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THE CYANIDE ION CATALYZED DISPROPORTIONATION OF 4-NITROBENZALDEHYDE IN METHANOL

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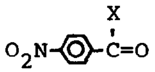
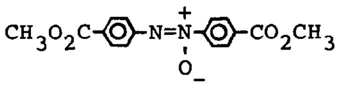
Waldrup and Yager[1] recently reported that 4-nitrobenzaldehyde (1a) reacts with aqueous sodium cyanide in refluxing methanol to yield dimethyl 4,4'-azoxydibenzoate (2) and 4-nitrobenzoic acid (1b). More recently, Castells and coworkers[2] observed that 1a undergoes a reaction with methanol (60°, 4 days), catalyzed by the conjugate base of 3,4,5-trimethylthiazolium iodide, to form methyl 4-nitrobenzoate (1c), 2 and dimethyl 4,4'-azodibenzoate (3).



1a, X = H
1b, X = OH
1c, X = OCH_3



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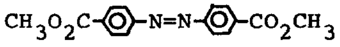

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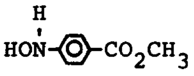
Prompted by these reports, we wish to make known at this time the preliminary findings from our study of the cyanide catalyzed disproportionation of 1a in methanol. It is our observation that the reaction leads to the formation of 1c, methyl 4-hydroxylaminobenzoate (4) [mp 118-120°; nmr (δ, $CDCl_3$), 7.90 and 7.00 (2d, 4H, J = 8 Hz, $-C_6H_4-$), 3.85 (s, 3H, $-OCH_3$); ir (cm^{-1}), 3420 (-OH), 3250 (>N-H), 1700 (ester); ms (m/e), 167 (M^+)], α-(4-nitrophenyl)-N-(4-carbomethoxyphenyl)nitrone (5) [mp 229-231°; ir (cm^{-1}), 1720 (ester), 1530 and 1350 ($-NO_2$); ms (m/e), 300 (M^+)], and 2 (trace quantities).



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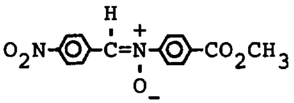

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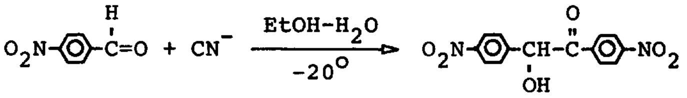
In a typical procedure, a solution of sodium cyanide (0.151 g, 1.0 mmol) in methanol (150 ml) was rapidly added to a solution of 1 (0.049 g, 1.0 mmol) in methanol (50 ml) under an atmosphere of purified nitrogen.[3] Products were separated utilizing the technique of preparative TLC (Silica Gel PF, chloroform).

While the yield of 1c (≈50%) is generally insensitive to the reaction conditions employed, relative yields of 4 and 5 are highly dependent on the ratio of aldehyde to cyanide. For example, changing the reactant mole ratio from 1:1 to 10:1 caused a drop in yield of 4 from 40% to less than 10%. At the same time 5 increased in yield from a trace to more than 20%. Obviously under the latter conditions, 4 was generated in the presence of unreacted starting material (1), further reaction between which yielded the nitrone 5. In a separate reaction, an authentic sample of 5 was conveniently prepared by allowing 4 to react with 1a under the reaction conditions.[4]

It is our feeling that apparent inconsistencies between the results reported herein and those obtained by others[1,2] are best accounted for by taking note of differences in reaction conditions. For example, we have observed that unless oxygen is rigorously excluded from the system[3], products obtained from the reaction are 1c and 2. Furthermore, it is easily demonstrated that the azoxy compound 2 arises from the oxidation of the hydroxylamine 4. Thus, it may be observed that alcoholic solutions of 4 produce 2 in high yield on standing for a few minutes in the presence of atmospheric oxygen. These data are consistent with those of Castells and co-workers[2] with the exception that we have not detected 3 among the reaction products.

It seems reasonable that 3 results from further reduction of 2 under the more vigorous conditions employed. The results reported by Waldrup and Yager[1] are in agreement if one considers that, in addition to the reaction having been carried out in an atmosphere containing oxygen, the products were further subjected to a period of reflux in a system now containing water and base. While 2 likely precipitated immediately after forming and was therefore resistant to further reaction, 1c, being soluble in aqueous ethanol, should have been saponified to the corresponding acid.

In 1972, Banas and Scrowaczewska[5] reported that 4-nitrobenzaldehyde (1a), under proper conditions, is able to undergo a normal benzoin condensation to yield 4,4'-dinitrobenzoin (6). The reaction was carried out by adding a 10%



1a 6

aqueous potassium cyanide solution (quantity not specified) to an ethanolic solution of 1a (0.2 M) at -20° (nitrogen atmosphere) and allowing the system to stand for 24-48 hours while maintaining the low temperature. Our attempts to reproduce these results have thus far been without success. However, the reaction described herein between 1a and cyanide occured normally at -20° yet provided no new products although the rate of reaction was retarded.

Work is continuing on the reaction mechanism and will be reported in a later publication.

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1. D. Waldrup and B. J. Yager, Texas J. Science, 27, 397 (1976).
2. J. Castells, H. Llitjos and M. Moreno-Manas, Tetrahedron Lett., 205 (1977).
3. A stream of nitrogen, carefully deoxygenated with Fieser's solution [L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley and Sons, Inc., New York, N. Y., 1967, p 393], was bubbled through a methanolic solution of each reactant for a period of approximately one hour prior to reaction.
4. The reaction of N-substituted hydroxylamines with aldehydes to form nitrones in high yields is well established. For a review of the preparation and chemistry of nitrones, see: J. Hamer and A. Macaluso, Chem. Rev., 64, 473 (1964).
5. T. Banas and Z. Skrowaczewska, Roczniki Chem., 46, 179 (1972).