

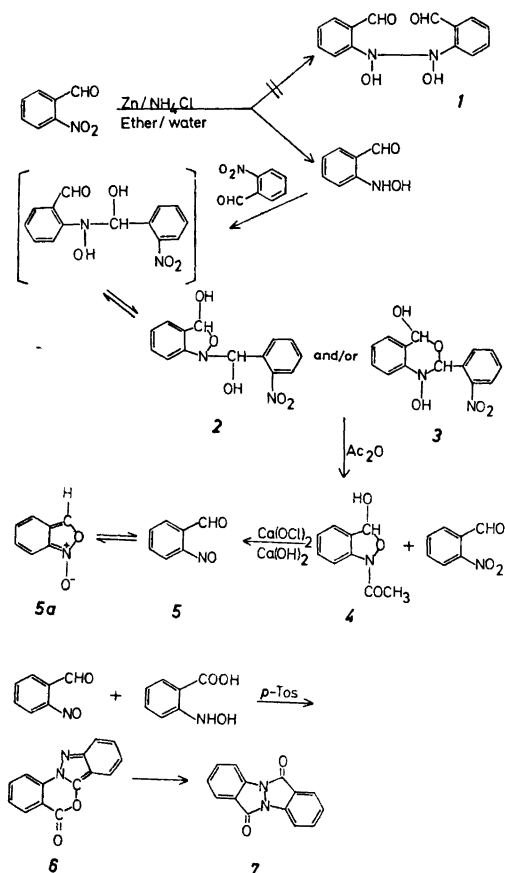
o-Nitrosobenzaldehyde, Reactions under Acidic Conditions

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In a study of the reactions of *o*-nitrosobenzyl alcohol under acidic conditions, *o*-nitrosobenzaldehyde was suggested as a possible intermediate.¹ This compound was synthesised at the beginning of the century, but no conclusive evidence as to its authenticity was given. Thus only the elemental analyses were reported.^{2,3} No later studies have been reported, except for the recording of the mass spectrum.⁴ Modern techniques should make it possible to establish the structure, and also to determine if the open structure **5** or the cyclic form **5a** is predominant.⁵

Bamberger reduced *o*-nitrosobenzaldehyde with zinc in ethyl ether/water, and obtained a com-



ound called agnotobenzaldehyde. On reaction with acetic anhydride, agnotobenzaldehyde gave one mol of *o*-nitrosobenzaldehyde and one of a substance believed to be *N*-acetyl-*o*-hydroxylaminobenzaldehyde. Oxidation of this compound with calcium hypochlorite gave the product identified as *o*-nitrosobenzaldehyde.³ On repetition, the synthetic steps proceeded as described by Bamberger.

The spectra (Experimental) of the product *o*-nitrosobenzaldehyde showed the structural assignment by Bamberger to be correct. The unusually large anisotropic effect of the nitroso group, giving an upfield shift for the *ortho* benzene hydrogen, and a downfield shift for benzyl hydrogens has been reported.⁶ The same effect is found in *o*-nitrosobenzaldehyde, a doublet at δ 6.5 being due to the hydrogen *ortho* to the nitroso group and a singlet at δ 12.1 to the aldehyde hydrogen. This appears to be the lowest δ -value reported for an aldehyde hydrogen.

o-Nitrosobenzaldehyde seems to consist entirely of the open form (**5**), as shown by the strong carbonyl band in the IR spectrum and the normal extinction coefficient in the electronic spectrum. No indications of the nitrone form **5a** could be found by IR^{10,11} or NMR spectroscopy.

Spectroscopic investigations of the synthetic intermediates showed agnotobenzaldehyde not to be **1** as proposed by Bamberger³ but probably **2** or **3**. The IR spectrum showed no carbonyl groups to be present but NH or OH together with nitro groups. In solution, the spectrum changed and had the bands of *o*-nitrosobenzaldehyde together with bands possibly due to *o*-hydroxylaminobenzaldehyde.

The compound from acetylation of agnotobenzaldehyde was not *N*-acetyl-*o*-hydroxylaminobenzaldehyde,³ but the isomeric compound **4**. IR showed no aldehyde band, but an NH or OH band together with an amide band. NMR contained an AB pattern, which collapsed to a singlet on addition of deuterium oxide (methine proton).

In the reaction of *o*-nitrosobenzyl alcohol, 6*H*, 12*H*-indazolo[2,1-*a*]indazole-6,12-dione (**7**) was a product. A possible reaction path was proposed to proceed *via* *o*-nitrosobenzaldehyde which gave **7** *via* **6**.¹ To test this proposal, *o*-nitrosobenzaldehyde and *o*-hydroxylaminobenzoic acid^{1,10} were reacted together in refluxing toluene with *p*-toluenesulfonic acid. After 5 min reflux, *o*-nitrosobenzaldehyde had reacted completely and **6** (22%) and **7** (14%) were formed. On continued reflux (0.5 h), the yield of **7** was 18% and of **6** 13%.

The compound **7** was also formed (29%) when *o*-nitrosobenzaldehyde was refluxed alone with *p*-toluenesulfonic acid in toluene. Traces (2%) of the lactone **6** were formed, as in the reaction of *o*-nitrosobenzyl alcohol.¹ *o*-Hydroxylaminobenzoic acid refluxed alone with *p*-toluenesulfonic acid, did not give **6** or **7**.

