

## Conversion of 2-Nitrobenzonitrile into Benzoic Acid

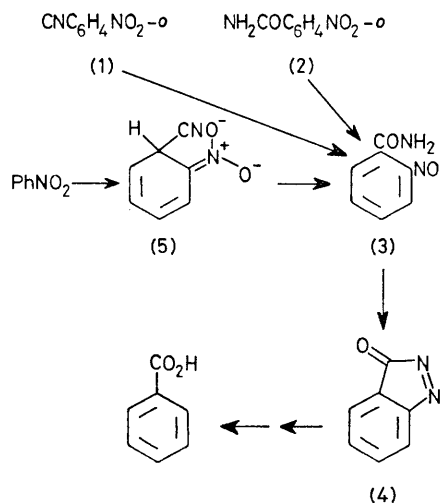
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**Summary** 2-Nitrobenzonitrile and 2-nitrobenzamide, when heated with aqueous-alcoholic sodium hydroxide, give benzoic acid; the reaction is believed to proceed *via* 2-nitrosobenzamide as does the von Richter reaction.

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<sub>2</sub>O was used in place of H<sub>2</sub>O, 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

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<sup>1</sup> V. von Richter, *Ber.*, 1871, **4**, 21, 459, 553; M. Rosenblum, *J. Amer. Chem. Soc.*, 1960, **82**, 3796.

<sup>2</sup> K. M. Ibne-Rasa and E. Koubek, *J. Org. Chem.*, 1963, **28**, 3240.

<sup>3</sup> E. F. Ullman and E. A. Bartkus, *Chem. and Ind.*, 1962, 93.

<sup>4</sup> C. M. Suter and F. B. Dains, *J. Amer. Chem. Soc.*, 1928, **50**, 2733.

<sup>5</sup> E. E. Reid, *Amer. Chem. J.*, 1899, **21**, 284; 1900, **24**, 397.

<sup>6</sup> E. E. Reid, 'My First One Hundred Years,' Chemical Publishing Co., New York, 1972, p. 85.

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<sup>1</sup> in which a nitrile group enters *ortho* to  $\text{NO}_2$  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)<sup>2</sup> and indazol-3-one (4)<sup>3</sup> as shown in the Scheme. The reduction of an aromatic nitro-group by alcoholic base is well known.<sup>4</sup> 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.<sup>5</sup> Reid, in his autobiography, mentions 'a by-product of the alkaline hydrolysis of *ortho*-nitrobenzamide' which remained unidentified.<sup>6</sup>