that separated was dissolved in ether and the aqueous layer was extracted twice with ether. The ether was evaporated from the combined solutions and the residue was steam distilled until all quinoline and pyridine were removed. The residue was dissolved in dilute hydrochloric acid, the acid solution extracted once with ether, and the amine regenerated by adding aqueous sodium hydroxide. The amine was extracted with ether. After evaporation of the solvent, the residual oil solidified and was recrystallized from methanol-water; white crystals, m.p. 96—97°. The yield was 5.4 g. (53%).

TABLE I

Diaryl Thioethers

Halogen Compound	Reaction Product	Yield %	M. p. °C	Analysis		
				Calcd.	Found	
4-Chloroaniline	4-Phenylmercaptoaniline ^a	53	96—97	C H	71.60 5.51	71.24 5.67
2-Chloroanisole	2-Phenylmercaptoanisole ^b	68		C H	72.18 5.60	72.31 5.46
4-Chloroanisole	4-Phenylmercaptoanisole ^c	82		C	72.18	72.04
4-Bromoanisole		88		H	5.60	5.55
2-Chloroanthraquinone	2-Phenylmercaptoanthraquinone	96	159—161	C H	75.93 3.82	75.61 3.65
2-Chlorobenzanilide	2-Phenylmercaptobenzanilide	49	75—76	C H N	74.72 4.95 4.58	74.68 5.24 4.52
4-Chlorobenzoic Acid	4-Phenylmercaptobenzoic Acid ^d	91	176—177	C H	67.80 4.38	67.95 4.15
4-Chlorobiphenyl	4-Phenylmercapto-biphenyl	90	70	C H	82.40 5.38	82.80 5.52
2-Chloro-6-methyl- <i>p</i> -phenylenedibenzamide	2-Phenylmercapto-6-methyl- <i>p</i> -phenylene-dibenzamide	68	217—219	C H N	73.94 5.06 6.39	73.64 4.92 6.44
2-Chloronitrobenzene	2-Phenylmercapto-nitrobenzene ^e	49	77			

Halogen Compound	Reaction Product	Yield %	M. p. °C	Analysis		
				Calcd.	Found	
3-Chloronitrobenzene	3-Phenylmercapto-nitrobenzene ^f	78	41—42	C H	62.32 3.92	62.78 3.89
4-Chlorophenol	4-Phenylmercapto-phenol ^g	48	53—54			
2-Chloro- <i>p</i> -phenylene-dibenzamide	2-Phenylmercapto- <i>p</i> -phenylenedibenzamide ^h	86	197—197.5	C H	73.56 4.75	73.83 4.92
2-Chloro- <i>p</i> -phenylene-dibenzenesulfonamide	2-Phenylmercapto- <i>p</i> -phenylenedibenzene-sulfonamide ⁱ	48	167—168			
2,5-Dichlorobenzanilide	2,5-Diphenylmercapto-benzanilide	87	90—91	C H	72.61 4.63	72.47 5.00
<i>o</i> -Dichlorobenzene	<i>o</i> -Diphenylmercapto-benzene ^j	61		C H	73.43 4.79	73.56 4.64
<i>p</i> -Dichlorobenzene	<i>p</i> -Diphenylmercapto-benzene ^k	72 83	82—83	C H	73.43 4.79	73.68 4.80
4,4'-Dichlorobiphenyl	4,4'-Diphenylmercapto-biphenyl	99	117—118	C H	77.80 4.90	77.79 5.12
3,5-Dichlorotoluene	3,5-Diphenylmercapto-toluene ^l	88		C H	73.98 5.23	73.38 5.15
1,2,4,5-Tetrachloro-benzene	1,2,4,5-Tetraphenyl-mercaptobenzene	98	143—144	C H	70.55 4.34	70.36 4.32
Hexachlorobenzene	Hexaphenylmercapto-benzene	74	182—184	C	69.38	69.25
Hexabromobenzene		86		H	4.16	4.10
4-Bromoacetanilide	4-Phenylmercapto-acetanilide ^m	48	149—149.5	C H	69.10 5.38	69.13 5.76
<i>N</i> -Benzenesulfonyl-1-amino-2-methyl-4-bromonaphthalene	<i>N</i> -Benzenesulfonyl-1-amino-2-methyl-4-mercaptanaphthalene ^m	68	195.5—196.6	C H	68.12 4.72	68.39 4.80
3-Bromobenzoic Acid	3-Phenylmercapto-benzoic Acid	81	108—109	C H	67.80 4.38	67.61 4.51
2-Bromonaphthalene	2-Phenylmercapto-naphthalene ⁿ	96	54—55	C H	81.31 5.12	81.32 5.17
2-Bromotoluene	2-Phenylmercapto-toluene ^o	93		C H	77.95 6.04	77.78 6.17
3-Bromotoluene	3-Phenylmercapto-toluene ^p	93		C H	77.95 6.04	77.28 6.46
Tribromomesitylene	Triphenylmercapto-mesitylene	89	150—151	C H	72.93 5.44	73.17 5.53

