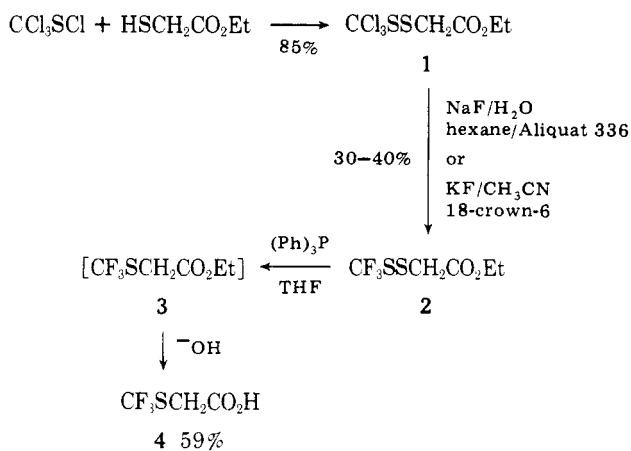


pared by condensing trichloromethylsulfenyl chloride with ethyl mercaptoacetate, with a twofold excess of aqueous sodium fluoride at room temperature in the presence of a catalytic amount of Aliquat 336⁶ gave the trifluoro disulfide **2** in 35% yield. Alternatively, addition of **1** to a cold suspension of



potassium fluoride in acetonitrile containing a catalytic amount of 18-crown-6 also yielded **2** (41%). To our knowledge this represents one of the first examples of a phase-transfer mediated trisubstitution of fluorine for chlorine, and it occurs under unusually mild conditions.⁷⁻⁹ Treatment of disulfide **2** with an aminophosphine¹⁰ resulted in an extremely exothermic reaction which produced only traces of sulfide **3**. However, when disulfide **2** was added to a THF solution of triphenylphosphine it was smoothly desulfurized to **3**. With one recent exception¹¹ reports of desulfurizations of disulfides with triphenylphosphine had been limited to acyl or vinylogous disulfides.¹² In the present case, the extremely electronegative trifluoromethyl group may polarize the disulfide sufficiently to render it labile to attack by triphenylphosphine. Since ester **3** was difficult to isolate in good yield because of its tendency to codistill with a variety of solvents, it was hydrolyzed in situ with 5% sodium hydroxide to produce pure trifluoromethylthioacetic acid in 59% yield (from **2**).

Experimental Section

Infrared spectra were obtained in CHCl_3 using a Perkin-Elmer Infracord; NMR spectra were obtained in CDCl_3 on a Varian T-60 spectrometer using Me_4Si as an internal standard; VPC analyses were carried out on a F & M 700 gas chromatograph with a 6 ft SE-30 column. MgSO_4 was used as drying agent for organic extracts.

Ethyl Trichloromethylthioacetate (1). Ethyl mercaptoacetate (36 g, 0.3 mol) was added dropwise with stirring over 1 h to trichloromethylsulfenyl chloride (55.8 g, 0.3 mol). The mixture was stirred at room temperature for an additional 1 h and then distilled to yield 69 g (85%) of **1** as a pale yellow oil: bp 94–96 °C (0.3 mm); NMR δ 4.20 (q, 2, $J = 7$ Hz), 3.90 (s, 2), 1.35 ppm (t, 3, $J = 7$ Hz); IR 1725, 845 cm^{-1} . Anal. Calcd for $\text{C}_5\text{H}_7\text{Cl}_3\text{O}_2\text{S}_2$: C, 22.28; H, 2.62; Cl, 39.45. Found: C, 22.68; H, 2.67; Cl, 39.83.

Ethyl Trifluoromethylthioacetate (2). A. A mixture of 30 mL of hexane containing 5.40 g (20 mmol) of disulfide **1** and 30 mL of H_2O containing 5.04 g (120 mmol) of NaF was stirred at room temperature while about 0.7 g of Aliquat 336 in 1 mL of hexane was added. After stirring at room temperature overnight the mixture was diluted with 100 mL of hexane and the organic layer separated, washed with H_2O , dried, filtered, and evaporated. The residue was distilled under aspirator pressure to give 1.4 g (35%) of **2** as a pale yellow liquid: bp 72–74 °C (10 mm); NMR δ 4.24 (q, 2, $J = 7$ Hz), 3.72 (s, 2), 1.30 ppm (t, 3, $J = 7$ Hz); IR 1725, 1145 cm^{-1} ; m/e M^+ 220.

