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A CONVENIENT SYNTHESIS OF BIS(o-ARYLMERCAPTOPHENYL)SULFIDES

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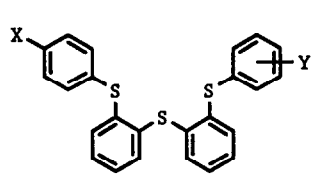
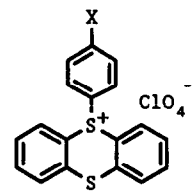
Summary: Reactions of 5-arylthianthrenium perchlorates with arylthiolates in tetrahydrofuran at ambient temperature under nitrogen atmosphere afforded bis(o-arylmercaptophenyl)sulfides in excellent yields.

Synthesis of polyaryl thioethers such as bis(m-phenylmercaptophenyl)sulfide and m-bis(m-phenylmercaptophenylmercapto)benzene has attracted much interests because they can be utilized not only as additives for the polyphenyl ethers and phenoxybiphenyls to improve the oxidation stability but also as high-temperature hydraulic fluids, lubricants, and heat-transfer fluids.[1] These compounds and other polyaryl thioethers have generally been synthesized by the nucleophilic displacement of aryl halides with an alkali metal thiolate in an amide solvent by heating at high temperature for the longer reaction time.[2]

Although synthesis of bis(o-phenylmercaptophenyl)sulfide (1, X=Y=H) has been reported,[1] no experimental details for its synthesis were described. Severe steric hindrance is expected for the synthesis of 1 (X=Y=H) from the reaction of o-chlorophenyl phenyl sulfide with sodium o-phenylmercaptobenzenethiolate.



1

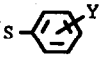


2

Recently hypervalent sulfur species (sulfurane) have received much attention owing to not only mechanistic senses but also synthetic utility.[3] We utilized 5-arylthianthrenium perchlorates (2) which were readily obtained from the reaction of thianthrene cation radical perchlorate with either activated aromatics[4] or organomercurials[5] for the synthesis of 1 by sulfurane mechanism. Reactions of 2 with arylthiolates in tetrahydrofuran (THF) at ambient temperature under nitrogen atmosphere gave excellent yields of 1. The results are summarized in Table 1.[6]

5-(p-Anisyl)thianthrenium perchlorate (2a) also reacted with n-propanethiolate to give o-(p-anisylmercapto)phenyl o-n-propylmercaptophenyl sulfide in 90% yield under the same reaction condition. However, reactions of 2a with 2-thiazolin-2-thiolate and methyl-4H-1,2,4-triazol-3-thiolate failed to give the corresponding polyaryl thioethers either at ambient or reflux temperature. Only 2a was recovered quantitatively. The scope of the synthesis of polyaryl thioethers via sulfurane is presently under investigation.

Table 1. Preparation of bis(o-arylmercaptophenyl)sulfides (1)

Substrate 2		Isolated yield (%) 1
a, X = OCH_3	Y = p-CH_3	92
b, X = OCH_3	Y = p-OCH_3	95
c, X = OCH_3	Y = o-Cl	94
d, X = OCH_3	Y = o-NH_2	78
e, X = OCH_2CH_3	Y = p-CH_3	90
f, X = OCH_2CH_3	Y = p-OCH_2CH_3	93
g, X = $OCH_2CH_2CH_3$	Y = p-CH_3	93
h, X = $OCH(CH_3)_2$	Y = p-CH_3	80
i, X = $OCH_2CH_2CH_2CH_3$	Y = p-CH_3	97
j, X = $OCH_2CH_2CH_2CH_3$	Y = p-$OCH_2CH_2CH_2CH_3$	91

All new compounds were satisfactorily characterized by the spectroscopic methods.

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References and Notes

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6. General procedure: To a stirred solution of p-thiocresol(0.603 g, 4.831 mmol) and sodium hydride (0.104 g, 4.250 mmol) in dry THF(50 ml) at ambient temperature under nitrogen atmosphere for 2 h was added 5-(p-anisyl)thianthrenium perchlorate(2a, 1.075 g, 2.541 mmol). The mixture was stirred for 2.5 h, followed by the addition of water(5 ml). Evaporation of the solvent under vacuo, followed by the extraction with chloroform gave a residue, chromatographed on silica gel. Elution with n-hexane, followed by benzene gave 1a(1.038 g, 2.328 mmol).

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