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Ring-Nitrosation of a Secondary Aromatic Amine, 1,3,5-Tris(phenylamino)benzene.

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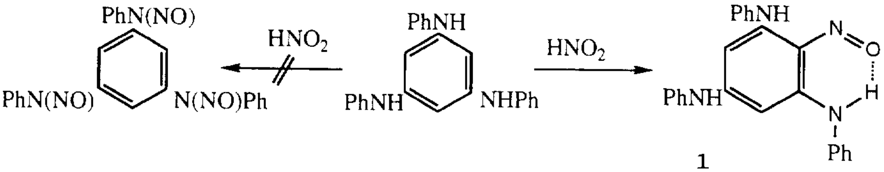
Abstract: Nitrosation of 1,3,5-tris(phenylamino)benzene with nitrous acid or an alkyl nitrite afforded the red-black 2,4,6-tris(phenylamino)nitrosobenzene. Copyright © 1996 Elsevier Science Ltd

One of the well-established rules in the chemistry of amines is that NO^+, or an equivalent reagent, gives diazonium salts with primary amines and N-nitrosamines with secondary amines; tertiary amines give nitroso ring substitution (if aromatic) or cleavage products (if aliphatic).[1,2]

We attempted to prepare a tris-nitroso derivative of 1,3,5-tris(phenylamino)benzene (TPAB) by addition (<5°C) of aqueous sodium nitrite to an ethanolic solution of the amine containing hydrochloric acid. The first drop of nitrite solution produced a black color. Workup gave a difficultly soluble, black solid whose ^{1}H-NMR spectrum ($CDCl_3$) revealed a strong absorption at δ11.9, inconsistent with the tris-N-nitroso structure proposed by Minunni.[3]

When the reaction was repeated with one equivalent of nitrite,[4] a dark solid was again isolated. It gave a red microcrystalline powder upon recrystallization from toluene or ethanol, or black hair-like needles by slow evaporation of a solution in N,N-dimethylformamide.



1

The recrystallized compound, assigned structure 1, melted at 242-5°C and was sparingly soluble in most organic solvents. The ^{13}C-NMR spectrum displayed 18 peaks as expected for the structure as drawn. A resonance at 156 ppm is ascribed to the carbon bearing the nitroso group. However, nitrosation with ^{15}N-enriched $NaNO_2$ gave 1 with an ^{15}N resonance at 549 ppm (adjusted to $NH_{3,liq}$), a position characteristic of N-nitroso compounds.

The following evidence supports, but does not prove, formation of 1 by a direct nitrosation of the aromatic ring, rather than by a rearrangement of a labile N-nitroso intermediate:

(1) Addition of sodium nitrite solution to a solution of TPAB in methanol/HCl at -78°C gave the characteristic dark color of **1** instantly,

(2) TPAB with isopentyl nitrite (redistilled and base-washed) alone gave 1 readily,[5] whereas the rearrangement of aromatic N-nitroso to C-nitroso compounds generally requires acid catalysts,[6]

(3) The *slope* of the curve of absorbance *vs* time from **1** (λ_{max} = 514nm, logϵ = 3.65), monitored directly in benzene at 24C in a solution 0.010**M** each in TPAB and n-butyl nitrite without added acid, was at a *maximum* at the beginning of the reaction and decreased smoothly to zero after 400s.

A o- or p-quinoid structure assigned initially to 1, based on its color and spectral data in solution, is ruled out in the solid phase by the X-ray crystal structure of the black DMF solvate, which shows H-atoms on each amine nitrogen, a C-N(O) bond distance of 1.57Å, and a (C)N=O distance of 1.13Å.[7]

REFERENCES AND NOTES

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4. TPAB (1.0g, 2.9 mmol) and hydrochloric acid (1.0mL) in absolute ethanol (30mL) were treated <5°C with 0.23g (3.3mmol) sodium nitrite in 2mL water in one portion. After 0.5h the solid was filtered off and washed successively with water and methanol: 1.1g (100%), mp 238-44°C. IR (Nujol): 3340(br), 3244(br), 1664, 1621, 1585, 1494, 1296, 1142, 720, 690 cm^{-1}
^{13}C-NMR (recrystallized product in DMSO-d$_6$) δ83.20, 87.20, 122.42, 123.06, 123.40, 123.62, 124.15, 124.69, 128.75, 128.97, 129.20, 137.74, 138.69, 139.39, 139.86, 142.78, 150.20, 155.95.
^{1}H-NMR (DMSO-d$_6$): δ6.22 (s, 1H), 6.47 (s, 1H), 7.41-7.79 (m, 15H), 9.75(s, 1H), 9.89(s, 1H).
Anal. Calcd. $C_{24}H_{20}N_4O$: C, 75.78%; H, 5.26%; N, 14.73%. Found: C, 75.54%; H, 5.44%; N, 14.47%.

5. TPAB (3.5g, 10mmol) and *iso*pentyl nitrite (3.5g, 30mmol) in toluene (100mL)at 23°C for 15h gave a 90% yield of 1 in two crops.

6. Fischer-Hepp rearrangement: March, J. *"Advanced Organic Chemistry"* John Wiley & Sons, NY, 4th ed, **1992**, p. 558.

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