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The Preparation of Some Diaryl Sulfides and Sulfones

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Some new diaryl sulfides have been synthesized from sodium thiophenolates and aryl bromides by a simple nucleophilic displacement reaction. All were converted into the corresponding sulfones. Preparation of a bissulfide and sulfone is described.

Several new diaryl sulfides and the corresponding sulfones were prepared for study in one extensive program in this Laboratory. Preparation of the sulfides was somewhat different from published procedures. However, conversion of these sulfides to their sulfones was accomplished by the standard hydrogen peroxide oxidation.

Metal thiophenolates have often been employed to displace the halogen in aryl halides forming diaryl sulfides. Aromatic bromides react with lead thiophenolates at high temperatures.[1] A variety of sulfides has been obtained from cuprous thiophenolate and aromatic chlorides in quinoline.[2] When copper is used as a catalyst, sodium thiophenolates replace activated halogens in aromatic halides.[1] Without copper sodium thiophenolate will react with aryl halides providing the halogen is highly activated by nitro groups.[3]

All the diaryl sulfides reported here were synthesized from aryl bromides and sodium thiophenolates in dimethylformamide in the absence of any catalyst. The general procedure involves simply refluxing these reactants (thiophenolates prepared *in situ*) in dimethylformamide for several hours, distilling solvent and isolating the product. The sulfides made by this method are listed in Table I. The first column, R, denotes the substituent arising from the aryl bromide and the second column, R′, that from the thiophenolate.

Somewhat surprising is the effect R has on the reactivity of the halide. In every instance a trifluoromethyl group in the *meta* position gave good to excellent yields of the sulfide. No resonance effect can be exerted by this substituent from its position in the nucleus. The inductive effect must account for the high yields by promoting attack of the nucleophilic thiophenolate ions. The case of *m*-nitrophenyl *m*-tolyl sulfide presents an anomaly since the yield was so low. Here, a nitro group has replaced the trifluoromethyl substituent, but inductive effect should not change.

An attempt was made to prepare pentachlorophenyl *α,α,α,*-trifluoro-*m*-tolyl sulfide from sodium pentachlorothiophenolate and *m*-bromobenzotrifluoride, but no reaction occurred. Evidently the superabundance of electronegative chlorines practically eliminates nucleophilic character in this thiophenol.

The mechanism of the reaction is probably a simple nucleophilic displacement with little, if any, occurring through a benzyne mechanism. Infrared studies of both sulfides and sulfones gave no indication of isomers which could form *via* the benzyne reaction.

A bissulfide, 4,4′-bis(*α,α,α*-trifluoro-*m*-toluenemercapto)biphenyl, was also synthesized by the described procedure. Starting materials were *m*-bromobenzotrifluoride and 4,4′-biphenyldithiol, which was obtained from the corresponding disulfonic acid *via* disulfonyl chloride.

EXPERIMENTAL[4]

General procedure for synthesis of diaryl sulfides. To a solution of 0.11 mole of aryl bromide and 0.15 mole of thiophenol in about 100 ml. of dimethylformamide was added 0.15 mole of sodium hydroxide in one portion. There was an initial mild exothermic reaction after which the mixture was stirred at room temperature until all sodium hydroxide had disappeared. It was then heated to reflux (145–155°) which was maintained for approximately 5 hr. Salt precipitated during this period. Dimethylformamide was distilled down to a thick residue which was treated with cold water. The oil that separated was removed with ether. The ether was washed with water, dried and evaporated to a residue, which was distilled. In Table I are given the diaryl sulfides with their properties and analyses.

2-Naphthyl α,α,α-trifluoro-m-tolyl sulfide. Following the above method 24.2 g. (0.11 mole) of *m*-bromobenzotrifluoride, 20.8 g. (0.13 mole) of 2-naphthalenethiol and 5.2 g. (0.13 mole) of sodium hydroxide yielded 30 g. (90%) of light yellow crystals. They melt at 65–66° when recrystallized from ethanol.

