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NITRO-GROUP DISPLACEMENT FROM 1-NITRONAPHTHALENE BY REACTION WITH SULPHUR

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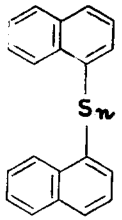
Although displacement of the nitro-group from activated aromatic compounds is well known (1), it has recently been reported that a nitro-group could also be displaced from unactivated nitro compounds such as p-nitrotoluene by the reaction with triethyl phosphite (2).

We now report that elemental sulphur is also effective in displacing the nitro-group from an unactivated aromatic compound, namely, from 1-nitronaphthalene. This reaction can be carried out in a sulphur- 1-nitronaphthalene melt (230°) or in a high boiling solvent such as 1,2,4-trichlorobenzene (b.p. 210°) and gives rise to a mixture of 1,1'-dinaphthyl sulphide (I), 1,1'-dinaphthyl disulphide (II) and trisulphide (III), several highly coloured unidentified products, sulphur dioxide, oxides of nitrogen and polymeric material. A partial separation of the products could be achieved by preparative thin layer chromatography but the sulphide-polysulphide components of the mixture all had very similar R_F's and could not be resolved.



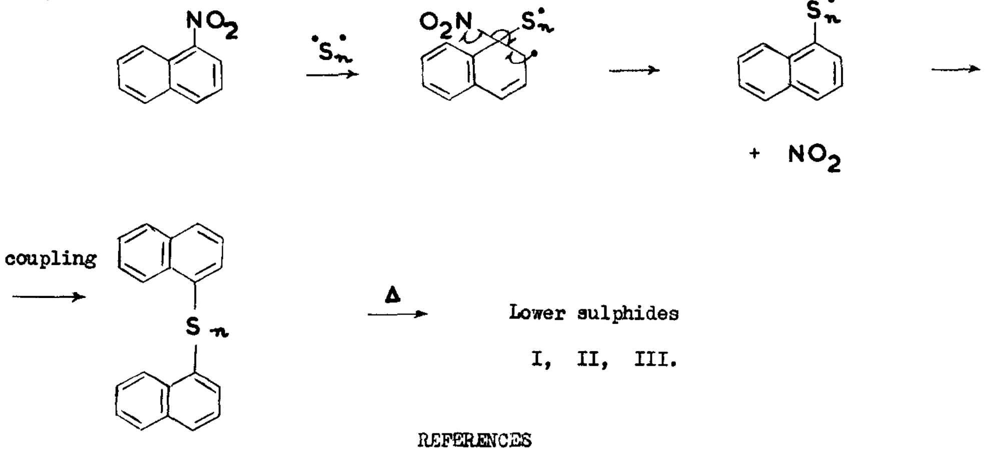
I, n=1

II, n=2

III, n=3

The overall yield of the sulphide-polysulphide mixture was ca. 10%. The mass spectrum of this mixture showed molecular ion peaks at m/e 286, 318, 350 due to the sulphide (I), disulphide (II) and trisulphide (III) respectively. The identity of these components was confirmed by comparison with the spectral and chromatographic properties of authentic samples of (I) (3), (II) (4) and (III) (5). Elemental analysis of this mixture (24.7% S) revealed that the major components were in fact the disulphide (II) and trisulphide (III). It is possible however, that smaller quantities of higher polysulphides may also be present, but they exhibit no molecular ion in the mass spectrum.

Since 1-nitronaphthalene is unactivated towards nucleophilic attack, the direct nucleophilic replacement of the nitro-group by sulphur appears unlikely. However sulphur has previously been shown to be effective in replacing $^{35}SO_2$ from ^{35}S labelled diphenyl sulphone, and a radical mechanism has been suggested (6). Similarly, the dinaphthyl sulphides (I), (II) and (III) may result from attack by sulphur radicals on 1-nitronaphthalene and this mechanism is outlined below.



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