Conversion of 2-Nitrobenzonitrile into Benzoic Acid

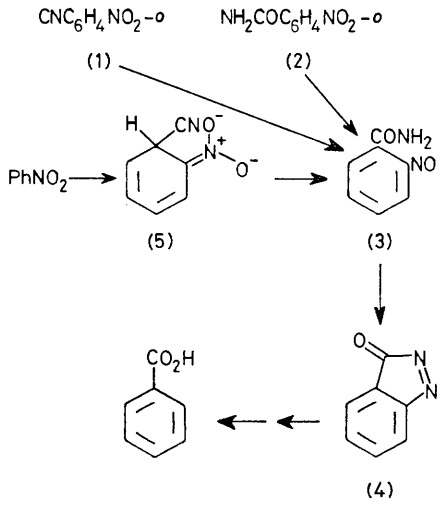
By ANDREA C. ELLIS and IAN D. RAE*

(*Chemistry Department, Monash University, Clayton, Victoria* 3168, *Australia*)

Summary 2-Nitrobenzonitrile and 2-nitrobenzamide, when heated with aqueous-alcoholic sodium hydroxide, give benzoic acid; the reaction is believed to proceed *via* 2-nitrosobenzamide as does the von Richter reaction.

WHEN 2-nitrobenzonitrile (**1**) was heated with aqueous-ethanolic sodium hydroxide, a 70% yield of benzoic acid was obtained. An equivalent amount of nitrogen was evolved and, when D_2O was used in place of H_2O, a single deuterium

was found in the *ortho* position of the benzoic acid. 2-Nitrobenzoic acid was stable under these conditions but 2-nitrobenzamide (**2**) reacted to give benzoic acid (78%).



SCHEME

The ethanol could be replaced by methanol or isopropyl alcohol but the reaction did not proceed in water or in aqueous t-butyl alcohol. 2,4-Dimethyl-6-nitrobenzonitrile was converted into 2,4-dimethylbenzoic acid in 87% yield.

These reactions resemble the von Richter reaction[1] in which a nitrile group enters *ortho* to NO_2 followed by removal of the nitro-group and hydrolysis of the nitrile. The von Richter reaction has been found to proceed *via* 2-nitrosobenzamide (**3**)[2] and indazol-3-one (**4**)[3] as shown in the Scheme. The reduction of an aromatic nitro-group by alcoholic base is well known.[4] Thus the formation of 2-nitrosobenzamide from the nitro-compounds (**1**) and (**2**), and subsequent reaction by the von Richter pathway, can explain this unusual loss of a nitro-group. Alternatively, the ion (**5**) might be produced by hydride donation from the solvent, allowing an earlier access to the von Richter pathway.

We find it remarkable that such a reaction has not been previously reported, despite reports of hydrolyses of 2-nitrobenzamide.[5] Reid, in his autobiography, mentions 'a by-product of the alkaline hydrolysis of *ortho*-nitrobenzamide' which remained unidentified.[6]

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[5] E. E. Reid, *Amer. Chem. J.*, 1899, **21**, 284; 1900, **24**, 397.
[6] E. E. Reid, 'My First One Hundred Years,' Chemical Publishing Co., New York, 1972, p. 85.