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A FACILE SYNTHESIS OF ARYL SULFIDES BY IRON-CATALYZED AROMATIC SULFURATION

T. Fujisawa, N. Ohtsuka, T. Kobori and G. Tsuchihashi
Sagami Chemical Research Center
Ohnuma, Sagamihara-shi, Kanagawa, Japan

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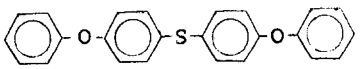
Several methods for the preparation of aryl sulfides have been reported, but they are lacking in general applicability because severe reaction conditions, complicated procedures and/or activated reactants are required (1,2). As for the method by direct sulfuration to aromatic nuclei, no catalyst is required in the reactions of phenols (3) or anilines (4) with sulfur chlorides to give the corresponding sulfides (5). Aluminum chloride is necessitated to synthesize diphenyl sulfide (1) or bis(4-methoxyphenyl) sulfide (6) by the reactions of benzene or anisole with such reagents as sulfur, sulfur chlorides or thionyl chloride. But the reactions catalyzed by aluminum chloride suffer from rather narrow applicability because of forming complexes with hetero atoms and of the poor selectivity in orientation, so that previously known aryl sulfides, especially those with electron-releasing substituents, are limited. We now develop a facile method for the preparation of aryl sulfides by a direct aromatic sulfuration with sulfur chlorides catalyzed by a trace amount of iron-powder.

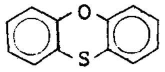
$$2ArH \quad + \quad \underset{x\,=\,1\text{ or }2}{S_xCl_2} \quad \xrightarrow{Fe} \quad ArSAr \quad + \quad 2HCl \quad + \quad (S)$$

Addition of a trace amount of iron-powder to a mixture of sulfur monochloride and anisole resulted in a vigorous reaction after an induction period of a few minutes giving bis(4-methoxyphenyl) sulfide (7) and its isomer, 2-methoxyphenyl 4-methoxyphenyl sulfide, mp 46-7°, (8) with the release of hydrogen chloride. Bis(4-methoxyphenyl) trisulfide and 4-chloroanisole were formed as by-products. It was observed that even solid iron like a nail promotes this sulfuration. The reaction was also successful with a trace amount of ferric chloride as catalyst. The use of sulfur dichloride instead of sulfur monochloride led also to a rapid formation of the sulfide, where no induction period was observed in the presence of iron-powder, different from the reaction with sulfur monochloride. This reaction was most advantageously carried out in the absence of light, for avoiding the formation of by-products from the disproportionation of the sulfur chlorides. The general pattern of the procedure is as follows. A red glass flask, which shields light of wave length below 6000 Å, fitted with a magnetic stirring bar, a red-glass dropping funnel and a condenser was flushed with nitrogen. In the flask were placed 1.0 mol of anisole and ca 30 mg of iron-powder at room temperature. Then a solution of 0.1 mol of an appropriate sulfur chloride in 20 ml of carbon tetrachloride was added in portions over a period of 2 hr. The mixture was stirred until the evolution of hydrogen chloride was complete (ca 1 hr). The products were isolated by distillation followed by recrystallization from ethanol. The yields of the products were as follows; Fe-S_2Cl_2 system, bis(4-methoxyphenyl) sulfide 74%, 2-methoxyphenyl 4-methoxyphenyl sulfide 5%, and bis(4-methoxyphenyl) trisulfide 18%; $FeCl_3$-S_2Cl_2 system, 77, 5, and 14%; Fe-SCl_2 system, bis(4-methoxyphenyl) sulfide 65%, 2-methoxyphenyl 4-methoxyphenyl sulfide 5%, and 4-chloroanisole 3%; $FeCl_3$-SCl_2 system, 57, 4, and 7%.

The sulfuration was tried for various types of aromatic compounds. Phenetole gave bis(4-ethoxyphenyl) sulfide and 2-ethoxyphenyl 4-ethoxyphenyl sulfide, mp 98-9°, (8) in yields of 74 and 8%, respectively with Fe-S_2Cl_2 system and 78 and 5% with Fe-SCl_2 system along with by-products resembled to the case of anisole. Diphenyl ether was converted to the extent of 70% into bis(4-phenoxyphenyl) sulfide, I, mp 100-2°, ($C_{24}H_{18}O_2S$ requires C, 77.84, H, 4.86. Found: C, 77.39, H, 4.98%. Sulfone, mp 136-8°, $C_{24}H_{18}O_4S$ requires C, 71.63, H, 4.51. Found: C, 71.36, H, 4.28%) with Fe-S_2Cl_2 system, and 58% with Fe-SCl_2 system. This type of sulfide has never been obtained by the reaction with aluminum catalysts, because the reaction of sulfur or sulfur monochloride with diphenyl ether or diphenyl sulfide in the presence of aluminum chloride, aluminum amalgam or aluminum metal gives such cyclization products as phenoxthine, II, (9) or thianthrene, III, (10) by attacking on their ortho positions. Iron catalysts as iron-powder or ferric chloride, however, facilitate the sulfuration with sulfur chlorides to the para positions giving open-chain aryl sulfides. Thus, diphenyl sulfide afforded the para sulfurated compound, i.e. bis(4-phenylthiophenyl) sulfide, IV, in 27% yield.



I



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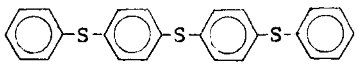

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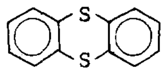
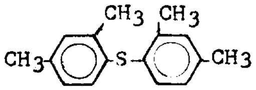
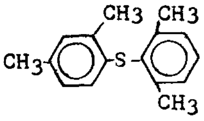


III

Among six positional isomers of sym-xylyl sulfides, only two compounds, i.e. bis(2,3-dimethylphenyl) sulfide (11) and bis(2,6-dimethylphenyl) sulfide (12) have been disclosed by this time, but the method for the preparation has been described only in the case of 2,6-isomer. According to the present method, addition of iron-powder to a mixture of sulfur monochloride and m-xylene at room temperature led to the formation of bis(2,4-dimethylphenyl) sulfide, V, bp 125-7°/0.36mm, ($C_{16}H_{18}S$ requires C, 79.31, H, 7.49. Found: C, 79.12, H, 7.41%) in 71% yield along with its structural isomer, i.e. 2,4-dimethylphenyl 2,6-dimethylphenyl sulfide, VI, mp 53-4°, (8) (6% yield) and bis(2,4-dimethylphenyl) disulfide (7% yield).



V



VI

This method of sulfuration thus appears to be of rather general utility and is particularly suited for the synthesis of symmetrical aryl sulfides with electron releasing substituents. In contrast with aluminum chloride, the iron-powder does not form the complex with aryl sulfide. Thus, there are several advantages in the present reaction: these include that a trace amount of iron-powder as catalyst is enough to promote the reaction, the procedure is so simple that the complicated treatment such as hydrolysis is not required, and the procedure is suited for a large scale synthesis of sulfides.

We consider that the sulfuration in the present paper is a type of electrophilic aromatic substitution analogous to the halogenation. It seems likely that sulfur chlorides behave similarly to chlorine in their aromatic substitution catalyzed by iron-powder, because the bond energy of sulfur-chlorine bond (59.7 Kcal/mol) is very close to that of chlorine-chlorine bond (58 Kcal/mol) (13).

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