

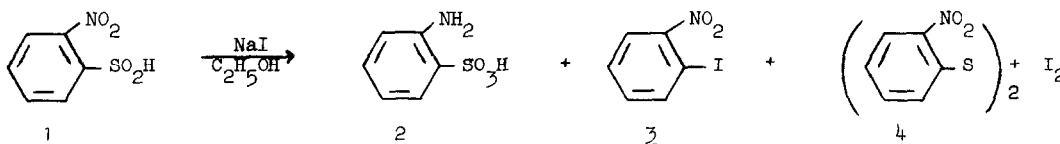
ORTHANILIC ACID FROM THE REACTION OF o-NITROBENZENESULFINIC
ACID WITH SODIUM IODIDE

A. Wagenaar and Jan B.F.N. Engberts*

Department of Organic Chemistry, The University,
Zernikelaan, Groningen, The Netherlands.

(Received in UK 25 September 1973; accepted for publication 10 October 1973)

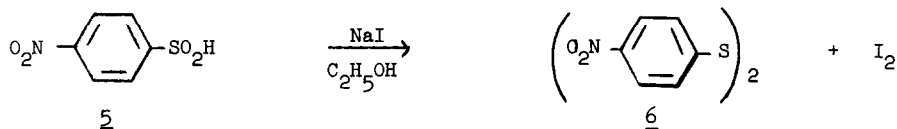
We wish to report a novel redox reaction in which o-nitrobenzenesulfinic acid (1) is transformed into orthanilic acid (2). Thus, reaction of 1 with six equivalents of sodium iodide in ethanol at 70° for 17 hours afforded 2 (49%) as the major product while the other products identified were o-iodonitrobenzene (3, 37%), the disulfide 4 (2%) and iodine. For complete conversion of 1 approximately two equivalents of sodium iodide were necessary.²



No reaction occurs when 1 is treated under the same conditions with sodium chloride, sodium bromide or sodium hydroxide. The conversion of 1 with sodium iodide is clearly dependent on the acidity of the medium since sodium o-nitrobenzenesulfinate remains unchanged under the employed reaction conditions while in the presence of 0.75 N hydrogen chloride 4 becomes the dominant product and no 2 is formed. The stability of both ethyl o-nitrobenzenesulfinate and methyl o-nitrophenyl sulfide toward sodium iodide in neutral ethanol at 70° indicates that the redox reaction is rather specific for 1.

No decision on the precise mechanism of formation of 2 can be made at the moment. In view of the well documented ability of iodide anions to act as reducing agents,³ we tentatively suggest that the (di)anion radical derived from 1 or its anion by one electron transfer from iodide should be invoked as an initial short-lived intermediate.⁴ The formation of iodine might also be

accounted for by this hypothesis. Although labelling studies are clearly needed to establish an intramolecular oxygen transfer process, it is plausible to suppose neighbouring group interaction⁵ since the reaction of p-nitrobenzenesulfinic acid (5) under analogous conditions yielded the disulfide 6 (80%) and iodine.⁶ No sulfonic acid could be detected.



Intramolecular transfer of oxygen in o-substituted nitrobenzene derivatives has been found previously⁵, the photochemical isomerization of o-nitrobenzaldehyde into o-nitrosobenzoic acid being the classical example.⁷

The selective reduction of the sulfinic acid functionalities of 1 and 5 to the disulfides 4 and 6, respectively, is noteworthy. Disulfides have formerly been produced from sulfinic acids by electrolytic⁸ and aluminium hydride reduction.⁹ The reaction of sulfinic acids with hydrogen bromide in acetic acid is known to afford the corresponding sulfenyl bromide and bromine.¹⁰

References and footnotes.

1. All organic reaction products were identified by comparison of their m.p.'s and IR and NMR spectral data with those of authentic materials.
2. Determined by careful titration of iodine with sodium thiosulfate.
3. See, for instance, S.L. Walters and T.C. Bruice, *J. Amer. Chem. Soc.* **93**, 2269 (1971).
4. A paramagnetic species is easily generated upon electrolysis of 1 in DMF and showed the following ESR hyperfine splitting constants: $a_{\text{N}} = 9.6$ gauss, $a_{\text{H}} = 3.8$ (1H), 3.2 (1H) and 1.1 (2H) gauss. Since the sodium salt of 1 gives the same spectrum, the species is most likely the dianion radical $\text{O}-\text{NO}_2\text{C}_6\text{H}_4\text{SO}_2^{2-}$.
5. For an extensive review, see P.N. Preston and G. Tennant, *Chem. Revs.* **72**, 627 (1972).
6. Reduction of a nitro function to an amino group has been accomplished with amino-iminomethanesulfinic acid as the reducing agent: P.H. Gore, *Chem. Ind.* 1355 (1954).
7. D.C. Neckers, "Mechanistic Organic Photochemistry", Reinhold Publ. Corp., New York, N.Y. p. 207 (1967).
8. S. Takagi, T. Suzuki, and K. Imaeda, *J. Pharm. Soc. Japan*, **69**, 358 (1949).
9. J. Strating and H.J. Backer, *Rec. Trav. Chim.*, **69**, 638 (1950).
10. K. Fries and G. Schürmann, *Chem. Ber.* **47**, 1195 (1914).