## o-Nitrosobenzaldehyde, Reactions under Acidic Conditions

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In a study of the reactions of o-nitrobenzyl alcohol under acidic conditions, o-nitrosobenzaldehyde was suggested as a possible intermediate. 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. No later studies have been reported, except for the recording of the mass spectrum. 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.

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

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pound called agnotobenzaldehyde. On reaction with acetic anhydride, agnotobenzaldehyde gave one mol of o-nitrobenzaldehyde 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.<sup>3</sup> 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. The same effect is found in o-nitrosobenzaldehyde, a doublet at  $\delta$  6.5 being due to the hydrogen ortho to the nitroso group and a singlet at  $\delta$  12.1 to the aldehyde hydrogen. This appears to be the lowest  $\delta$ -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 <sup>10,11</sup> or NMR spectroscopy.

Spectroscopic investigations of the synthetic intermediates showed agnotobenzaldehyde not to be 1 as proposed by Bamberger 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-nitrobenzaldehyde together with bands possibly due to o-hydroxylaminobenzaldehyde.

The compound from acetylation of agnotobenzaldehyde was not N-acetyl-o-hydroxylaminobenzaldehyde, 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-nitrobenzyl alcohol, 6H, 12H-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 %)

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-nitrobenzyl alcohol. o-Hydroxylaminobenzoic acid refluxed alone with p-toluenesulfonic acid, did not give 6 or 7.

Both 6 and 7 are reduced as compared to onitrosobenzaldehyde and o-hydroxylaminobenzoic acid. An oxidised compound, azoxybenzene-o,o'-dicarboxylic acid was formed by the reaction of these substances. This compound was also formed in the reaction of o-nitrobenzyl alcohol.1

These results are thus in agreement with the hypothesis advanced earlier, that o-nitrosobenzaldehyde is an intermediate in the reaction of o-nitrobenzyl alcohol under acidic conditions.1

Experimental. o-Nitrosobenzaldehyde prepared as described earlier. Agnotobenzaldehyde (2 or 3) (m.p.  $99-99.5\,^{\circ}\text{C}$ ) had IR (KBr): 3300, 1610, 1530, 1355 cm<sup>-1</sup>; IR (acetonitrile): 3400, 1710, 1670, 1610, 1540, 1350 cm<sup>-1</sup>; NMR ( $d_{\text{e}}$ -acetone):  $\delta$  10.4 (s), 9.9 (s), 7-8 (m). 4 (m.p.  $126.5-127\,^{\circ}\text{C}$ ) had IR (KBr): 3320, 1650, 1440 cm<sup>-1</sup>; NMR ( $d_{\text{e}}$ -acetone):  $\delta$  7-8 (4 H, m), 6.65 and 6.55 (2 H, AB,  $J_{\text{AB}}=9\text{Hz}$ ), 2.22 (3 H, s). The AB pattern collapsed to singlet ( $\delta$  6.65, 1 H) on D<sub>2</sub>O addition. MS: m/e 179 (C<sub>e</sub>H<sub>e</sub>NO<sub>3</sub>). o-Nitrosobenzaldehyde (m.p.  $111-112\,^{\circ}\text{C}$ ) had IR (KBr): 1700, 1610, 1270 cm<sup>-1</sup> (trans-azo dioxide): 7 IR prepared as  $\mathbf{described}$ earlier.3 1700, 1610, 1270 cm<sup>-1</sup> (trans-azo dioxide); <sup>6,7</sup> IR (CHCl<sub>3</sub>): 1700, 1510, 1490 cm<sup>-1</sup> (nitroso mono-(CHCl<sub>3</sub>): NMR (CDCl<sub>3</sub>):  $\delta$  12.1 (1 H, s), 8.3 – 7.5 (3 H, m), 6.5 (1 H, d, J= 8Hz); MS: m/e 135 (C<sub>7</sub>H<sub>5</sub>NO<sub>2</sub>). Electronic spectrum (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$ : 780 nm (3.72 m<sup>2</sup> mol<sup>-1</sup>). The reactions of o-nitrosobenzaldehyde were performed as described for o-nitrobenzyl alcohol.1

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## Synthesis of Some Substituted Picolinimidovl Chloride Hydrochlorides

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Imidoyl chlorides are useful as reactive intermediates, and our intention is to use some 4-amino substituted picolinimidoyl chlorides as such for studies on unsymmetrical imides. Even though a large variety of imidoyl chlorides are known, the only picolinimidoyl chloride which has been reported 2 is N-phenylpicolinimidoyl chloride hydrochloride. This compound was prepared by Beckmann rearrangement of 2-pyridyl phenyl ketone. However, chlorination of amides is the most widely used method for preparing imidoyl chlorides, and the best known reagents are phosphorus(V) chloride (PPC), carbonyl dichloride, thionyl chloride (TC) or a combination of triphenylphosphine and tetrachloromethane.3

Preliminary experiments with some picolinamides showed that these compounds were resistant to chlorination by TC, the reagent of greatest convenience. They also gave addition complexes with other chlorinating agents, e.g. with triphenylphosphine and tetrachloromethane.

Scheme 1.

We here show that the series of picolinamides 1 can be converted to the corresponding picolinimidoyl chloride hydrochlorides 2, cf. Scheme 1, by using different combinations of chlorinating agents and different reaction temperatures and reaction periods.

Results. We have prepared the nine picolinamides 1a-i (Table 1) from the corresponding