ml. of 50% aqueous potassium hydroxide solution was added. The yellow ether layer was slowly decanted into a solution of 5.6 g. (0.007 mole) of the tricyclotetradecane dicarboxylic acid **7** in 50 ml. of methanol. After 15 min., the cooling bath was removed and 1.7 ml. of glacial acetic acid was added to the yellow solution. After another 15 min., the solution was concentrated under reduced pressure to a thick orange-yellow oil, 5.5 g. This was taken up in carbon tetrachloride, and a semicrystalline solid separated when the solution was diluted with Skellysolve B. This solid was then recrystallized once from 200 ml. of chloroform and 800 ml. of Skellysolve B, and once from 70 ml. of chloroform and 100 ml. of ether. When the filtrate from the second recrystallization was diluted with Skellysolve B, a small amount (0.5 g.) of a white crystalline solid was obtained, m.p. 136.7–138.6° dec.; λ_{max}^{MeOH} 283 mμ (ϵ 8650); ν_{max}^{KBr} 3400 (NH), 2900–3100 (CH), 1745 (C=O), 1665 (C=O), 1525 (NH) 1255 (Ph-O), and 1115 cm.$^{-1}$ (CH_3O). No color change with 5% aqueous ferric chloride reagent was produced and iodine–sodium azide reagent was not decolored. N.m.r. data shows δ 1.5 (CH_3) 12H; 3.8 (OCH_3) 18H, (N-CH) 6H; 6.6 (NH) 2H, (=CH-) 4H; 7.3 (=CH-) 3H (theory requires 2H). No inflection of the titration curve was observed when this solid was titrated with perchloric acid in glacial acetic acid.

Anal. Calcd. for $C_{36}H_{44}N_4O_{12}S_2$: C, 54.82; H, 5.62; N, 7.10; mol. wt., 788.9. Found: C, 55.30; H, 5.78; N, 7.28; mol. wt. (in 95% ethanol), 798.

Synthesis of Thioethers. Amide Solvent-Promoted Nucleophilic Displacement of Halide by Thiolate Ion

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Received December 26, 1963

A new general procedure for synthesizing aryl thioethers *via* nucleophilic displacement of aryl halide by thiolate ion is reported. The reaction is shown to be dependent upon amide solvents exclusively with more than simple catalysis involved. Many different thioethers, both old and new, have been prepared in very good yield by this method.

Methods for the preparation of aryl thioethers have generally suffered from limited applicability in that activated reactants, severe reaction conditions, complicated procedures, or a combination of these requirements were involved.[1-5] Parker[6] has stated that unsymmetrical aryl sulfides can be prepared in high yields providing the halogen substrate is activated by at least one powerful electron-withdrawing substituent.

A recent method[7] developed in these laboratories involving reaction of disulfides with copper in the presence of halides has provided a means of synthesizing many different thioethers in a convenient way. An even more convenient and general sulfide preparation is described in the present paper. The method involves simply heating an alkali metal thiolate (either aliphatic or aromatic) and a halide together in an amide solvent. Results are summarized in Tables I and II.

$$\underset{(R)}{\mathrm{ArSK}} + \mathrm{Ar'X} \xrightarrow[\text{solvent}]{\text{amide}} \underset{(R)}{\mathrm{ArSAr'}} + \mathrm{KX}$$

An indication of the generality of the method is evident from the variety of sulfides reported. Not only is the method valuable for the preparation of polyaryl sulfides, but it also provides a convenient way to alkyl aryl sulfides from alkane thiols and aryl halides.

Examination of the data in Table I covering experiments on the preparation of bis(phenylmercapto)benzenes in certain solvents illustrates this method's amide solvent dependency. First attempts at aryl thioether synthesis involved Ullmann-like conditions found in aryl ether preparations where aryl halide and potassium aryl thiolate were heated in excess thiol at temperatures above 200° in the presence of copper salts. No reaction occurred, presumably because of the extreme insolubility of the potassium thiolate even under drastic conditions. Various high boiling solvents then were employed to attempt solution of the salt, but without avail until dimethylformamide was employed. The effectiveness of this solvent in solubilizing all reactants and in promoting formation of aryl thioethers from aryl thiolates and activated aryl halides has been described previously,[5,8] but was thought to be limited to activated halides. As shown in Table I, dimethylformamide serves in unactivated cases also, giving poorer yields of product.

