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IRON-CATALYZED AROMATIC SULFURATION WITH SULFENYL CHLORIDES*

Tamotsu Fujisawa, Takeo Kobori, Noriko Ohtsuka and Gen-ichi Tsuchihashi
Sagami Chemical Research Center
Ohnuma, Sagamihara-shi, Kanagawa, 229, Japan

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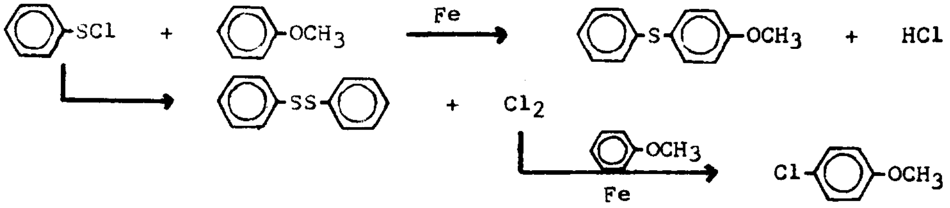
Although the study on aromatic substitution with sulfenyl halides has been well documented (1), a limited number of sulfenyl halides were used in the reaction. Almost all of them have electron with-drawing groups such as 2,4-dinitrophenyl (2), anthraquinonyl (3) or trichloromethyl (4) groups. Little is known about the reaction with sulfenyl chlorides having electron releasing groups (5) and aromatic sulfuration with benzenesulfenyl chloride or p-toluenesulfenyl chloride promoted by catalyst such as aluminum chloride has been reported to be unsuccessful (6). We have recently found that one of the mildest methods available for the sulfuration of aromatic compounds to sulfides consists in their iron-catalyzed reaction with sulfur chlorides (7). This observation prompted us to investigate a new route to the synthesis of asymmetrical aryl sulfides by iron-catalyzed reaction with various types of sulfenyl chlorides as starting materials.

Addition of a trace amount of iron-powder to a mixture of benzenesulfenyl chloride and excess anisole at room temperature led to the formation of a 43% yield of 4-methoxyphenyl phenyl sulfide (8) with the release of hydrogen chloride. Diphenyl disulfide (41% yield) and 4-chloroanisole (37% yield) were simultaneously obtained as by-products, formed by homolytic fission of the sulfenyl chloride.

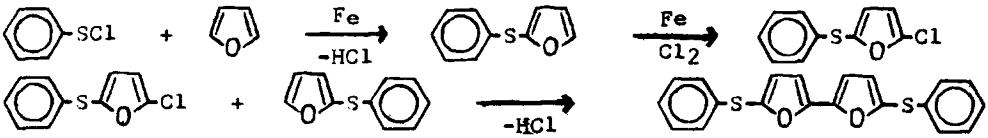


The suppression of this side-reaction was achieved by slow dropping (ca 30 min) of the sulfenyl chloride (0.1 mol) to a mixture of anisole (1.0 mol) and the catalyst (0.0005 g-atom) in absence of light (7) in a nitrogen atmosphere at room temperature. This resulted in a higher yield of 4-methoxyphenyl phenyl sulfide of 78%. The yields of diphenyl disulfide and 4-chloroanisole decreased to 20 and 2%, respectively. The similar reaction was also obserbed with a trace amount of ferric chloride as catalyst to give the sulfide in a yield of 72%. Thus the electrophilic aromatic substitution with benzenesulfenyl chloride proceeds smoothly in the presence of iron catalyst diffrent from the use of aluminum chloride as catalyst.