^a Lit. m. p. 99^o, ref. 2b. ^b B. p. 118—120^o (1 mm.), lit. b. p. 150—152^o (3 mm.), ref. 6d. ^c B. p. 138—140^o (2 mm.), lit. b. p. 150—152^o (3 mm.) ref. 6d. ^d Lit. m. p. 177^o, W. S. Weedon and H. W. Doughty, *Am. Chem. J.*, **33** (1905) 424. ^e Lit. m. p. 77^o, F. Mauthner, *Ber.*, **39** (1906) 3597. ^f Lit. m. p. 42.5^o, D. L. Hammick and R. B. Williams, *J. Chem. Soc.*, **1938**, 211. ^g Lit. m. p. 50—51^o, ref. 6d. ^h Lit. m. p. 197—197.5^o, R. Adams and D. S. Acker, *J. Am. Chem. Soc.* **74** (1952) 5872. ⁱ Lit. m. p. 167—168.5^o, R. Adams, E. F. Elslager and T. E. Young, *J. Am. Chem. Soc.*, **75** (1953) 663. ^j B. p. 187^o (1 mm.). ^k Lit. m. p. 80^o, O. Hinsberg, *Ber.*, **79B** (1936) 492. ^l B. p. 145^o (0.5 mm.). ^m Compounds prepared by H. H. Gibbs, *Ph. D. Thesis*, University of Illinois (1956). ⁿ Lit. m. p. 51.8^o, ref. 5b. ^o B. p. 164^o (12 mm.), lit. b. p. 160.5 (11 mm.), E. Bourgeois, *Ber.* **28** (1895) 2322. ^p B. p. 167^o (12 mm.), lit. b. p. 164.5^o (11 mm.), E. Bourgeois, *Ber.* **28** (1895) 2323.

Reaction of 2,6-Dichloro-p-phenylenedibenzamide with Cuprous Thiophenolate; 2,7-Dibenzamido-5,10-dibenzoyl-4,9-diphenylmercaptophenazine and 2,6-Diphenylmercapto-p-phenylenedibenzamide

A mixture of 4.0 g. of 2,6-dichloro-*p*-phenylenedibenzamide,¹⁴ 3.8 g. of cuprous thiophenolate, 20 ml. of quinoline and 2 ml. of pyridine was heated in a Woods-metal bath to 200—210^o (inside temp.) for 4 hours. The hot solution was poured into cracked ice and excess conc. hydrochloric acid. After standing for 2 hours, the solid was collected by filtration, dried and repeatedly extracted with ether. The ether extract was washed twice with dilute hydrochloric acid and once with water and dried. Upon evaporation of the solvent 1.5 g. (34%) of white crystalline 2,7-dibenzamido-5,10-dibenzoyl-4,9-diphenylmercaptophenazine resulted, which was recrystallized from ethanol, m. p. 184—185^o.

Calcd. for C₅₂H₃₆N₄O₄S₂: C 73.91; H 4.30; N 6.63.
Found: C 73.77; H 4.46; N 6.45.

After the ether extraction, the remaining solid was extracted with chloroform. The chloroform solution was washed with dilute hydrochloric acid and water, dried and the chloroform was evaporated. The residue of 2,6-diphenylmercapto-*p*-phenylenedibenzamide crystallized and was recrystallized from ethanol, m. p. 223—224^o. The yield was 1.9 g. (34%).

