

ORTHO EFFECT OF THE NITRO GROUP ON IRON-CATALYZED
AROMATIC SULFURATION WITH SUBSTITUTED BENZENETHIOSULFENYL CHLORIDES*

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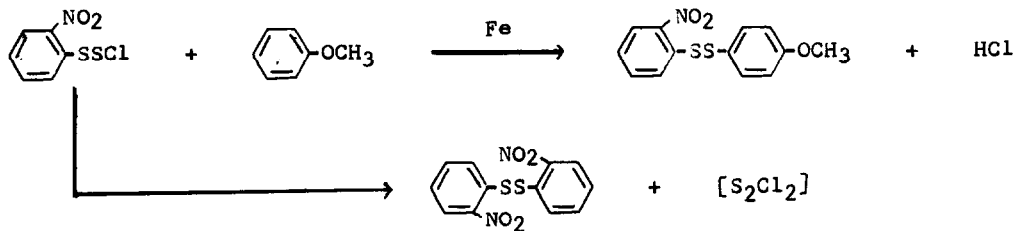
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The direct sulfuration of aromatic nucleus with sulfur chlorides in the presence of a trace amount of iron-powder provides a convenient method for the preparation of symmetrical sulfides (1), and the reaction proceeds through thio-sulfenyl chloride and sulfenyl chloride as intermediates (2). This observation was quickly followed by the development of iron-catalyzed aromatic sulfuration with sulfenyl chlorides, which provides a facile synthetic route for unsymmetrical aryl sulfides (3). Further, during the course of the study on aromatic sulfuration with substituted benzenethiosulfenyl chlorides, the product composition of the reaction of anisole with nitrobenzenethiosulfenyl chlorides was found to depend on whether the nitro group was ortho or para. We now wish to report on the latter observation in this letter.

Addition of 2-nitrobenzenethiosulfenyl chloride (4) to a mixture of anisole and a trace amount of iron-powder in the absence of light (1) in an argon atmosphere at room temperature led to the release of hydrogen chloride. After completion of the reaction, unreacted anisole was removed by distillation, and the residue was extracted with ether. The extract was evaporated and the resulting solid was recrystallized from ethanol. This crystalline material was shown to be 4-methoxyphenyl 2-nitrophenyl disulfide by elementary analyses and nmr and ir spectra (mp 73-5°, $C_{13}H_{11}NO_3S_2$ requires C, 53.24, H, 3.75, N, 4.78, S, 21.84%. Found: C, 53.05, H, 3.83, N, 4.88, S, 21.99%). The unextracted residue was identified as bis(2-nitrophenyl) disulfide by comparing its ir and nmr spectra with those of an authentic sample. The bis(2-nitrophenyl) disulfide may have been formed by decomposition of the thiosulfenyl chloride. The yields of the



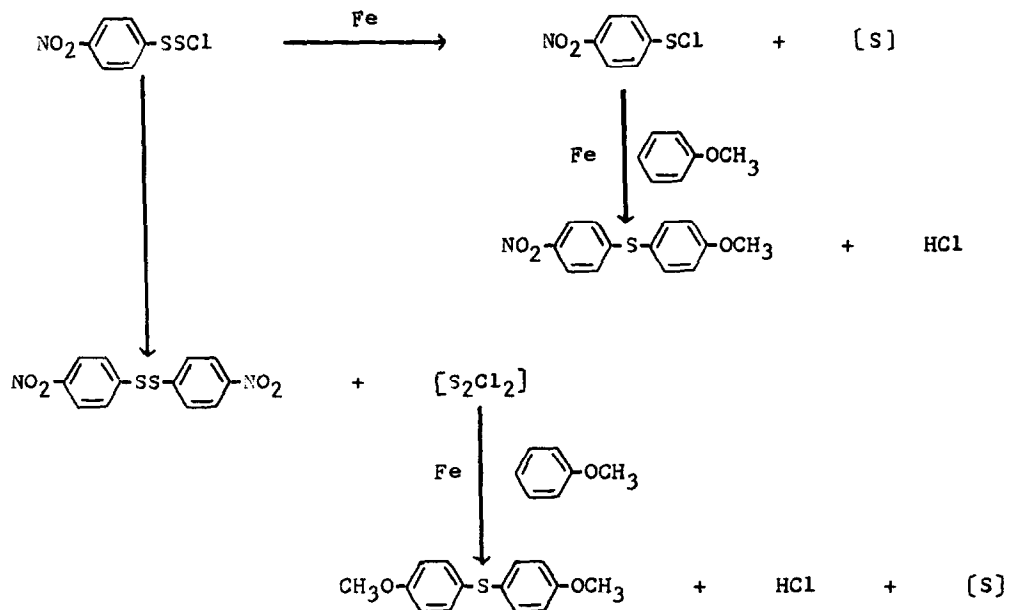
unsymmetrical disulfide and symmetrical disulfide were 61 and 7%, respectively.

