# Isolation of an Intermediate during Formation of 4,4′,4″-Trinitrohydrobenzamide in the Reaction of 4-Nitrobenzaldehyde with Ammonia

ANNE-MARIE WEIDLER-KUBANEK
Corporate Chemical Research Laboratory, Allied Chemical Corp., Morristown, N. J. 07960

**N-(4-nitrobenzylidene)-α-alkoxy-4-nitrobenzylamines were prepared through the condensation of 4-nitrobenzaldehyde with ammonium acetate in solution in some alcohols at room temperature. The new compounds were identified by spectral data.**

Aromatic aldehydes do not form a simple addition product with ammonia, but give a more complex product, a hydrobenzamide (*1*).

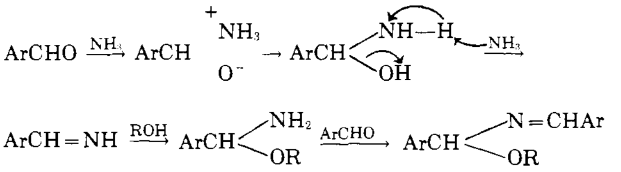
When a methanol solution of 4-nitrobenzaldehyde is added to a solution of ammonium acetate in the same solvent, a compound crystallizes out shortly after the two solutions are mixed at room temperature. The product was identified as *N*-(4-nitrobenzylidene)-α-methoxy-4-nitrobenzylamine (1a).

The reaction was quantitative in the presence of an excess of ammonium acetate. The yield was lowered somewhat by the addition of a small amount of acetic acid.

In ethanol, the corresponding ethoxy compound was formed in much lower yield. Polycondensation took place, and hydrobenzamide was isolated as one of the reaction products. With benzaldehyde, no reaction was observed under these conditions.

The condensation products were characterized by infrared, ultraviolet, and NMR spectroscopy. The mass spectrum of 1a also confirmed the structure.

One may visualize the formation of the intermediates as follows:



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1a. R=$CH_3$, Ar=4-nitrophenyl
1b. R=$C_2H_5$, Ar=4-nitrophenyl

Further reaction of 1a or 1b with the aldehyde gives rise to 4,4′,4″-trinitrohydrobenzamide, ArCH(N=CAr)$_2$.

## EXPERIMENTAL

The infrared spectra were recorded on a Perkin-Elmer IR21 spectrometer, the ultraviolet spectrum on a Beckman CKI spectrometer, the mass spectrum on an AEI MS 902, and the NMR spectra on a Varian A-60 spectrometer with TMS as internal standard.

**Preparation of 1a.** 4-Nitrobenzaldehyde (6.04 grams, 0.04 mole) was dissolved with heating in 75 cc of absolute methanol. The solution was cooled and mixed at room temperature under a stream of nitrogen with a solution of ammonium acetate (3.08 grams 0.04 mole) in 25 cc of absolute methanol. After a few minutes, white needles started to separate. The solution was cooled and filtered, and the solid collected, yielding 6.7 grams of crude material (m.p. 121.5–24.5° C). Recrystallization from methanol gave pure 1a (5.7 grams, 90%) (m.p. 127–27.5° C). TLC (silica, ethyl acetate : benzene, 5:2) $R_f$ = 0.45. Infrared (KBr) 1650, 1515, 1345, 1065 cm$^{-1}$, ultraviolet max ($CH_3OH$) 278 mμ (log ε = 4.20). NMR ($CDCl_3$) δ 3.56 (singlet, $CH_3$), 5.80 (doublet, *J* = 1.7 Hz, CH), 8.58 (doublet, *J* = 1.7 Hz, =CH), 7.69 to 8.32 (4 doublets, *J* = 9.0 and 8.75 Hz, aromatic protons). Mass spectrum (70 ev). *m/e* (relative intensity) 315(17), 314(31), 300(9), 284(4), 268(12), 166(90), 150(100).

Anal. Calcd. for $C_{15}H_{13}N_3O_5$: C, 57.16; H, 4.16; N, 13.32. Found: C, 57.16; H, 4.28; N, 12.90.

**Preparation of 1b and 4,4′,4″-Trinitrohydrobenzamide.** The same procedure was used as for the methoxy compound, with the exception of the solvent, which was absolute ethanol. The 5.7 grams of crude product were recrystallized from 1 to 1 ethanol-benzene. Yield, 1.35 grams (21%), colorless (m.p. 87.5–88.5° C); (1b) TLC (silica gel, ethyl acetate : benzene, 5:2). $R_f$ = 0.39, infrared (KBr) 1650, 1515, 1345, 1065 cm$^{-1}$. NMR ($CDCl_3$) δ 1.37 (triplet, *J* = 7.0 Hz, $CH_3$), 3.74 (quartet, *J* = 7.0 Hz, $CH_2$), 5.93 (—CH—), 8.70 (=CH), 7.71 – 8.32 (4 doublets, *J* = 9.0 Hz, aromatic protons).

Anal. Calcd. for $C_{16}H_{15}N_3O_5$: C, 58.36; H, 4.49; N, 12.76. Found: C, 58.38; H, 4.40; N, 13.12.

From the mother liquor, a yellow crystalline compound was isolated and identified as 4,4′,4″-trinitrohydrobenzamide, 3.8 grams (66%) [m.p. 114–16° C (with decomposition)]. The decomposition temperature was dependent on the rate of heating of the sample (for the melting point of reported 2° per minute) which might explain the variation in reported melting point (*1*). Attempts to recrystallize the compound gave high-melting, unidentifiable material. TLC (silica, ethyl acetate: benzene, 5:2). $R_f$ = 0.45. Infrared (KBr) 1640, 1515, 1340 cm$^{-1}$. NMR (DMSO-$d_6$) δ 5.85 (—$\overset{|}{\mathrm{C}}$H), 7.36 – 8.39 (multiplet, =$\overset{|}{\mathrm{C}}$H and aromatic protons).

Anal. Calcd. for $C_{21}H_{15}N_5O_6$: C, 57.68; H, 3.49; N, 16.16. Found: C, 57.68; H, 3.46; N, 16.02. Molecular weight calculated: 433. Found: 440 ± 5.

## ACKNOWLEDGMENT

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## LITERATURE CITED

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