B. To an ice-cold solution of 1.6 g (6 mmol) of 18-crown-6 in 50 mL of dry CH_3CN was added 7.0 g (120 mmol) of KF and the suspension stirred for 30 min. To this rapidly stirred solution was added dropwise over ~20 min a solution of 5.4 g (20 mmol) of disulfide **1** in 10 mL of CH_3CN . The mixture was stirred in the cold for an additional 1 h and then at room temperature for 2 h. Suspended solids were removed by filtration and the filtrate was evaporated. The residue was triturated

with petroleum ether and filtered and the filtrate was concentrated and distilled to give 1.8 g (41%) of **2** as a light tan oil.

Trifluoromethylthioacetic Acid (4). The disulfide **2** (4.4 g, 20 mmol) dissolved in 20 mL of THF was added dropwise to a stirred solution of 5.8 g (22 mmol) of triphenylphosphine in 50 mL of THF. After addition was complete, the mixture was stirred at room temperature for 30 min. An additional 1 g of triphenylphosphine was added in 0.5-g portions and stirring continued for 15 min longer until VPC indicated complete consumption of starting material. Fifty milliliters of 5% NaOH was added and the mixture stirred rapidly for 1 h. Most of the THF was removed under vacuum and the mixture diluted with 200 mL of H_2O . It was washed twice with benzene and twice with Et_2O , acidified to pH 1.5 with 3 N HCl, and extracted with three portions of Et_2O . The latter extracts were combined, dried, filtered, and evaporated to give a brown oil which was distilled to give 1.9 g (59%) of **4** as a pale yellow oil: bp 87–88 °C (11 mm) [lit.¹ 101 °C (31 mm)]; NMR δ 10.25 (s, 1), 3.80 ppm (s, 2); IR 1710, 1240 cm^{-1} .

Registry No.—**1**, 61915-55-7; **2**, 61915-56-8; **4**, 2408-17-5; ethyl mercaptoacetate, 623-51-8; trichloromethylsulfenyl chloride, 594-42-3.

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- The remarkable ease of this substitution might be accounted for by an initial sulfur-sulfur bond cleavage followed by halogen exchange to produce a trifluoromethylsulfenyl halide which could then recombine with ethyl mercaptoacetate producing **3**. Tullock and Coffman [*J. Org. Chem.*, **25**, 2016 (1960)] report the conversion of trichloromethylsulfenyl chloride to trifluoromethylsulfenyl chloride with sodium fluoride in hot tetramethylene sulfone. Trifluoromethylsulfenyl chloride readily combines with thiols to give disulfides.
- Trifluoromethylsulfenyl halides are extremely toxic substances. Caution must be exercised if they are used or if they may be present as side products in these reactions.
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Neighboring Sulfide Group in Thermal Decomposition of Aryldiazonium Salts

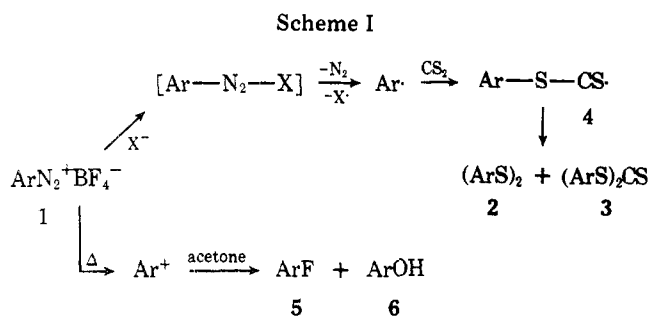
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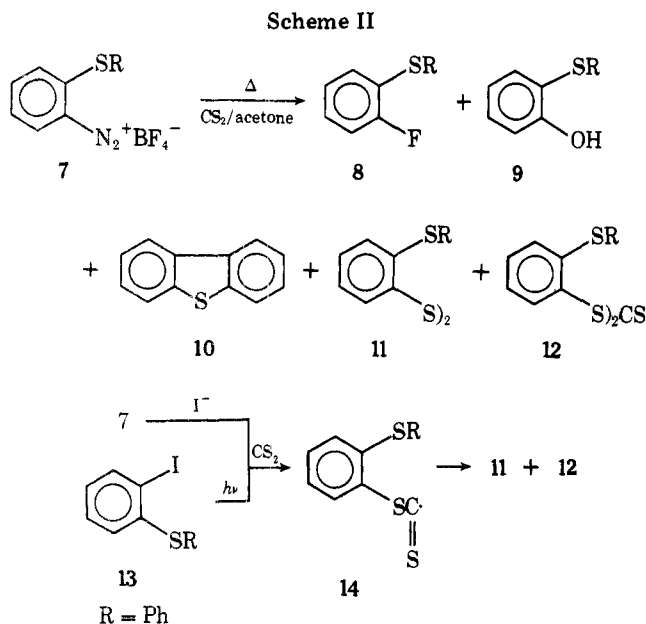
Received November 2, 1976