Calcd. for C₃₂H₂₄N₂O₂S₂: C 72.15; H 4.54.
Found: C 72.02; H 4.52.

2,5-Dichloro-p-phenylenedibenzamide

A mixture of 1.77 g. of 2,5-dichloro-*p*-phenylenediamine,¹⁵ 4.8 g. of benzoyl chloride and 50 ml. of reagent pyridine was refluxed for 90 min., cooled and poured into cracked ice and conc. hydrochloric acid. The precipitate was collected by filtration, washed and dried to give 3.7 g. (96%) of product. Recrystallization from dimethylformamide gave colorless plates, m. p. 303—304^o.

Calcd. for C₂₀H₁₄Cl₂N₂O₂: C 62.34; H 3.66; N 7.27.
Found: C 62.24; H 3.61; N 7.39.

Reaction of 2,5-Dichloro-p-phenylenedibenzamide with Cuprous Thiophenolate; 2,7-Dibenzamido-5,10-dibenzoyl-3,8-diphenylmercaptophenazine and 2,5-Diphenylmercapto-p-phenylenedibenzamide

A mixture of 0.7 g. of 2,5-dichloro-*p*-phenylenedibenzamide, 0.7 g. of cuprous thiophenolate, 8 ml. of quinoline and 1 ml. of pyridine was treated as described for the reaction of 2,6-dichloro-*p*-phenylenedibenzamide with cuprous thiophenolate.

From the ether extract 0.2 g. (26%) of 2,7-dibenzamido-5,10-dibenzoyl-3,8-diphenylmercaptophenazine was obtained. The compound was recrystallized from ethanol, m. p. 176—177^o.

Calcd. for C₅₂H₃₆N₄O₄S₂: C 73.91; H 4.30; N 6.63.
Found: C 73.71; H 4.29; N 6.45.

The chloroform extract contained 0.25 g. (35%) of 2,5-diphenylmercapto-*p*-phenylenedibenzamide. The substance was recrystallized from ethanol, m. p. 200—201°.

Calcd. for $C_{32}H_{24}N_2O_2S_2$: C 72.15; H 4.54.

Found: C 72.35; H 4.74.

Oxidation of Phenylmercapto Compounds to Sulfones

General Procedure: To a solution of 0.01 mole of phenylmercapto compound in 25 ml. of acetic acid, a twofold excess of 30% hydrogen peroxide was added and the mixture was heated under reflux for 2 hours. The solvent was then evaporated *in vacuo* and the residue was recrystallized from ethanol or acetic acid.

TABLE II
Diaryl Sulfones

Sulfone	Yield %	M. p. °C	Analysis		
			Calcd.	Found	
2-Benzenesulfonylanisole	92	141—142	C	62.88	62.84
			H	4.88	4.83
4-Benzenesulfonylanisole ^a	89	91—92	C	62.88	62.73
			H	4.88	5.03
2-Benzenesulfonylanthraquinone	96	220—221	C	68.95	68.96
			H	3.47	3.60
2-Benzenesulfonylbenzanilide	76	113—114	C	67.64	67.47
			H	4.48	4.49
			N	4.15	3.98
4-Benzenesulfonylbenzoic Acid ^b	97	277—278	C	59.53	59.57
			H	3.85	4.09
4-Benzenesulfonylbiphenyl ^c	95	149—150	C	73.44	73.60
			H	4.80	4.98
2-Benzenesulfonyl-6-methyl- <i>p</i> -phenylenedibenzamide	92	223—224	C	68.92	69.22
			H	4.71	4.92
2-Benzenesulfonylnitrobenzene ^d	88	147			
3-Benzenesulfonylnitrobenzene ^e	94	84—85	C	54.76	54.72
			H	3.45	3.24
2-Benzenesulfonyl- <i>p</i> -phenylenedibenzamide ^f	97	193-193.5			
2-Benzenesulfonyl- <i>p</i> -phenylenedibenzene-sulfonamide ^g	80	154.5-156			
2,5-Dibenzenesulfonylbenzanilide	95	210—211	C	62.88	62.85
			H	4.01	4.16
			N	2.93	2.83
<i>o</i> -Dibenzenesulfonylbenzene	95	165—166	C	60.32	60.31
			H	3.94	4.00
<i>p</i> -Dibenzenesulfonylbenzene ^h	95	237—238	C	60.32	60.49
			H	3.94	3.91
4,4'-Dibenzenesulfonylbiphenyl ⁱ	95	301—304	C	73.44	73.60
			H	4.80	4.98
3,5-Dibenzenesulfonyltoluene	85	256—257	C	61.27	61.14
			H	4.33	4.27
1,2,4,5-Tetrabenzenesulfonylbenzene ^j	94	308—310	C	56.41	56.21
			H	3.47	3.54

