Hydroxydenitration by a Nef-type Process; the More General Case

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Summary With CN⁻ anions in dipolar aprotic solvents 2- and 4-nitroisophthalonitriles yield 2- and 4-hydroxy-isophthalonitriles through an induced Nef-type disruption of the nitro-group; halide ions (Br⁻ and I⁻) under the same conditions yield 5-halogeno-2-hydroxy- and 5-halogeno-4-hydroxy-isophthalonitrile, respectively.

We previously[1] reported the synthesis of *o*-cyanophenols by the action of KCN in dimethyl sulphoxide on compounds containing an activated nitro-group. The mechanism of this reaction when 2-hydroxy-isophthalonitrile (1) is formed from *o*-cyanonitrobenzene has been explained[2] in terms of the breakdown of an anionic intermediate (2) in a Nef-type process involving evolution of nitrous oxide; the overall reaction is represented by equation (1). While our recent

$$R(H) \cdot NO_2 + KCN \longrightarrow R(CN) \cdot OK + \tfrac{1}{2}N_2O + \tfrac{1}{2}H_2O \quad (1)$$

observations support this interpretation we have additionally studied the reaction of KCN with 2-nitroisophthalonitrile in which either (a) direct displacement of NO_2 by CN, or (b) attack by CN⁻ ion at the *para*-position to the NO_2-group followed by hydroxydenitration[3] might be expected. In Me_2SO or dimethylformamide at 100 °C formation of benzene-1,2,3-tricarbonitrile† (*ca.* 15%) takes place by route (a) but evidence for reaction by route (b) has not been found. The main product (65—75%) is (1). A rapidly evolved gaseous mixture contains N_2O, CO_2 (>20%), and HCN (12%) with minor components probably including NO, NO_2, and $(CN)_2$; a black resinous material (*ca.* 10%) is also produced. 2-Nitroisophthalonitrile has thus to be

† New compounds have given satisfactory analytical and spectroscopic data.

considered as a possible intermediate in the formation of (1) from *o*-cyanonitrobenzene when an excess of KCN is present, prior oxidation of (2) being postulated.[1] However, since benzene-1,2,3-tricarbonitrile, HCN, or CO_2 have not been found among the reaction products this possibility is eliminated and the mechanism suggested by Chapas *et al.*[2] is supported.


(1)   (2)   (3)

(4), X = I or Br   (5), X = I or Br   (6)
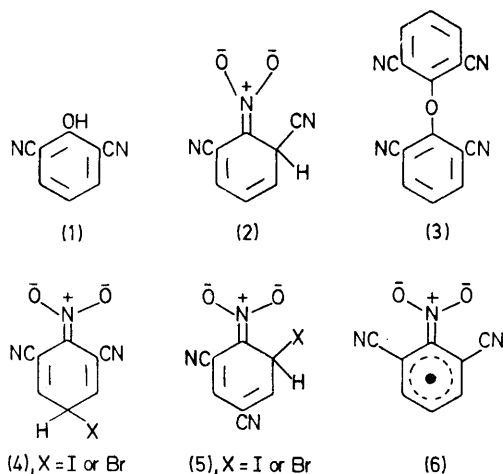
2-Nitroisophthalonitrile is known to undergo normal displacement of the nitro-group by phenolate anions in Me_2SO[4] and the formation of (3) when the foregoing reaction is conducted with < 1 mol of KCN therefore provides evidence for the presence of the anion of (1) in the solution before work-up. Similarly with LiCl in Me_2SO at 100 °C reaction occurs mainly by route (a) to give 2-chloro-

isophthalonitrile (60%). With KI, however, it seems that route (b) is operative; at 100 °C oxides of nitrogen are rapidly evolved and 2-hydroxy-5-iodoisophthalonitrile (60%) is formed, presumably through the intermediate (4). With NaBr at 100 °C the reaction is slower and gives rise to both 2-bromoisophthalonitrile and 5-bromo-2-hydroxy-isophthalonitrile.

4-Nitroisophthalonitrile also reacts anomalously with KCN in Me_2SO at 100 °C even though one *ortho*-position is unsubstituted; the product is 4-hydroxy-isophthalonitrile (70—80%) and a gaseous mixture similar to that obtained with the 2-isomer is rapidly evolved. With NaBr and with KI, however, the main reaction products in Me_2SO at 100 °C are 4-hydroxy-5-bromo- (*ca.* 65%) and 4-hydroxy-5-iodo-isophthalonitrile (*ca.* 45%) respectively, presumably formed through the intermediate (5), oxides of nitrogen being evolved.

The failure of the CN^- anion to react at the unoccupied *para*- or *ortho*-positions in these examples, while it yet induces disruption of the nitro-group, suggests that CN^- may discharge to CN· radical at an early stage in the reaction and that fragmentation then occurs in a radical anion (*e.g.* 6) to yield the dicyanophenolate anion. Evolution of HCN indicates reaction of CN· radical with solvent and the CO_2 is an expected end-product since the reaction represents overall a reduction by KCN as shown in equation (2). In the novel iodinations described above formation of

$$R{\cdot}NO_2 + KCN \rightarrow R{\cdot}OK + \tfrac{1}{2}N_2O + \tfrac{1}{2}O + CN \qquad (2)$$
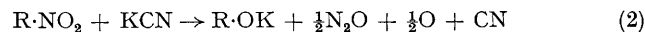
isolable amounts of unhalogenated dicyanophenol also occurs.

[1] J. H. Gorvin, *Chem. Comm.,* 1971, 1120; B.P. 1,395,893 (1975).
[2] R. B. Chapas, R. D. Knudsen, R. F. Nystrom, and H. R. Snyder, *J. Org. Chem.,* 1975, **40**, 3746.
[3] R. G. Landolt and H. R. Snyder, *J. Org. Chem.,* 1968, **33**, 403.
[4] H. F. Hodson, J. F. Batchelor, and J. H. Gorvin, B.P. 1,414,621 (1975).