Higher amide solvents, *i.e.*, N,N-dimethylacetamide, N,N-dimethylbutyramide, N,N-dibutylacetamide, and N-methyl-2-pyrrolidone, proved even more effective presumably because of their higher boiling points, thus higher reaction temperatures. For reasons of availability and ease of removal, dimethylacetamide was considered to be the solvent of choice and then was used most frequently. The utility of these amides apparently stems from two properties: (1) their ability to solubilize potassium aryl thiolates, and (2) their evident participation in the reaction. The first property has already been mentioned, but the second requires elaboration.

Prior to discussion of solvent participation it should be pointed out that the reaction appears to be a bimolecular nucleophilic substitution. Examination of data in Table I shows that it differs from an Ullmann-type reaction since no copper catalyst is really necessary. Preliminary kinetic and spectral data indicate the reaction is second order and that no other mechanisms are operating. Detailed kinetics and a suggested

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[1] E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. II, Chemical Publishing Co., Inc., New York, N. Y., 1960, p. 28.

[2] E. Müller, *et al.*, "Methoden der Organischen Chemie" (Houben-Weyl), Vol. IX, Georg Thieme Verlag, Stuttgart, 1955, pp. 97-118.

[3] J. F. Bunnett and W. D. Merritt, Jr., *J. Am. Chem. Soc.*, **79**, 5967 (1957).

[4] R. Adams, W. Reifschneider, and M. D. Nair, *Croat. Chem. Acta*, **29**, 277 (1957); R. Adams and A. Ferretti, *J. Am. Chem. Soc.*, **81**, 4927 (1959).

[5] J. H. Uhlenbrock, *Rec. trav. chim.*, **80**, 1057 (1961).

[6] N. Kharasch, "Organic Sulfur Compounds," Vol. I, Pergamon Press, Inc., New York, N. Y., 1961, p. 107.

[7] J. R. Campbell, *J. Org. Chem.*, **27**, 2207 (1962).

[8] J. R. Campbell and R. E. Hatton, *ibid.*, **26**, 2480 (1961).

TABLE I

m- or *p*-Bis(PHENYLMERCAPTO)BENZENES

$$m\text{- or } p\text{-}XC_6H_4Y + C_6H_5SK \longrightarrow \underset{A}{m\text{- or } p\text{-}C_6H_5SC_6H_4SC_6H_5} + \underset{B}{m\text{- or } p\text{-}XC_6H_4SC_6H_5}$$

