

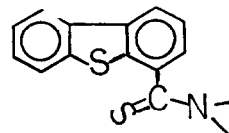
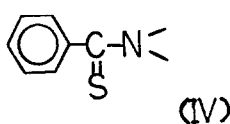
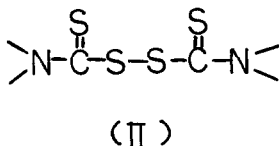
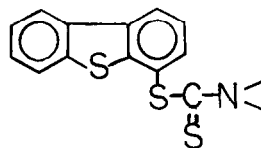
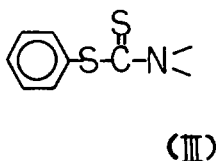
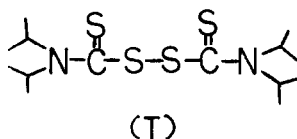
A NEW SYNTHESIS OF AROMATIC THIOLS

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Summary Benzenoid and heterocyclic lithio derivatives react smoothly with tetraisopropylthiuram disulfide to give highly crystalline and readily purified S-aryl-N,N-diisopropyl-dithiocarbamates, which yield aromatic thiols on alkaline hydrolysis.

The literature ¹ contains various examples of the synthesis of thiols by the direct thiation of organomagnesium or organolithium reagents with elemental sulfur. This type of reaction has been of limited utility, since clean products are usually not obtained, and sulfides are formed as significant by-products ². In contrast, the reaction of organometallic reagents with either dimethyl disulfide or diphenyl disulfide affords an excellent route to the corresponding mixed sulfides. We now report a new disulfide reagent, tetraisopropylthiuram disulfide (I, TITD), ³ which allows the clean conversion of aryllithiums into the corresponding thiols by way of highly crystalline and easily purified dithiocarbamate intermediates



It has been known for many years that tetramethylthiuram disulfide (II, TMTD) suffers nucleophilic attack at the disulfide bond when treated with cyanide ion ⁴ or amines ⁵. More recently, Grignard reagents have been reported to react similarly to give modest yields (26 - 75%) of dithiocarbamates. ⁶ We have now examined the reaction of TMTD with phenyllithium and with 4-lithiodibenzothiophene. In both cases the product was a mixture of about equal amounts of the desired arylthiocarbamate (III) and the corresponding thio-

amide (IV), formed by a competing nucleophilic attack at the thione carbon of the TMTD.

Table (I)

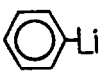
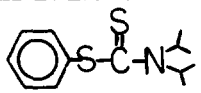
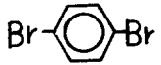
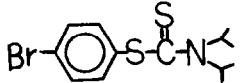
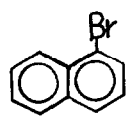
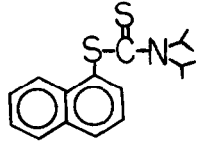
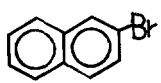
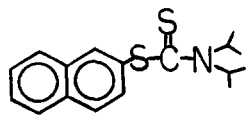
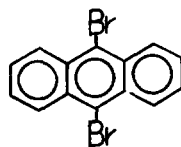
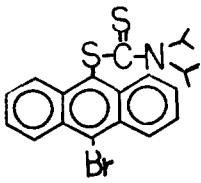
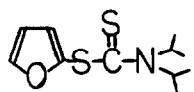
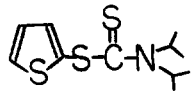
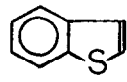
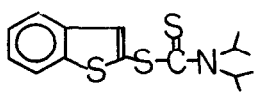
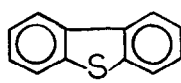
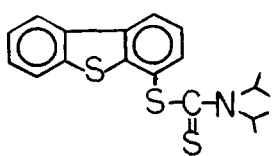
Starting Material	Products	mp(°C)	Yield(%)
		135-136	50
		172-174	81
		149-151	71
		145-147	85
		195-196	83
		114-115	95
		119-121	96
		187-189	92
		145-147	61

Table (II)

Starting Material	Products	mp or bp(°C)	Yield(%)
		68(20mm)	83
		70-71	92
		85-87	86
		80-81	87

When TMTD was replaced by its homolog tetraisopropylthiuram disulfide (I, TITD), the thione carbonyl became highly hindered to nucleophilic attack, and a variety of aryllithiums, both benzenoid and heterocyclic, reacted exclusively at the disulfide bond. The resulting S-aryl-N, N-diisopropylthiuram disulfides (see Table I) generally crystallized directly on work-up without chromatography. Several representative dithiocarbamates were hydrolyzed by 20% ethanolic KOH, followed by acidification, to give the corresponding pure thiols in high yield, as shown in Table II above

The reaction of TITD with functionally substituted aliphatic carbanions should lead to synthetically useful intermediates. Studies along these lines are being pursued in our laboratory.

ACKNOWLEDGEMENT. This work was supported by the National Science Foundation MRL program under Grant DMR 7923647.

References and Notes

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(Received in USA 26 January 1982)