Aryldiazonium tetrafluoroborates (**1**) are a well-known source of aryl radicals when they undergo reduction by nucleophilic species.¹ The mechanism proposed² involves the attack of nucleophilic species at the β nitrogen of the diazonium group to form an intermediate which then fragments homolytically, releasing $\text{X}\cdot$, N_2 , and aryl radicals. Recently, we studied³ this reaction in carbon disulfide and we found that this solvent is a good scavenger for aryl radicals, which add to the carbon-sulfur double bond to give diaryl disulfide (**2**) and diaryl trithiocarbonate (**3**) through an intermediate arylthiothiocarbonyl radical (**4**). Otherwise, the thermal decomposition of **1** gives the aryl cation.⁴ When the reaction was carried out in acetone, fluoroarenes (**5**) and phenols (**6**) were obtained;⁴ no addition products on the carbon-sulfur double

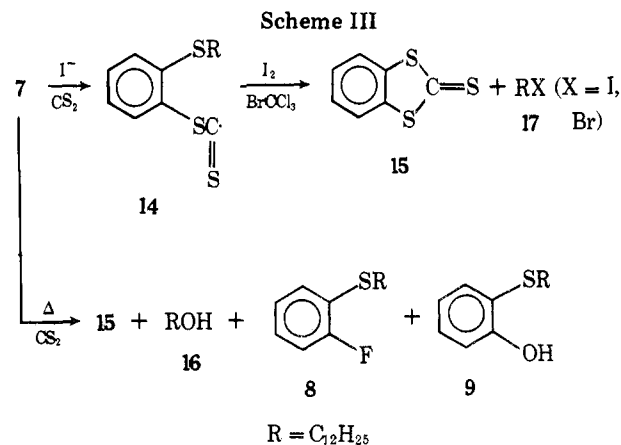
bond were isolated when the thermal decomposition was carried out in the presence of carbon disulfide (Scheme I).



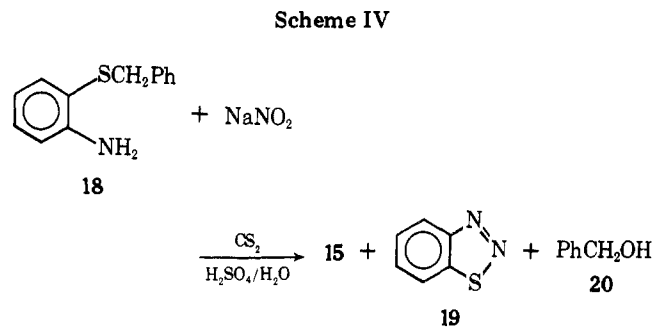
We now wish to report the thermal decomposition of *o*-aryl- and *o*-alkylthioaryldiazo tetrafluoroborates in carbon disulfide and discuss the influence of neighboring sulfide group on the reaction mechanism. When *o*-phenylthiobenzenediazonium tetrafluoroborate (7, R = Ph) was heated at 45 °C for 24 h in an acetone/carbon disulfide mixture, we obtained, besides 2-fluorodiphenyl sulfide (8, R = Ph) and 2-hydroxydiphenyl sulfide (9, R = Ph), dibenzothiophene (10), bis-*o*-phenylthiophenyl disulfide (11, R = Ph), and di-*o*-phenylthiophenyl trithiocarbonate (12, R = Ph). Compounds 11 and 12 were also obtained by reduction of 7, R = Ph, with iodide ions or by photolysis of 2-iododiphenyl sulfide (13, R = Ph) in carbon disulfide, through the radical (14, R = Ph) as intermediate (Scheme II).