Isomer	Halide X	Halide Y	Halide mole	Thiol, mole	Solvent	Catalyst, ml.	Time, hr.	Yield A, %	Yield B, g.	Starting halide recovered, %
p	Cl	C_6H_5S	0.16	0.2	DMF[a]	None	24	25.7		40.3
m	Br	Br	0.11	0.21	DEA[b]	$CuCl_2$	10	57[c]	11.2	
m	Cl	C_6H_5S	0.32	0.6	DEA	$CuCl_2$	20	15		66.5
m	Cl	Cl	0.20	0.5	DEA	None	15	Trace		
m	Cl	Cl	0.50	1.1	DMA[d]	CuCl–KI	24	40.7	57.9	
m	Br	Br	0.11	0.3	DMA	$CuCl_2$	24	97	2.8	0
m	Br	Br	0.11	0.3	DMA	$CuCl_2$	13	98	0	0
m	Br	Br	0.65	1.8	DMA	$CuCl_2$	13	95	13.2	0
m	Cl	Cl	0.65	1.8	DMA	$CuCl_2$	14	79.3	31.4	
m	Br	Br	0.11	0.3	DMA	None	20	Quant.	0	0
m	Cl	Cl	0.2	0.5	DMA	None	15	92.7	18.8	
p	Cl	Cl	0.2	0.5	DMB[e]	None	15	81	0	0
p	Cl	Cl	0.2	0.5	NMP[f]	None	15	94.5	0	0
m	Cl	Cl	0.2	0.5	EG[g]	None	15	0	0	74.8
m	Cl	Cl	0.2	0.5	EG	$CuCl_2$	15	0	0	86.1
m	Cl	Cl	0.2	0.5	EG	DMA (25)	15	0	*h*	77.6
m	Cl	Cl	0.2	0.5	EG	DMA (50)	15	0	*h*	85.8
m	Cl	Cl	0.2	0.5	DG[i]	None	15	0	2.3	88.5
m	Cl	Cl	0.2	0.5	DG	DMA (50)	15	11.2	32	
m	Cl	Cl	0.2	0.5	DG	NMP (15)	15	0	12	72.2
m	Cl	Cl	0.2	0.5	DG	NMP (50)	15	14.8	31.5	34.7

[a] Dimethylformamide, reaction temp. *ca.* 160°. [b] Diethylaniline, reaction temp. 210–216°. [c] Product contained many amine impurities. [d] N,N-Dimethylacetamide, reaction temp. 170–175°. [e] N,N-Dimethylbutyramide, reaction temp. *ca.* 180°. [f] N-Methyl-2-pyrrolidone, reaction temp. 185–190°. [g] Ethylene glycol, reaction temp. 180–190°. [h] Only product was $C_6H_5SCH_2CH_2OH$, b.p. 85–88° (0.25 mm.), n^{22}_D 1.5915; W. R. Kirner and G. H. Richter [*J. Am. Chem. Soc.*, **51**, 3409 (1929)] report b.p. 115–116° (2 mm.), n^{20}_D 1.5917. [i] Diglyme, reaction temp. 155–160°.

reaction mechanism consistent with results will be the subject of the second paper of this series.

The last eight examples of Table I illustrate very well the peculiar ability of amide solvents in this thioether synthesis. Solvents employed in these examples were ethylene glycol and diglyme both of which differed from most solvents in that they dissolved potassium benzenethiolate when employed in optimum quantities. It is noteworthy that no reaction occurred in the neat solvents with or without cupric chloride! When dimethylacetamide was added to the reaction in ethylene glycol (25–50 ml. to 200 ml.), a most unusual product, 2-phenylmercaptoethanol, was the only material isolated. Evidently displacement of one of ethylene glycol's hydroxy groups by the thiophenoxide ion is promoted by dimethylacetamide. This may constitute the first example of hydroxyl displacement by thiol, especially among aliphatic alcohols.

More important is the effect that added amide solvents had on the nucleophilic substitution in diglyme. Some intermediate monosubstituted product, B, was produced at low concentrations of amide (15 ml. to 200 ml. diglyme), but as the quantity of added amide was increased, the yield of B almost trebled and 11–15% yield of bissulfide, A, was realized. Although the exact function of amide solvent is not known, it is definitely not one of catalysis here. Zaugg and co-workers[9] have found that less than 5% concentrations of amides exert profound catalytic effects in alkylations of certain enolate anions.

The unique solvent characteristics of dimethylformamide have been known for many years, but only recently has it achieved distinction as a solvent for aromatic nucleophilic substitution reactions. Friedman and Schechter[10] found it was very efficient in the preparation of aryl nitriles from aryl halides and cuprous cyanide. Similar results have also been reported by Newman and Boden[11] for N-methyl-2-pyrrolidone. An investigation by Bacon and Hill[12] on copper-catalyzed aromatic displacements in polar solvents placed dimethylformamide better than dimethylsulfoxide but not so good as pyridines. Finally, Uhlenbrock[5] has shown dimethylformamide to be the preferred solvent in the preparation of halo aryl sulfides from aryl thiolates and aryl halides. This latter procedure is similar to that reported here and deserves some comment: (1) the scope is generally limited to sulfides which could be formed from activated halides, (2) a very large excess of thiolate was employed, and (3) yields were usually only fair.

