Displacement of Mobile Nitro-groups in Reactions with Cyanide Ion. A New Route to *o*-Cyanophenols†

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Summary Aromatic compounds containing a mobile nitro-group may be converted into *o*-cyanophenols by cyanide ion in dipolar aprotic solvents.

ALTHOUGH in dipolar aprotic solvents a mobile aromatic nitro-group is readily replaced by an alkoxy-group,[1] its replacement by a cyano-group occurs only exceptionally,

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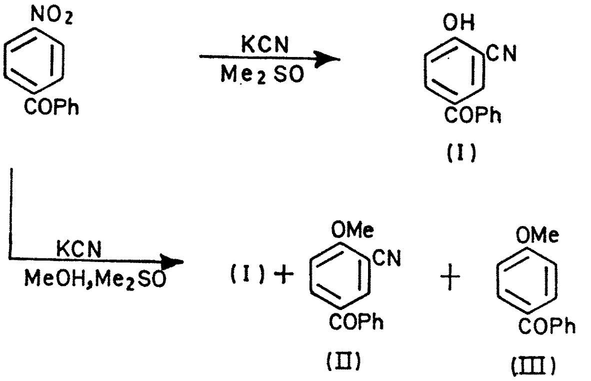
† Application has been made for provisional patent.

e.g. in 1-nitroxanthone which with KCN in dimethyl sulphoxide gives 1-cyanoxanthone‡ in 75% yield. It has now been found that the predominating reaction with 3-nitroxanthone and other compounds studied is attack by CN^- ion *ortho* to the nitro-group, as in the von Richter reaction, followed by replacement of NO_2 by OH. Thus in a typical reaction, when 4-nitrobenzophenone is heated with KCN (3 mols) in Me_2SO at 100° for 3 h the acidic fraction of the product consists of 5-benzoylsalicylonitrile (I) (55—60%);§ a complex mixture of azoxy- and azo-compounds is formed as a neutral fraction. A similar but slower reaction occurs in dimethylformamide and in hexamethylphosphoramide. If methanol (10 mols) is added to the initial reaction mixture the yield of (I) is reduced and the neutral azo-fraction contains 5-benzoyl-2-methoxybenzonitrile (II) (*ca.* 10%)§ in addition to the expected[1] 4-methoxybenzophenone (III) (5%).



The known formation of 2-cyano-3-methoxynitrobenzene from 1,3-dinitrobenzene in methanol has been explained[2] by intermolecular hydride transfer induced by CN^- followed by displacement of the nitro-group by OMe^-. Although in the present reactions no intermediate such as 5-benzoyl-2-nitrobenzonitrile has been isolated, its formation and rapid reaction with hydroxyl ion (or added OMe^-) is a reasonable supposition. Intensive drying of solvent and reagents does not impede the reaction but hydroxyl ions are inevitably present as a result of the reduction (presumably by hydride ion) of a proportion of the nitro-groups to azoxy- and azo-groups.

In the related reactions with 4-nitroquinoline 1-oxides recently described by Himeno, Noda, and Yamazaki[3] it would appear that, after attack by CN^- ion at the 3-position, hydride ion is preferentially removed by reduction of amine oxide to amine. Among various nucleophiles which can then displace the nitro-group the authors do not mention the hydroxyl ion: on the other hand they report attack by a second CN^- ion to give a 3,4-dicyanoquinoline to which I have found no parallel in the benzene series.

Results with a series of nitrobenzenes containing such activating substituents as *p*-$PhSO_2$, *o*- and *p*-CN, and *p*-CO_2Et indicate some generality in this route to *o*-cyanophenols,¶ which in the first three instances are produced in *ca.* 60% yield (concurrent ester hydrolysis reduces the yield from ethyl *p*-nitrobenzoate). On acidic hydrolysis the products afford 5-benzenesulphonylsalicylic acid,[6] 2-hydroxyisophthalic acid, and 4-hydroxyisophthalic acid respectively. From 3-nitroxanthone with KCN in $HCONMe_2$ or Me_2SO is obtained 4-cyano-3-hydroxyxanthone (60—70%), and 1-nitroxanthone gives 2-cyano-1-hydroxyxanthone (10%) as a by-product from the reaction in Me_2SO. Compounds containing more than one mobile nitro-group seem, however, to give complex products.

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‡ Identical with material prepared from 1-aminoxanthone by the Sandmeyer reaction (*cf.* ref. 4.)

§ Identical with material prepared from salicylonitrile by method of Erndt.[5]

¶ New compounds have given satisfactory analytical and spectroscopic data.

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