

## A Convenient Two-Step Synthesis of Bis(polyalkylphenyl) Disulfides from Polyalkylbenzenes<sup>1)</sup>

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**Synopsis.** Heating of polyalkyliodobenzenes with copper(I) thiocyanate in phosphoric tris-dimethylamide at 180—190 °C for a short period of time gives the corresponding bis(polyalkylphenyl) disulfides in high yields.

Although the reaction of aryl halides with copper(I) thiocyanate was reported as early as in 1920 to yield a mixture of aryl cyanide, arenethiol, diaryl sulfide, and diaryl disulfide rather than the expected aryl thiocyanates,<sup>2)</sup> no attempts seem to have been made so far to extend the original work to synthetic purpose. This is probably due to the incomplete conversion coupled with the tedious work-up involved in the separation of the products.<sup>3)</sup>

We have found, however, that this reaction can be modified to provide a simple two-step method for the conversion of polyalkylbenzenes into the corresponding diaryl disulfides, which are otherwise less easy of access. Reported preparation of bis(polyalkylphenyl) disulfides is based on the mild oxidation of polyalkylbenzenethiols,<sup>4)</sup> the action of sulfur monochloride on polyalkylbenzenes,<sup>5)</sup> and the reaction of the diazonium compounds of polyalkylanilines with sodium polysulfide.<sup>6)</sup> Almost all these procedures, however, suffer from either

difficulty of access to appropriate starting materials or the lack of generality.

A mixture of a polyalkyliodobenzene and copper(I) thiocyanate (mole ratio, *ca.* 1.0: 1.1) in phosphoric tris-dimethylamide was heated in an oil bath and kept at 180—190 °C for a short period of time until the mixture turned dark and homogeneous. After cooling, the thick mixture was diluted with water and the precipitate was filtered off and extracted with hexane or benzene, giving the corresponding diaryl disulfides in good yields. Neither the replacement of iodoarene by bromoarene nor the use of other dipolar aprotic solvents such as *N*-methyl-2-pyrrolidone and *N,N*-dimethylformamide gave better results.

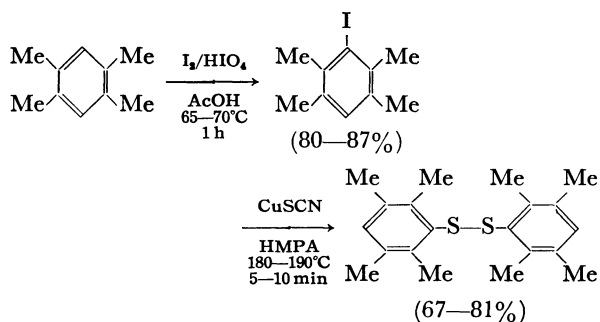
This method of preparation of diaryl disulfides has certain advantages, complementing the existing methods for disulfide synthesis: 1) It is a two-step synthesis from hydrocarbon. Each operation is quite simple and overall process can be carried out in half a day. 2) Starting materials are easily available and reagents are cheap. 3) Products are pure and yields are good, although no attempts have yet been made to optimize them.

TABLE 1. PHYSICAL PROPERTIES OF SOME BIS (POLYMETHYLPHENYL) DISULFIDES

Disulfide	Mp (°C)	Yield <sup>a)</sup> (%)	PMR spectra ( $\delta$ ) <sup>b)</sup>		IR <sup>c)</sup> spectra (cm <sup>-1</sup> )	Elemental analysis (%)			
			CH <sub>3</sub>	Aromatic H		Found C	Found H	Calcd C	Calcd H
Bis(2,3,4-trimethylphenyl) disulfide	128—130	91	2.19(1) 2.27(1) 2.38(1)	6.91(d) 7.32(d) <i>J</i> = 7.5 Hz	795 812 1005 1148	71.3	7.4	71.5	7.3
Bis(2,4,6-trimethylphenyl) disulfide	126—128 (lit, 125) <sup>4)</sup>	89	2.23(2) 2.25(1)	6.82	715 850 862 1032 1298	71.8	7.5	71.5	7.3
Bis(2,3,4,6-tetramethyl- phenyl) disulfide	90—91	83	2.10(1) 2.17(2) 2.24(1)	6.84	718 862 1012 1290	72.8	8.0	72.7	7.9
Bis(2,3,5,6-tetramethyl- phenyl) disulfide	99—101 (lit, 100—101) <sup>4)</sup>	81	2.12(2) 2.15(2)	6.90	718 872 1000	72.7	8.0	72.7	7.9
Bis(pentamethylphenyl) disulfide	190—193	87	2.16(2) 2.22(3)		1008 1062 1285	73.6	8.5	73.7	8.4

a) Based on the isolated product. b) Numerals in parentheses refer to the number of methyl groups.

c) Principal peaks in the region 650—1350 cm<sup>-1</sup>.



### Experimental

All melting points were determined on a hot stage and are uncorrected. The PMR spectra were recorded on a Varian T-60 spectrometer using deuteriochloroform solutions and TMS as internal standard. The IR spectra were measured in Nujol mulls with a Hitachi 215 spectrophotometer.

Iodoarenes were prepared by the direct iodination of arenes with iodine/periodic acid.<sup>7</sup> The structures of all the products were characterized by PMR and IR spectroscopy and elemental analysis. Physical properties and yields of some bis-(polymethylphenyl) disulfides obtained are given in Table 1.

The general procedure is illustrated below with the preparation of bis(2,3,4-trimethylphenyl) disulfide from 4-iodo-1,2,3-trimethylbenzene:

A mixture of 4-iodo-1,2,3-trimethylbenzene (3.8 g), copper

(I) thiocyanate (2.0 g), and phosphoric tris-dimethylamide (6 ml) was stirred and heated in an oil bath. At  $180-190^\circ C$  the mixture rapidly turned dark and homogeneous. Heating was then stopped and the mixture was allowed to cool with stirring. The black viscous mixture was diluted with water and the precipitated solid was collected by filtration and washed thoroughly with water. It was sucked as dry as possible and then placed in a filter thimble and extracted with hexane with a Soxhlet extractor. The extract was evaporated and the residue was crystallized from ethanol to give bis(2,3,4-trimethylphenyl) disulfide as fine prisms, mp  $127-129^\circ C$ . Yield, 2.12 g (91%).

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