

Nitrosamines and Hydrazones of Dinitroformaldehyde from *N,N*-Disubstituted
Hydrazines, a Dialkyl Nitroxide, and Tetranitromethane

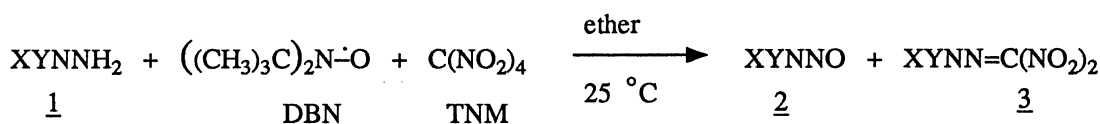
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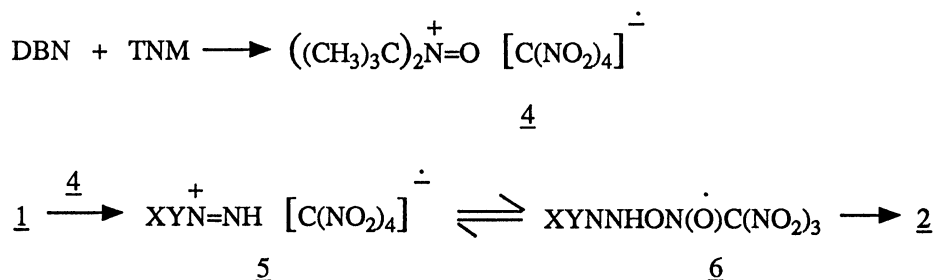
N,N-Disubstituted hydrazines reacted with a mixture of a dialkyl nitroxide and tetranitromethane to give nitrosamines and small amounts of hydrazones of dinitroformaldehyde.

Selected examples of *N,N*-disubstituted hydrazines 1 were converted to nitrosamines 2 on treatment with a mixture of di-*t*-butylnitroxide (DBN) and tetranitromethane (TNM) in an inert solvent at 25 °C and a similar conversion of *N*-methyl-*N*-phenylhydrazine 1a was brought about by replacing DBN with other nitroxides. This discovery constitutes the first example for the oxidation of a hydrazine to the corresponding nitrosamine and offers an innovative preparative route to nitrosamines heretofore obtained from secondary and tertiary amines by treatment with a nitrosating reagent. In the absence of DBN, the hydrazines 1 reacted with TNM to give the hydrazones 3.¹⁾ Under similar conditions DBN in the absence of TNM did not convert either hydrazines 1 or hydrazones 3 to nitrosamines 2. A thermal conversion of the hydrazones 3 to the nitrosamines 2 at 25 °C did not occur; in an inert solvent (2-(2-*n*-butoxyethoxy)ethanol) heating at 150-180 °C was required to convert the hydrazone 3a to an intractable mixture that contained the nitrosamine 2a in trace amounts detected by TLC. A photochemical conversion of the hydrazone 3a to the nitrosamine 2a was previously reported.¹⁾

On addition of TNM to an equimolar portion of DBN in pentane persistent absorption characteristic of a charge transfer complex 4 appeared in the region 340-370 nm, where TNM and DBN were individually transparent. The data was consistent with a proposed pathway in which a diazenium intermediate 5 \rightleftharpoons 6 was produced from a hydrazine 1 in hydride abstraction by the nitrosonium cation and underwent oxidative fragmentation to a nitrosamine 2. Neither identification of other products nor differentiation of the proposed fragmentation 5(6) \rightarrow 2, from stepwise dissociation of the tetranitromethane radical anion can be offered at this time.²⁾ Other oxidative dehydrogenations by nitrosonium salts were known.³⁾



(a) X = C₆H₅, Y = CH₃; (b) X = Y = C₆H₅; (c) XY = (CH₂)₅



A solution of *N*-methyl-*N*-phenylhydrazine 1a (0.5 g, 4 mmol) in ether (2.0 mL) was added dropwise at 0 °C to a deeply colored solution of a mixture of DBN (0.3 g, 2.0 mmol) and TNM (0.4 g, 2.0 mmol) in ether (10 mL). The reaction mixture was brought to 25 °C and stirred (3 h). Removal of ether left a gummy residue that yielded methylphenylnitrosamine 2a (0.2 g, 75%) and the methylphenylhydrazone 3a (0.05 g, 10%) of di-nitroformaldehyde on separation by preparative TLC [Analtech, Inc. precoated silica gel plates, 1000 microns thick; methylene chloride and hexane (60/40)]. The products 2a and 3a were identified by observing GC, mp, and IR data to be identical with authentic information.¹⁾ The product pairs: (1) *N*-nitrosodiphenylamine 2b (65%) and the diphenylhydrazone 3b (detected by TLC) and (2) *N*-nitrosopiperidine 2c (67%) and the hydrazone 3c (10%) were similarly obtained from *N,N*-diphenylhydrazine 1b and *N*-aminopiperidine 1c. *N*-Aminomorpholine 1d, XY = (CH₂)₂O(CH₂)₂, and *N*-amino-*N'*-methylpiperazine 1e, XY = (CH₂)₂N(CH₃)-(CH₂)₂, gave intractable mixtures on similar treatment with DNB and TNM.

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References

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