From thermal decomposition of tetrafluoroborate 7, R = *n*-C₁₂H₂₅, benzo-1,3-dithiol-2-thione (15) and 1-dodecanol (16) were formed together with *o*-fluorophenyl *n*-dodecyl sulfide (8, R = *n*-C₁₂H₂₅) and *o*-hydroxyphenyl *n*-dodecyl sulfide (9, R = C₁₂H₂₅); formation of 11 and 12 was not observed in this case. Moreover, reduction of 7, R = *n*-C₁₂H₂₅, gave compound 15 and iodododecane (17, R = *n*-C₁₂H₂₅; X = I) and no trace of 11, R = *n*-C₁₂H₂₅, and 12, R = *n*-C₁₂H₂₅; on the other hand, addition of bromotrichloromethane to the reaction mixture led to small amounts of bromododecane (17, R = *n*-C₁₂H₂₅; X = Br) (Scheme III). Formation of 15 in this reaction is in agreement with what was previously reported³ on the reduction of 7, R = CH₃, in carbon disulfide, and could be rationalized by assuming that the radical 14, R = *n*-C₁₂H₂₅, instead of undergoing the usual reaction leading to 11 and 12, prefers to undergo intramolecular homolytic addition on the



sulfur atom of the ortho alkylthio group, followed by loss of a dodecyl radical which can be trapped by iodine or bromotrichloromethane. However, this route appears to be different from that observed with 7, R = *n*-C₁₂H₂₅, which gives 15 by thermal decomposition; formation of 16 would suggest that in this case dodecyl cations, rather than dodecyl radicals, are displaced, thus indicating that the reaction intermediate must be different from 14. Attempts to obtain the tetrafluoroborate 7, R = PhCH₂, were not successful because the diazotization of 2-aminophenyl benzyl sulfide (18) led very rapidly to 1,2,3-benzothiadiazole (19) and benzyl alcohol (20),^{5,6} however, when the diazotization of 18 was carried out in a mixture of sulfuric acid/carbon disulfide, we obtained traces of 15 as well as 19 and 20 (Scheme IV).

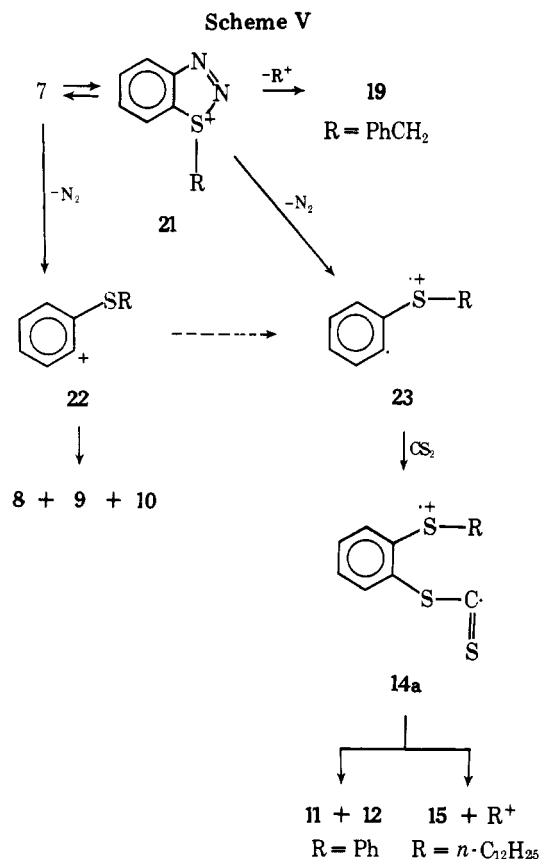


All these results appear to offer evidence of participation of the neighboring sulfur atom in the thermal decomposition of diazonium salts; a plausible mechanism could be a nucleophilic attack by the sulfur atom on the β nitrogen of the diazonium group, to afford a benzodiazothiolum salt (21) in equilibrium with the "open" diazonium salt 7; in fact 7, by nitrogen loss, can lead to the aryl cation (22), from which products 8, 9, and 10 are formed. Two kinds of reactions seem to be possible for intermediate 21: loss of R⁺ leading to 19, when R⁺ is a stable cation such as the benzyl cation, or nitrogen loss giving the radical intermediate 23. By reaction with carbon disulfide, radical 23 would then form the radical 14a, from which products 11 and 12, when R = Ph, and 15, when R = alkyl, can be produced (Scheme V).

Another possible route leading to 23 could be an intramolecular charge transfer process from cation 22. This alternative mechanism can be ruled out at least in one case investigated; in fact, the thermal decomposition of 7, R = CH₃, afforded 15, but no traces of 8, R = CH₃, and 9, R = CH₃. These results appear to exclude the formation of aryl cation 22, R = CH₃, and thus the formation of 23 by a charge transfer process.