Dimethylacetamide did not prove so beneficial in typical Ullmann reactions as it did in our thioether synthesis. For instance, a very poor yield of a five-membered ring polyphenyl ether was obtained from potassium *m*-phenoxyphenate and *m*-dihalo benzenes in dimethylacetamide according to usual Ullmann procedures. Without solvent except for excess phenol this preparation proceeded in good yield. Such results again point out the unique function of amide solvents in thioether formation. This can probably be ascribed in part to specific solvation of the cation by solvent in accord with the work and suggestions of others.[9,13,14] Part of the success could also be due to the efficacy of the benzenethiolate ion which is cer-

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(9) H. E. Zaugg, B. W. Horrom, and S. Borgwardt, *J. Am. Chem. Soc.*, **82**, 2895 (1960); H. E. Zaugg, *et al.*, *J. Org. Chem.*, **26**, 644 (1961).

(10) L. Friedman and H. Shechter, *ibid.*, **26**, 2522 (1961).

(11) M. S. Newman and H. Boden, *ibid.*, **26**, 2525 (1961).

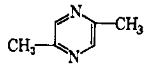
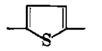
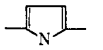
(12) R. G. R. Bacon and H. A. O. Hill, *Proc. Chem. Soc.*, 113 (1962).

(13) H. E. Zaugg, *J. Am. Chem. Soc.*, **83**, 837 (1961).

(14) T. J. Wallace and A. Schriesheim, *J. Org. Chem.* **27**, 1514 (1962).

TABLE II

YIELDS, PHYSICAL PROPERTIES, AND ANALYSES OF THIOETHERS

R	X	Ar	Yield, %	M.p. and b.p. (mm.), °C.	Formula	Sulfur, % Calcd.	Sulfur, % Found
Monosulfides							
$RBr(Cl) + C_6H_5SH \longrightarrow R—S—C_6H_5$							
3,4-$(CH_3)_2C_6H_3$			30.4	117–120 (0.45)[a]			
C_6H_5			64.8	173–183 (30)[b]			
2-C_5H_4N			97.8	107–110 (0.3)[c]			
2-CH_3-5-$(CH_3)_2CH—C_6H_3$			78.2	115–120 (0.3)[c]	$C_{16}H_{18}S$	13.23	13.60
			89.0	190–192 (26)	$C_{12}H_{12}N_2S$	14.82	14.70
Bissulfides							
$RC_6H_4SH + ArX_2 \longrightarrow Ar(SC_6H_4R)_2$							
p-$(CH_3)C$	m-Cl	C_6H_4	67.1	210–237 (0.55)[d]	$C_{26}H_{30}S_2$	15.77	15.60
H	o-Cl[e]	C_6H_4	92.0	180–187 (0.25)	$C_{18}H_{14}S_2$	21.79	22.00
H	m-Cl	C_6H_4	92.7	180–185 (0.35)[f]			
H	p-Cl	C_6H_4	94.5	82–83 [f,g]			
H	p-Br	$—C_6H_4OC_6H_4—$	81.6	82–84 [h]	$C_{24}H_{18}OS_2$	16.59	16.90
H	p-Br	$—C_6H_4C_6H_4—$	98.7	119–120 [h]	$C_{24}H_{18}S_2$	17.37	17.21
H	Br		74.3	189–195 (0.5)	$C_{16}H_{12}S_3$	32.02	31.79
H	Cl		89.0	51–52[h]	$C_{17}H_{13}NS_2$	21.71	21.27
Trissulfide							
$3C_6H_5SH + 1,2,4\text{-}C_6H_3Cl_3 \longrightarrow 1,2,4\text{-}C_6H_3(SC_6H_5)_3$							
			94	243–248 (0.2)	$C_{24}H_{18}S_3$	23.89	23.64

