The physical and chemical properties of compound IVb are quite similar to those of compound IVa. The hydrochloride of compound IVb was obtained by suspending the base in ethyl ether with 10% methanol and passing through the suspension a stream of hydrogen chloride; IVb hydrochloride separated as a white crystalline powder melting at 187–188°.

Anal. Calcd. for $C_{27}H_{26}N_4O_4S_2\cdot HCl$: N, 9.81; Cl, 6.20. Found: N, 9.78; Cl, 5.95.

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Thioethers. III. Preparation of Aromatic Di- and Tri-mercapto Compounds by Dealkylation of Aryl Alkyl Thioethers

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Aromatic di- and tri-mercaptans have been synthesized by dealkylation of the corresponding aryl alkyl thioethers with sodium in liquid ammonia.

The synthesis of aromatic di- and tri-alkylmercapto compounds from the corresponding di- and tri-bromo compounds and cuprous alkylmercaptides has been described in previous papers.[2] Since these thioethers are readily accessible, their possible uses as intermediates in a synthetic approach to aromatic di- and tri-mercapto compounds has been explored.

The dealkylation of 1,2- and 1,4-diethylmercaptobenzenes was first investigated with each of the three reagents, sodium in liquid ammonia, lithium in monomethylamine, and sodium in pyridine. The first two reagents proved to be equally satisfactory and better than the third one. Sodium in liquid ammonia was selected as the method of choice for subsequent studies. From the appropriate diethylmercapto derivatives by this means 1,2- and 1,4-dimercaptobenzenes, 4,4′-dimercaptobiphenyl, 4,4′-dimercaptobibenzyl, 2,5-dimercaptotoluene, 1,3,5-trimercaptobenzene and 2,4,6-trimercaptomesitylene were synthesized in 70–99% yields.

The use of sodium in liquid ammonia has been extensively and successfully applied to the debenzylation of alkyl benzyl sulfides[3] and for hydrogenolysis of alkyl sulfides,[4] and in a single instance for hydrogenolysis of an aryl alkyl sulfide, namely, thioanisole.[5] Aryl alkyl sulfides are reported to be cleaved in excellent yields into thiophenol and alkanes with lithium in monomethylamine.[6]

Di- and tri-mercapto aromatic compounds have usually been prepared by reduction of the corresponding sulfonyl chlorides.[7–18] A second method, applicable when the required disulfonic acids cannot be formed by direct sulfonation,[7,8,15] involves the use of an aminosulfonic acid. The amino group is diazotized and allowed to react with potassium ethyl xanthate. Upon hydrolysis of the product, the resulting mercapto sulfonic acid is transformed into the dimercaptan in one of two ways: oxidation with potassium permanganate converts the product to a disulfonic acid which is reduced, through the acid chloride, to the dimercaptan. Mild oxidation may be used to convert the mercapto group to a disulfide; this is followed by formation of the sulfonyl chloride from the sulfonic acid group, and finally reduction of both the sulfonyl chloride and disulfide groups to the di- or tri-mercaptan.

The new method described in this Communication is definitely superior to those previously used whenever the corresponding bromo compounds are more readily available than the corresponding sulfonic acids or sulfonyl chlorides. Thus, 1,2- and 1,4-dimercaptobenzenes are synthesized preferably from the 1,2- and 1,4-dibromobenzenes rather than from the 1,2- and 1,4-benzenedisulfonic acids.

It is reported that an inactive halogen atom in aromatic halogen compounds will react with potassium hydrogen sulfide in presence of copper sulfate as catalyst to give a mercaptan, but a temperature of 250° is required for completion of the reaction.[19] This procedure has not been applied to dihalogen compounds. The vigorous conditions required would normally lead to a preference of the pathway through the alkylmer-