Experimental Section

GLC analyses were carried out with a Varian 1440/1 instrument (5% FFAP on a Varaport column). The reaction products were identified, when possible, by mixture melting points with prepared authentic



specimens, and by comparison of their IR spectra (Perkin-Elmer 257), or by low-resolution mass spectral analysis (JEOL JMS D100). Aryldiazonium tetrafluoroborates were all prepared from parent diazotized amines, as described by Hey and co-workers.⁷ Dibenzothiozophene (10), dodecanol (16), iodo- and bromododecane, benzyl alcohol (19), and 2-aminobiphenyl are commercial products.

2-biphenyllyl,⁸ 2-fluorobiphenyl,⁹ 2-hydroxydiphenyl sulfide (9, R = Ph),¹⁰ bis-*o*-phenylthiophenyl disulfide (11, R = Ph),¹¹ 2-iododiphenyl sulfide (13),¹² benzo-1,3-dithiol-2-thione (15),¹³ 1,2,3-benzothiadiazole (19),¹⁴ 2-aminodiphenyl sulfide,¹⁵ *o*-methylthioaniline,¹⁶ and *o*-aminophenyl benzyl sulfide (18)¹⁷ were prepared as described in the literature. Carbon disulfide was dried with calcium chloride and then distilled twice. Acetone was refluxed over $KMnO_4$ and distilled over P_2O_5 twice.

***o*-Aminophenyl *n*-Dedecyl Sulfide.** A solution of *o*-chloronitrobenzene (16 g, 0.1 mol) and sodium *n*-dodecylthiolate (22 g, 0.1 mol) in methanol (200 mL) was refluxed for 3 h, then poured in cold water. The *o*-nitrophenyl *n*-dodecyl sulfide obtained was extracted with ethyl ether and purified by chromatography on a silica gel column, yield 80%, mp 34 °C. Anal. Calcd for $C_{18}H_{29}NO_2S$: C, 66.83; H, 9.04; N, 4.33; S, 9.91. Found: C, 66.84; H, 8.99; N, 4.39; S, 9.96. The nitro derivative was reduced over palladium/charcoal in dichloromethane. Filtration, evaporation, and distillation gave the title product (22 g) as an oil. Anal. Calcd for $C_{18}H_{31}NS$: C, 73.66; H, 10.65; N, 4.77; S, 10.92. Found: C, 73.78; H, 10.68; N, 4.82; S, 11.04.

Thermal Decomposition of Aryldiazonium Tetrafluoroborates. The salt (0.005 mol) was dissolved in acetone (20 mL) and carbon disulfide (15 mL) was added; this solution was heated at 45 °C for 24 h. After this time, the fluoroborate was all decomposed (negative test with β -naphthol). The reaction mixture was then analyzed by GLC and/or chromatographed on a silica gel column.

A. From 1, Ar = *o*-PhPh. By column chromatography of the reaction mixture 2-fluorobiphenyl (12%) and 2-biphenyllyl (85%) were separated.

B. From 7, R = Ph. The following products were separated: 2-fluorodiphenyl sulfide (8, R = Ph, 12%) [bp 142 °C (16 mm). Anal. Calcd for $C_{12}H_9FS$: C, 70.56; H, 4.44; F, 9.30; S, 15.70. Found: C, 70.0; H, 4.49; F, 9.51; S, 15.58. Mass spectrum m/e 204 (M^+ , 100), 185 (17), 184 (12).]; 2-hydroxydiphenyl sulfide (9, R = Ph, 22%); dibenzothiozophene (10, 3%); bis-*o*-phenylthiophenyl disulfide (11, R = Ph, 17%); di-2-phenylthiophenyl trithiocarbonate (12, R = Ph, 14%) [mp 113 °C. Anal. Calcd for $C_{25}H_{18}S_5$: C, 62.73; H, 3.78; S, 33.49. Found: C, 62.7; H, 3.74; S, 33.39. Mass spectrum m/e 478 (M^+ , 1.5), 434 (0.3),

369 (92), 293 (7), 261 (100), 229 (28), 228 (35), 217 (35), 21 (40), 185 (65), 184 (85).].