The stability and reactivity of substituted benzenesulfenyl chlorides are related to the nature of the substituents. When 2,4-dinitrobenzenesulfenyl chloride, a very stable sulfenyl chloride, was treated with anisole in the presence of iron-powder, no noticeable reaction occurred at room temperature; while, when the same reagents were heated at 100° for 8 hr, 2,4-dinitrophenyl 4-methoxyphenyl sulfide was obtained in a yield of 75% even in the presence of light. Substituted benzenesulfenyl chloride with chloro-, methyl-, or methoxy-substituent reacted smoothly with anisole in the presence of iron-powder at room temperature in the absence of light. Thus, 4-chlorobenzenesulfenyl chloride gave 4-chlorophenyl 4-methoxyphenyl sulfide, mp 60-1°, ($C_{13}H_{11}ClOS$ requires C, 62.27, H, 4.42. Found: C, 62.36, H, 4.72%) in a yield of 89% and 2-chlorobenzenesulfenyl chloride gave 2-chlorophenyl 4-methoxyphenyl sulfide, mp 57-8°, (Found: C, 61.98, H, 4.68%. Sulfone, mp 93-5°, $C_{13}H_{11}ClO_3S$ requires C, 55.22, H, 3.92. Found: C, 55.33, H, 4.14%) in a yield of 90%. Reaction of p-toluenesulfenyl chloride afforded 4-methylphenyl 4-methoxyphenyl sulfide, mp 47-8°, ($C_{14}H_{14}OS$ requires C, 73.02, H, 6.13. Found: C, 73.01, H, 6.14%) in 73% yield and similar treatment of o-toluenesulfenyl chloride gave 2-methylphenyl 4-methoxyphenyl sulfide in 75% yield. 4-Methoxybenzenesulfenyl chloride (9) was converted in a yield of 39% into bis(4-methoxyphenyl) sulfide along with bis(4-methoxyphenyl) disulfide (36% yield). As an aliphatic derivative, methanesulfenyl chloride reacted with anisole in the presence of iron-powder at room temperature giving 4-methoxyphenyl methyl sulfide in 30% yield.

The sulfuration of various types of aromatic compounds with benzenesulfenyl chloride was studied. Phenetole reacted in the presence of iron-powder giving 4-ethoxyphenyl phenyl sulfide, bp 126-7°/0.15mm, ($C_{14}H_{14}OS$ requires C, 73.02, H, 6.13. Found: C, 73.19, H, 6.12%. Sulfone, mp 115-7°, $C_{14}H_{14}O_3S$ requires C, 64.11, H, 5.38. Found: C, 64.55, H, 5.13%) in 77% yield. The reaction of diphenyl ether gave 4-phenoxyphenyl phenyl sulfide, mp 54-6°, in a yield of 79%. With aromatic hydrocarbons, m-xylene gave 2,4-dimethylphenyl phenyl sulfide in a yield of 83% along with its structural isomer, 2,6-dimethylphenyl phenyl sulfide (3% yield). The reaction of p-xylene with benzenesulfenyl chloride in the presence of iron-powder, however, gave expected 2,5-dimethylphenyl phenyl sulfide in a yield of only 3%, but the main product was 1,4-bis(phenylthio)-2,5-dimethylbenzene in 46% yield. This result shows that the initial sulfuration leads to the increase of the reactivity of the free position para to the sulfur atom, resulting in further sulfuration with the sulfenyl chloride to form the compound with two sulfide linkages.

This sulfuration technique has been applied to heterocyclic aromatic compounds. The reaction of thiophene with benzenesulfenyl chloride in the presence of the catalyst at room temperature gave phenyl 2-thienyl sulfide and 2,5-bis(phenylthio)thiophene in yields of 33 and 40%, respectively. The latter compound was formed by the double sulfuration as mentioned above. On the other hand, the sulfuration of furan gave 5,5'-bis(phenylthio)-2,2'-bifuryl, mp 134-5°, ($C_{20}H_{14}S_2$ requires C, 68.46, H,3.96. Found: C, 68.57, H, 4.03%. Sulfone, mp 197-8°, $C_{20}H_{14}O_4S_2$ requires C, 57.77, H, 3.32. Found: C, 57.98, H, 3.41%) in 13% yield along with 2-furyl phenyl sulfide (3% yield), but the doubly sulfurated compound i. e. 2,5-bis(phenylthio)furan could not be obtained. In this case, the formation of a considerable amount of polymeric substance and diphenyl disulfide (51% yield) was observed. Since 5-position of the furan ring in 2-furyl phenyl sulfide is quite reactive, the bifuryl derivative might be formed according to the following equation.



The present reaction provides a facile synthetic route for asymmetrical aryl sulfides, whereas the method in the preceding letter (7) is suited for the synthesis of symmetrical aryl sulfides. Further development of this mild and selective sulfuration technique will shortly be reported in detail.

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8. The structures of all compounds described in this letter were determined by the study of their infrared and nmr spectra. Yield determinations were carried out by glpc.
9. Since the compound was decomposed in vacuum distillation, it was used without purification.