

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.

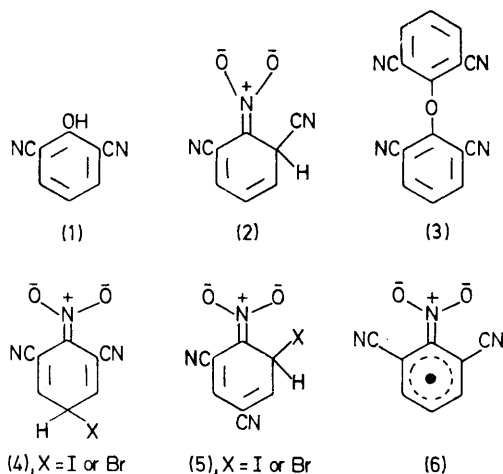
We previously¹ reported the synthesis of *o*-cyanophenols by the action of KCN in dimethyl sulphoxide on compounds containing an activated nitro-group. The mechanism of this reaction when 2-hydroxy-isophthalonitrile (**1**) is formed from *o*-cyanonitrobenzene has been explained² in terms of the breakdown 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



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 hydroxydenitration³ 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 $(\text{CN})_2$; 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 CO₂ have not been found among the reaction products this possibility is eliminated and the mechanism suggested by Chapas *et al.*² is supported.

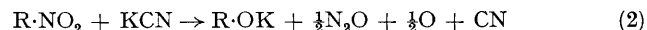


2-Nitrosophthalonitrile is known to undergo normal displacement of the nitro-group by phenolate anions in Me₂SO⁴ and the formation of (3) when the foregoing reaction is conducted with < 1 mol of KCN therefore provides evidence for the presence of the anion of (1) in the solution before work-up. Similarly with LiCl in Me₂SO 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-Nitrosophthalonitrile also reacts anomalously with KCN in Me₂SO 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 Me₂SO 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 CO₂ 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



isolable amounts of unhalogenated dicyanophenol also occurs.

(Received, 10th September 1976; Com. 1033.)

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).