Sulfone	Yield %	M. p. °C	Analysis		
			Calcd.	Found	
Hexabenzenesulfonylbenzene	74	277—279	C	54.89	54.06
			H	3.30	3.90
3-Benzenesulfonylbenzoic Acid	95	188—189	C	59.53	59.38
			H	3.85	4.20
2-Benzenesulfonylnaphthalene ^k	98	119—120	C	71.62	71.70
			H	4.51	4.80
2-Benzenesulfonyltoluene ^l	96	81—82	C	67.21	67.25
			H	5.21	5.14
3-Benzenesulfonyltoluene ^m	98	121—122	C	67.21	67.15
			H	5.21	5.15
Tribenzenesulfonylmesitylene	91	181—183	C	59.98	60.11
			H	4.47	4.51
2,5-Dibenzenesulfonyl- <i>p</i> -phenylenedibenzamide	90	269—271	C	64.41	64.53
			H	4.05	4.24
2,6-Dibenzenesulfonyl- <i>p</i> -phenylenedibenzamide ⁿ	89	263—264	C	64.41	64.11
			H	4.05	3.93
2,7-Dibenzamido-5,10-dibenzoyl-3,8-dibenzenesulfonylphenazine	84	266—268	C	68.71	68.50
			H	3.99	3.93
			N	6.17	6.04
2,7-Dibenzamido-5,10-dibenzoyl-4,9-dibenzenesulfonylphenazine	91	276	C	68.71	68.63
			H	3.99	3.88
			N	6.17	6.07

^a Lit. m. p. 90—91^o, ref. 6d. ^b Lit. m. p. 277^o, W. S. Weedon and H. W. Doughty, *Am. Chem. J.* **33** (1905) 425. ^c Lit. m. p. 148^o, J. Huismann, *D. R. P.* **701**, 954 (1941); *C. A.* **36** (1942) 98. ^d Lit. m. p. 147^o, E. Roberts and E. E. Turner, *J. Chem. Soc.* **1926**, 1208. ^e Lit. m. p. 85^o, ref. in footnote c. ^f Lit. m. p. 193—193.5^o, R. Adams and M. D. Nair, *J. Am. Chem. Soc.*, **78** (1956) 5927. ^g Lit. m. p. 154.5—156^o, R. Adams, T. E. Young and R. W. P. Short, *J. Am. Chem. Soc.*, **76** (1954) 1114. ^h Lit. m. p. 229^o, O. Hinsberg, *Ber.*, **69B** (1936) 492. ⁱ Lit. m. p. 299^o, ref. in footnote c. ^j Lit. m. p. 305^o, A. Livingston and J. D. Loudon, *J. Chem. Soc.* **1937**, 246. ^k Lit. m. p. 115—116^o, ref. 5b. ^l Lit. m. p. 81^o, ref. 5b. ^m Lit. m. p. 109^o, C. Courtot and P. Frenkiel, *Compt. rend.* **199** (1934) 557. ⁿ Lit. m. p. 263—264^o, ref. 12.

2-Benzamidodiphenylsulfone

A mixture of 2.0 g. of 2-aminodiphenylsulfone,¹⁶ 1.13 ml. of benzoyl chloride and 30 ml. of reagent pyridine was heated under reflux for 1.5 hours. The solution was poured into cracked ice and hydrochloric acid. The precipitated material was filtered, washed with water and recrystallized from dilute ethanol to give 2.0 g. (88%) of white crystals, m. p. 114^o.

Calcd. for C₁₉H₁₅NO₂S: C 67.64; H 4.48; N 4.15.

Found: C 67.47; H 4.49; N 3.98.