C. From 7, R = $C_{12}H_{25}$. The reaction mixture was analyzed by GLC, and *n*-dodecanol was identified. Then, from column chromatography, it was separated: *o*-fluorophenyl *n*-dodecyl sulfide (8, R = $C_{12}H_{25}$, 14%) [bp 144 °C (16 mm). Anal. Calcd for $C_{18}H_{29}FS$: C, 72.92; H, 9.86; F, 6.41; S, 10.81. Found: C, 72.88; H, 9.81; F, 6.26; S, 10.94. Mass spectrum m/e 296 (M^+ , 92), 128 (100).]; *o*-hydroxyphenyl *n*-dodecyl sulfide (9, R = $C_{12}H_{25}$, 25%) [bp 122 °C (1 mm). Anal. Calcd for $C_{18}H_{30}OS$: C, 73.41; H, 10.27; S, 10.89. Found: C, 73.35; H, 10.21; S, 10.81. Mass spectrum m/e 294 (M^+ , 100), 126 (80).]; benzo-1,3-dithiol-2-thione (15, 30%).

D. From 7, R = CH_3 . Only benzo-1,3-dithiol-2-thione (15, 35%) was separated from column chromatography, together with other heavy products not identified. No *o*-methylthiofluorobenzene and *o*-methylthiophenol were found.

Reduction of Aryldiazonium Tetrafluoroborates with Iodide Ions. The salt (0.005 mol) was dissolved in an acetone (15 mL)/carbon disulfide (15 mL) mixture under stirring. Sodium iodide (0.8 g) was added slowly and, after nitrogen evolution, the mixture was refluxed for 0.5 h. It was then poured in water and the organic layer separated. The crude obtained by solvent evaporation was chromatographed on a silica gel column.

A. From 7, R = Ph. *o*-Iododiphenyl sulfide (3.3%), bis-*o*-phenylthiophenyl disulfide (11, R = Ph, 46%), and di-*o*-phenylthiophenyl trithiocarbonate (12, R = Ph, 33%) were obtained.

B. From 7, R = *n*- $C_{12}H_{25}$. This reaction was carried out in the presence of bromotrichloromethane (0.01 mol). From column chromatography iodododecane (37%), little amounts of bromododecane (detected by GLC/MS), and benzo-1,3-dithiol-2-thione (15, 53%) were separated. GLC analysis of the reaction mixture showed that 1-dodecanol was not present. No addition products of *n*-dodecyl radical on carbon disulfide were isolated.

Photolysis of 2-Iododiphenyl Sulfide (13). A solution of 13 (0.56 g, 0.002 mol) in carbon disulfide (3 mL) and ethyl ether (7 mL) mixture was photolyzed using a low-pressure mercury lamp Hanau Type P.L. 369 for 18 h. By column chromatography of the reaction mixture on silica gel, unreacted starting product (0.27 g), bis-*o*-phenylthiophenyl disulfide (11, R = Ph, 44%), and di-*o*-phenylthiophenyl trithiocarbonate (12, R = Ph, 35%) were separated.

Diazotization of *o*-Aminophenyl Benzyl Sulfide (18). The amine 18 (3.6 g) was suspended in a cold solution of concentrated H_2SO_4 (3 mL) in water (15 mL) and carbon disulfide (15 mL) was then added. To this mixture a solution of $NaNO_2$ (1.3 g) in water (5 mL) was added dropwise, under vigorous stirring, at 0–5 °C. After addition, the mixture was stirred for 0.5 h at 10–20 °C, and then warmed at 45 °C until the test with β -naphthol was negative. The organic layer was separated and the solvent evaporated. By column chromatography of the crude on silica gel with carbon disulfide as eluent, benzo-1,3-dithiol-2-thione (15, traces), 1,2,3-benzothiadiazole (19, 95%), and benzyl alcohol (20, 75%) were separated.

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Registry No.—1 (AR = *o*-PhPh), 318-13-8; 7 (R = Ph), 59014-91-4; 7 (R = $C_{12}H_{25}$), 61900-50-3; 7 (R = CH_3), 52959-17-8; 8 (R = Ph), 61900-51-4; 8 (R = $C_{12}H_{25}$), 61900-52-5; 9 (R = $C_{12}H_{25}$), 61900-53-6; 12 (R = Ph), 61900-54-7; 13, 2236-42-2; 18, 6325-92-4; *o*-aminophenyl *n*-dodecyl sulfide, 61900-55-8; *o*-chloronitrobenzene, 88-73-3; sodium *n*-dodecylthiolate, 26960-77-0; *o*-nitrophenyl *n*-dodecyl sulfide, 61900-56-9.

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