Anal. Calcd. for $C_{17}H_{11}F_3S$: S, 10.54. Found: S, 10.72.

4,4′Bis(α,α,α-trifluoro-m-toluenemercapto)biphenyl. A copious evolution of hydrogen chloride occurred when 83 g. (0.4 mole) of phosphorus pentachloride[5] was slowly added to 62.5 g. (0.2 mole) of 4,4′-biphenyldisulfonic acid. Following the addition, the mixture was heated slowly to 220° where homogeneity occurred. Hydrogen chloride and phosphorus oxychloride were removed under reduced pressure to a solid residue. Recrystallization of the solid from acetic acid gave 20.7 g. of 4,4′-biphenyldisulfonyl chloride, m.p. 200–202°. Literature[6] reports m.p. 203°.

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(1) E. E. Reid, *Organic Chemistry of Bivalent Sulfur*, Vol. II, Chemical Publishing Co., Inc., New York, 1960, p. 28.

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

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

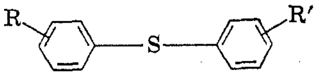
(4) All boiling points and melting points are uncorrected.

(5) Thionyl chloride failed in this reaction.

(6) S. Gabriel and A. Deutsch, *Ber.*, **13**, 390 (1880).

TABLE I

DIARYL SULFIDES

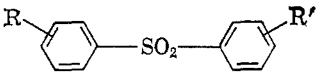


R	R′	M.P. B.P., (mm.)	Yield, %	Formula	Sulfur, %	
					Calcd.	Found
m-CF_3	H	146–158 (12–14)	93.5	$C_{13}H_9F_3S$	12.61	13.05
m-CF_3	p-CH_3	115 (1.5)	96.5	$C_{14}H_{11}F_3S$	11.95	11.95
m-CF_3	m-CH_3	99–110 (0.6)	90	$C_{14}H_{11}F_3S$	11.95	12.07
m-CF_3	o-CH_3	94–95 (0.5)	89.5	$C_{14}H_{11}F_3S$	—[a]	—
m-CF_3	p-t-C_4H_9	119–123 (0.7)	96.5	$C_{17}H_{17}F_3S$	10.33	10.46
m-CF_3	m-CF_3	93–100 (0.8)	77	$C_{14}H_8F_6S$	—[a]	—
m-CF_3	p-Cl	118–121 (1)	61	$C_{13}H_8ClF_3S$	11.10	11.24
CH_3	m-CH_3	114–116 (0.3)	—	$C_{14}H_{14}S$	14.96[b]	14.76
m-NO_2	m-CH_3	[a]	—	—	—	—
p-C_6H_5	m-CH_3	[a]	—	—	—	—
p-C_6H_5O	H	172–177 (0.5)[c]	46	$C_{18}H_{14}OS$	11.52	11.48

[a] Converted to sulfone without purification and/or identification. [b] % C: calcd.—78.46, found—78.10; % H: calcd.—6.58, found—7.09. [c] n_D^{24} 1.6440.

TABLE II

DIARYL SULFONES



R	R′	M.P.	Yield, %	Formula	Sulfur, %	
					Calcd.	Found
m-CF_3	H[a]	77–78	93	$C_{13}H_9F_3O_2S$	11.20	11.13
m-CF_3	p-CH_3	80–81[b] 101–102[c]	95	$C_{14}H_{11}F_3O_2S$	10.68	10.80
m-CF_3	m-CH_3	73–74[b]	90	$C_{14}H_{11}F_3O_2S$	10.68	11.13[d]
m-CF_3	o-CH_3	66–67[b]	75	$C_{14}H_{11}F_3O_2S$	10.68	10.65
m-CF_3	p-t-C_4H_9	101–102[c]	91	$C_{17}H_{17}F_3O_2S$	9.36	9.54
m-CF_3	m-CF_3	87–89[b]	93.5	$C_{14}H_8F_6O_2S$	9.05	9.15
m-CF_3	p-Cl	61–63[b]	81	$C_{13}H_8ClF_3O_2S$	10.00	9.80
m-CH_3	m-CH_3	94–95[c,e]	—	$C_{14}H_{14}O_2S$	14.96	14.76
m-NO_2	m-CH_3	95–96[f]	—	$C_{13}H_{11}NO_4S$	11.57	11.50
p-C_6H_5	m-CH_3	129[g]	39[h]	$C_{19}H_{16}O_2S$	10.39	10.87
p-C_6H_5O	H	92–93[i]	72	$C_{18}H_{14}O_3S$	10.33	10.57