Reaction of Aromatic Bromine Compounds with Cuprous Thiobutylate

The procedure described for the reaction of aromatic halogen compounds with cuprous thiophenolate was used. The reaction products were distilled *in vacuo*.

TABLE III
Aryl Butyl Thioethers

Bromine Compound	Reaction Product	Yield %	B. p. °C	Analysis	
				Calcd.	Found
4-Bromoanisole	4-Butylmercaptoanisole	92	94 (0.5 mm.)	C 67.30 H 8.22	67.35 8.22
p-Dibromo- benzene	p-Dibutylmercapto- benzene	68	142 (0.3 mm.)	C 66.08 H 8.72	66.06 8.94

REFERENCES

1. a) F. Mauthner, *Ber.* **39** (1906) 1347; b) M. T. Bogert and M. R. Mandelbaum, *J. Am. Chem. Soc.* **45** (1923) 3045; c) F. Mayer, *Ber.* **42** (1909) 3046.
2. J. Goldberg, *Ber.* **43** (1910) 584; b) E. Bourgeois and Huber, *Rec. trav. chim.* [3] **1** (1912) 33; c) E. Bourgeois and J. Henrion, *Bull. soc. chim. France*, [4] **51** (1932) 1416.
3. a) *D. R. P.* 251,709 (1911), *Frdl.* **11**, 601; b) *D. R. P.* 116,951 (1899), *Frdl.* **6**, 425; c) H. Decker and A. Würsch, *Ann.* **348** (1906) 239.
4. J. D. London, *J. Chem. Soc.* **1939**, 902.
5. a) F. Kraft, *Ber.* **23** (1890) 2364; b) F. Kraft and E. Bourgeois, *Ber.* **23** (1890) 3045; c) E. Bourgeois, *Ber.* **24** (1891) 2264; E. Bourgeois and A. Fouassin, *Bull. soc. chim. France*, [4] **9** (1911) 938.
6. a) *D. R. P.* 194,040 (1904), *Frdl.* **8**, 1370; b) *D. R. P.* 460,087 (1926), *Frdl.* **16**, 1250; c) *D. R. P.* 475,688 (1927), *Frdl.* **16**, 1360; d) G. E. Hilbert and T. B. Johnson, *J. Am. Chem. Soc.* **51** (1929) 1526.
7. a) M. J. Böeseken, *Rec. trav. chim.* **24** (1905) 17; b) G. Dougherty and P. D. Hammond, *J. Am. Chem. Soc.* **57** (1935) 117.
8. a) M. J. Böeseken, *Rec. trav. chim.* **24** (1905) 209; b) M. J. Böeseken and D. A. W. Koning, *Rec. trav. chim.* **30** (1911) 116.
9. a) K. Kries and G. Schürmann, *Ber.* **52** (1919) 2170; b) C. M. Bues and N. Kharasch, *J. Am. Chem. Soc.* **72** (1952) 3529.
10. H. Lecher, *Ber.* **58** (1925) 409.
11. R. Adams and H. H. Gibbs, *J. Am. Chem. Soc.* **79** (1957) 170.
12. R. Adams and M. D. Nair, *J. Am. Chem. Soc.* **78** (1956) 5932.
13. A. King, *Inorganic Preparations*, D. Van Nostrand Co, New York, 1930 p. 39.
14. R. Adams and D. S. Acker, *J. Am. Chem. Soc.* **74** (1952) 3029.
15. R. Adams, E. F. Elslager and K. F. Heumann, *J. Am. Chem. Soc.* **74** (1952) 2608.
16. F. Ullmann and G. Pasdermadjian, *Ber.* **34** (1901) 1153.

IZVOD

Priprema aril tioetera reakcijom aromatskih halogenida s kupro-fenolatom i kupro-tiobutilatom

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Čini se, da je reakcija kupro-tiofenolata s aril halogenidima u smjesi kinolina i piridina opća metoda, kojom se mogu prirediti aril tioeteri s visokim iskorištenjima. Samo dva halogenida upotrebljena u ovim radovima dali su neočekivane rezultate. Kupro-tiobutilat ne reagira s neaktiviranim aril kloridima, ali lagano reagira s aril bromidima, pri čemu se halogen zamjenjuje s butilmerkaptu grupom.

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