[a] E. Bourgeois [*Ber.*, **28**, 2312 (1895)] reports b.p. 182° (11 mm.). [b] D. R. Stull [*Ind. Eng. Chem.*, **39**, 517 (1947)] gives b.p. 162° (20 mm.) and 195° (40 mm.). [c] L. G. S. Brooker, *et al.* [*J. Am. Chem. Soc.*, **73**, 5326 (1951)], report b.p. 160–162° (8 mm.), 95% yield. [d] Solidified on standing. [e] Orthene. [f] Reported previously in ref. 7. [g] Reported previously in ref. 4. [h] From isopropyl alcohol.

tainly one of the most effective nucleophiles known,[6] especially in dimethylformamide.[15]

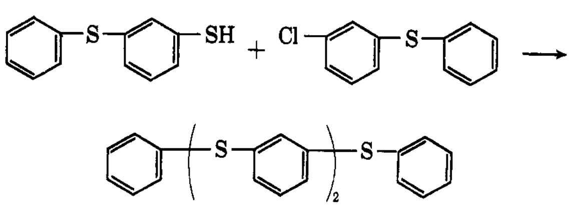
As expected, aryl bromides were more reactive than the chlorides. Thus, a 57% yield of bissulfide was obtained from dibromobenzene in diethylaniline whereas dichlorobenzene under identical circumstances gave none. Diethylaniline did not prove satisfactory as a reaction medium however; products were always contaminated with amine which could not be removed.

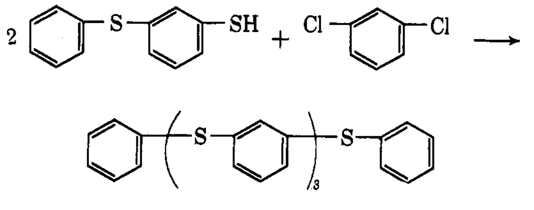
Reaction time in hours includes both the period of reflux and the time to distil excess solvent. Preliminary rate data suggest that this can be reduced significantly to a matter of a few hours.

Both expected and wholly unexpected by-products formed in many of the reactions between potassium thiolates and aryl halides. The intermediate monosubstituted material, halo phenyl aryl or alkyl sulfide (*cf.* Table I and Experimental), was often produced when a dihalo benzene was involved in the synthesis of bissulfides. Of course the largest quantities formed in cases where reaction conditions were below optimal or reactants were sluggish. Aryl disulfides were sometimes isolated, usually in small quantities only, *via* oxidation of starting thiols. Completely unexpected was the formation of diphenyl sulfide as the only product from the attempted reaction of potassium benzenethiolate and 2,5-dimethoxychlorobenzene. No reasonable interpretation of this result has been forthcoming.

The generality of this thioether synthesis is exemplified in the variety of compounds reported: various aryl mono-, bis-, tris-, and polysulfides; mono- and bisphenylmercapto heterocyclics; alkyl aryl sulfides; and phenylmercaptobiphenyl mixtures. It would appear that the only retarding influences to facile reaction and good yields might be (1) a weak thiolate nucleophile made impotent through electron-withdrawing groups, or (2) an unreactive halide containing strong electron donors which cause nucleophile repulsion.

The preparation of the four- and five-membered ring polyphenyl thioethers, bis(m-phenylmercaptophenyl) sulfide and m-bis(m-phenylmercaptophenylmercapto)-benzene, respectively, involved application of the amide procedure as the last step in both. The four-membered ring compound was obtained from potassium m-phenylmercaptobenzenethiolate and m-chlorophenyl phenyl sulfide in dimethylacetamide and the five-membered ring thioether from m-dichlorobenzene and potassium m-phenylmercaptobenzenethiolate in the same solvent.





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[15] A. J. Parker, *J. Chem. Soc.*, 4398 (1961).