In addition, the formation of unsymmetrical monosulfide, 4-methoxyphenyl 2-nitrophenyl sulfide, and bis(4-methoxyphenyl) sulfide was confirmed by glpc in yields of 27 and 17%, respectively (5).

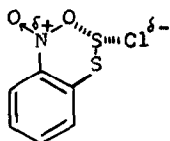
Harris (4) has reviewed the chemistry of 2-nitrobenzenethiosulfonyl chloride, which is stable and reacts with phenols (substitution) and olefins (addition) to give the corresponding disulfide compounds. Thus, the observed formation of the unsymmetrical disulfide, as a main product of iron-catalyzed aromatic sulfuration with the thiosulfonyl chloride, was to be expected.

On the other hand, the similar reaction of anisole with 4-nitrobenzenethiosulfonyl chloride (6), in the presence of a trace amount of iron-powder, affords an unsymmetrical monosulfide, 4-methoxyphenyl 4-nitrophenyl sulfide, in 50% yield. As by-products, bis(4-nitrophenyl) disulfide and bis(4-methoxyphenyl) sulfide were obtained in yields of 48 and 37%, respectively (5). However, the expected unsymmetrical disulfide, 4-methoxyphenyl 4-nitrophenyl disulfide, could not be detected. This reaction may be explained by the following scheme, involving an initial formation of the corresponding sulfonyl chloride by the decomposition of the thiosulfonyl chloride in the presence of iron-powder. The sulfonyl chloride subsequently reacts with anisole to form an unsymmetrical aryl sulfide by loss of hydrogen chloride. Moreover, homolytic fission of the thiosulfonyl chloride gives a symmetrical aryl disulfide and sulfur chloride. The latter reacts also with anisole in the presence of iron-powder to give bis(4-methoxyphenyl) sulfide as mentioned in the preceding paper (1).

This difference in the products of the two sulfuration reactions is attributable to an ortho effect of the nitro group of 2-nitrobenzenethiosulfonyl chloride



in which the thiosulfonyl chloride is stabilized by sulfur-oxygen interaction as shown:



Extensive study on the iron-catalyzed aromatic sulfuration with various types of thiosulfonyl chlorides is now in progress.

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3. T. Fujisawa, T. Kobori, N. Ohtsuka and G. Tsuchihashi, Tetrahedron Letters, 5071 (1968).
4. J. F. Harris, Jr., Doctoral Dissertation, Univ. of Pennsylvania (Univ. Microfilms, Pub. No. 4927); Dissertation Abstr., 13, 177 (1953); Chem. Abstr., 48, 2636e (1954).
5. The yields of the products were calculated based on the thiosulphenyl chlorides as starting materials.
6. This compound was prepared from the corresponding thiophenol and sulfur dichloride and had mp 35-7°. $C_6H_4ClNO_2S_2$ requires S, 28.96%. Found: S, 29.03%. Nmr (CCl_4): δ 7.64 (D) and 8.12 (D).