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TABLE I

ARYL DI- AND TRIMERCAPTANS FROM DI- AND TRIALKYLMERCAPTOBENZENES

Aryl alkyl thioether	Polymercaptan	Method	Yield, %	M.p. or b.p. (mm.), °C.	Analyses, % Calcd.	Analyses, % Found
p-Diethylmercaptobenzene	1,4-Dimercaptobenzene[a]	B 1	98	97.5–98.5	C 50.66	50.32
		A	85		H 4.25	4.31
		C	96			
o-Diethylmercaptobenzene	1,2-Dimercaptobenzene[b]	A	72	27–28	C 50.66	50.83
		B	70	102 (6.5)	H 4.25	4.38
		C	69	95 (5)		
2,5-Diethylmercaptotoluene	2,5-Dimercaptotoluene	B	82	38.5–39	C 53.80	53.78
				84 (0.5)	H 5.16	5.25
4,4′-Diethylmercaptobiphenyl	4,4′-Dimercaptobiphenyl[c]	B 2	99	180–181	C 66.01	66.11
					H 4.62	4.57
4,4′-Diethylmercaptobibenzyl	4,4′-Dimercaptobibenzyl[d]	B 2	97	130.5–131.5	C 68.25	68.59
					H 5.73	5.71
1,3,5-Triethylmercaptobenzene	1,3,5-Trimercaptobenzene[e]	B 1	85	59–60	C 41.34	40.99
					H 3.47	3.24
2,4,6-Triethylmercaptomesitylene	2,4,6-Trimercaptomesitylene	B	97	178–180	C 49.96	49.96
					H 5.59	5.48
2-Ethylmercaptomesitylene	Dimesityl disulfide[f]	[g]	77	124.5–125	C 71.47	71.83
					H 7.33	7.21

[a] Lit. m.p. 98°; J. Pollak, *Monatsh.*, **35**, 1457 (1914). [b] Lit.[7] m.p. 28°, b.p. 119–120° at 17 mm. [c] Sublimed at 160–165° at 0.1 mm.; lit.[17] m.p. 179–181°. [d] Sublimed at 120° at 0.3 mm. [e] Lit. m.p. 56–58°; J. Pollak and J. Carniol, *Ber.*, **42**, 3252 (1909). [f] Lit. m.p. 125°; A. Holtmeyer, *Z. Chem.*, 688 (1867). [g] The mercaptan was allowed to oxidize in the air.

capto compounds if di- or tri-mercaptans are desired.

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Experimental

All melting points are corrected.

Dealkylation of Aryl Alkyl Thioethers. A. With Sodium in Pyridine.—The procedure used by Hughes and Thompson[20] was followed.

B. With Sodium in Liquid Ammonia.—The thioether was suspended in liquid ammonia in a two-necked flask fitted with a Dry Ice–isopropyl alcohol condenser protected with a soda lime tube. Magnetic stirring was used. Small pieces of sodium were added until the blue color was permanent for at least 15 minutes (1.5 to 2 equivalents of sodium were necessary for each alkylmercapto group). Solid ammonium chloride was added to decompose the excess of sodium, and the ammonia was permitted to evaporate overnight in a stream of argon. The residue was dissolved in ice-water and excess hydrochloric acid. When the mercaptan was a liquid, it was extracted with benzene, the benzene solution was washed with water and dried. After elimination of the solvent, the mercaptan was distilled *in vacuo*, in the presence of argon. When the mercaptan was a solid, the precipitate obtained after pouring the residue into excess hydrochloric acid was treated according to (1) or (2):

(1) It was distilled with steam. The aqueous suspension of mercaptan was left overnight in the refrigerator under argon. The solution then was filtered, and the mercaptan was dried in a vacuum desiccator.

(2) It was filtered, added to a 5% aqueous sodium hydroxide, and then filtered through a sintered glass funnel into concentrated hydrochloric acid. This treatment was repeated and the product was then dried in a vacuum desiccator.

2,4,6-Trimercaptomesitylene, 4,4′-dimercaptobiphenyl and 4,4′-dimercaptobibenzyl were sublimed *in vacuo*.

C. With Lithium in Monomethylamine.—The procedure described by Truce and Tate[6] was used.

The data on yields, physical properties and analyses are presented in Table I.

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