Previous attempts to prepare these two polysulfides by other methods failed. Thus, no reaction occurred between *m*-chlorophenyl phenyl sulfide and sodium sulfide in trying to synthesize the four-membered ring compound, and only unidentifiable material resulted from an Ullmann reaction with *m*-dithioresorcinol and *m*-chlorophenyl phenyl sulfide for the five-membered ring compound.

Experimental[16]

General Procedure for Synthesis of Sulfides in Tables I and II.—Water of reaction and that from the starting alkali was distilled from a mixture of 0.5 mole of thiol, 0.5 mole of potassium hydroxide, and 200 ml. of dimethylacetamide until the vapor temperature reached 150°. Complete solution occurred from this point until the terminal part of the preparation when salts precipitated.

Very few solvents will dissolve an alkali metal thiolate and only the amides appear to be generally applicable. It can be seen from Table I that the only useful solvents are the carboxamides which include dimethylformamide, N,N-dimethylacetamide, N,N-dimethylbutyramide, N,N-dibutylacetamide, and N-methyl-2-pyrrolidone, whereas such solvents as ethylene glycol, diglyme, etc., are wholly unsatisfactory. With its lower boiling point, dimethylformamide is not so effective as the other high boiling amides.

After the water was removed, the solution of aryl thiolate was cooled to 120–130° and 0.2 mole of aryl dihalide (0.4 mole of aryl monohalide and approximately 0.14 mole of aryl trihalide) were added in one portion. Cooling was employed in this step only in cases where vigorous exothermic reactions occurred with highly reactive halides, *e.g.*, N-heterocyclic halides. The solution was heated immediately to reflux (170–175°) which was maintained for 5–10 hr. Solvent was distilled to a thick slurry to which was added water and benzene.

The benzene layer was separated, washed with water, and evaporated to a residue. Distillation or recrystallization of the latter isolated the pure thioethers. The mono-, bis-, and trissulfides prepared in this way together with physical properties and analytical data are presented in Table II.

In a few of the preparations of bissulfides, some monosubstituted intermediates were obtained along with desired products. These are listed in Table III.

TABLE III

Intermediate	B.p. (mm.), °C.	n^{25}_{D}
m-Chlorophenyl phenyl sulfide	108–117 (0.4)[a]	1.6363
p-Chlorophenyl phenyl sulfide	160–170 (10)[b]	1.6387
m-Chlorophenyl *p*-*t*-butylphenyl sulfide	150–170 (0.6)[c]	
3-Chloro-5-phenylmercaptopyridine	125–128 (0.5)[c]	

[a] M. Rolla, M. Sanesi, and G. Leandri [*Ann. Chim.*, **42**, 644 (1952)] report b.p. 173–174° (13 mm.). [b] The previous reference gives b.p. 167–168° (10 mm.). [c] No further identification was made.

Another by-product encountered in some of the syntheses was the disulfide corresponding to starting thiol, but it never amounted to very much.

***m*-Bis(*n*-dodecylmercapto)benzene and *m*-Chlorophenyl *n*-Dodecyl Sulfide.**—Using the above procedure, 163.5 g. (0.8 mole) of 1-dodecanethiol, 52.7 g. (0.8 mole) of 86% potassium hydroxide, and 71.2 g. (0.3 mole) of *m*-dibromobenzene in 300 ml. of dimethylacetamide yielded about 50 ml. of starting materials, b.p. 81–170° (0.4 mm.); 49.4 g. of intermediate *m*-chlorophenyl *n*-dodecyl sulfide, b.p. 175–200° (0.55 mm.); and a residue which solidified. This was recrystallized from isopropyl alcohol giving 85 g. (59%) of *m*-bis(*n*-dodecylmercapto)benzene as off-white crystals, m.p. 34–35°.

Anal. Calcd. for $C_{30}H_{54}S_2$: S, 13.39. Found: S, 13.2.