[a] G. W. Story and C. R. Bresson, *J. Org. Chem.*, **24**, 1892 (1959), report m.p. 77–78° and 49% yield by another way. [b] From petroleum ether (b.p. 77–98°). [c] From petroleum ether (b.p. 60–70°). [d] % C: calcd.—55.99, found—55.81; % H: calcd.—3.69, found—3.88. [e] M. T. Bogert and M. R. Mandelbaum, *J. Am. Chem. Soc.*, **45**, 3045 (1923) give m.p. 94°. [f] From ether. [g] From ethanol. [h] Based on 4-bromobiphenyl. [i] From benzene–petroleum ether (b.p. 77–98°).

Following the procedure of Marvel and Caesar[7] about 21 g. (0.06 mole) of the above disulfonyl chloride and 300 g. (1.35 mole) of stannous chloride dihydrate in 1200 ml. of acetic acid yielded 12 g. (92%) of slightly impure 4,4′-biphenyldithiol, m.p. 171–174°. Marvel and Caesar's value for pure product is 179–180°.

The general procedure above with one exception was employed to prepare this dithio ether. The reflux period was increased to about 15 hr. Thus, 12 g. (0.055 mole) of the dithiol, 33.7 g. (0.15 mole) of *m*-bromobenzotrifluoride, and 4.4 g. (0.11 mole) of sodium hydroxide in 150 ml. of dimethylformamide gave 18.3 g. (66%) of 4,4′-bis(α,α,α-trifluoro-*m*-toluenemercapto)biphenyl, b.p. 235–245° (0.2 mm.), which slowly solidified to a low melting solid. No other identification was attempted, but the product was oxidized to the disulfone below.

General procedure for synthesis of diaryl sulfones. The sulfides were dissolved in acetic acid and treated with a large excess of 30% hydrogen peroxide according to standard procedures. Table II reports the diaryl sulfones prepared together with properties and analyses.

2-Naphthyl α,α,α-trifluoro-m-tolyl sulfone. In the above way there was obtained 26.1 g. (78%) of tan solid from 30 g. (0.1 mole) of 2-naphthyl α,α,α-trifluoro-*m*-tolyl sulfide and 50 ml. of 30% hydrogen peroxide. The sulfone melts at 101–103° when recrystallized from ethanol, and at 104–105° from petroleum ether (b.p. 77-98°).

Anal. Calcd. for $C_{17}H_{11}F_3O_2S$: S, 9.53. Found: S, 9.99.

4,4′-Bis(α,α,α-trifluoro-m-toluenesulfonyl)biphenyl. The general method for synthesis of sulfones was utilized to prepare 20.9 g. (98%) of white crystals, m.p. 195–200°, from 18.3 g. (0.036 mole) of 4,4′-bis(α,α,α-trifluoro-*m*-toluenemercapto)biphenyl and 20 ml. of 30% hydrogen peroxide in 100 ml. of acetic acid. Recrystallization from benzene raised the melting point of the disulfone to 201–202°.

Anal. Calcd. for $C_{26}H_{16}F_6O_4S_2$: S, 11.26. Found: S, 11.68.

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[7] C. F. Marvel and P. D. Caesar, *J. Am. Chem. Soc.*, **73**, 1097 (1951).