Mixed Isomer, Bis(phenylmercaptobiphenyl).—A mixture of 0.5 mole of potassium benzenethiolate (from 55 g. of benzenethiol and 32.6 g. of 85% potassium hydroxide) and 57.6 g. (0.26 mole) of a dichlorinated biphenyl mixture in 200 ml. of dimethylacetamide was heated at reflux for 24 hr. Otherwise the method above was followed to give 26.3 g. of intermediate *x*-chloro-*x'*-phenylmercaptobiphenyl, b.p. 170–195° (0.25 mm.); and 46.3 g. (approx. 50%) of bis(phenylmercapto)biphenyl, a light yellow viscous oil with b.p. 205–250° (0.25 mm.).

Bis(*m*-phenylmercaptophenyl) Sulfide.—The Grignard of *m*-chlorophenyl phenyl sulfide was prepared in the usual manner from 63.4 g. (0.29 mole) of the halide and 7.8 g. (0.32 g.-atom) of magnesium ribbon in tetrahydrofuran with ethyl bromide as the initiator. It was cooled in an ice bath and treated with 9.2 g. (0.29 g.-atom) of sulfur, added at such a rate that the reaction temperature never exceeded 35°. The mixture was stirred for 5 min., solvent was evaporated *in vacuo*, and ether followed by 30 ml. of water and 80 ml. of 6 *N* hydrochloric acid was added. The organic layer and ether extract of the aqueous layer were combined and washed thoroughly with 200 ml. of 2 *N* sodium hydroxide. Acidification of the latter released the mercaptan which was separated with the aid of ether, washed with salt water, dried, and distilled. *m*-Phenylmercaptobenzenethiol was obtained in a yield of 30.1 g. (48%) as a colorless oil, b.p. 127–138° (0.35 mm.), n^{25}_{D} 1.6705.

Anal. Calcd. for $C_{12}H_{10}S_2$: C, 66.1; H, 4.6; S, 29.3. Found: C, 65.5; H, 4.5; S, 29.5.

Utilizing the method described previously, 0.28 mole of potassium *m*-phenylmercaptobenzenethiolate (from 62.2 g. of the above thiol and 18.3 g. of 87% potassium hydroxide) in 250 ml. of dimethylacetamide was treated with 50 g. (0.23 mole) of *m*-chlorophenyl phenyl sulfide for 36 hr. at 150 ± 5°. Isolation procedures provided an oil which was distilled giving 22.4 g. of unchanged halide and 38.8 g. (42%) of the four-membered ring thioether, b.p. 252–265° (0.25 mm.).

Anal. Calcd. for $C_{24}H_{18}S_3$: C, 71.8; H, 4.5; S, 23.8. Found: C, 71.3; H, 4.4; S, 23.9.

***m*-Bis(*m*-phenylmercaptophenylmercapto)benzene.**—The same procedure was employed to synthesize this orange viscous five-membered ring thioether from 0.23 mole of potassium *m*-phenylmercaptobenzenethiolate and 15.3 g. (0.104 mole) of *m*-dichlorobenzene in 200 ml. of dimethylacetamide. It was obtained in a yield of 9 g. (17%) with b.p. 300–308° (0.18 mm.).

Anal. Calcd. for $C_{30}H_{22}S_4$: C, 70.6; H, 4.35; S, 25.1. Found: C, 70.0; H, 4.28; S, 25.4.

Polymer from Pentachlorobenzenethiol.—In an attempt to synthesize *m*-bis(pentachlorophenylmercapto)benzene from 0.11 mole of *m*-dibromobenzene and 0.3 mole of potassium pentachlorobenzenethiolate, 73 g. of a yellow amorphous polymer was obtained. It melted above 300° and was insoluble in every solvent tried including water, alcohols, hydrocarbons, ethers, diglyme, amides, pyridine, chlorobenzene, ethyl acetate, etc. No solvent has yet been found to dissolve even a part of it.

Acknowledgment.—The author wishes to express his gratitude to Dr. F. S. Clark for some of the preparations and to our Analytical Group for all of the analytical determinations.

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(16) All melting and boiling points are uncorrected.