CHEMISTRY LETTERS, pp. 569-570, 1991

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 dialkylnitroxide 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.$^{3)}$

$$\underset{\underline{1}}{XYNNH_2} + \underset{DBN}{((CH_3)_3C)_2N\text{-}\dot{O}} + \underset{TNM}{C(NO_2)_4} \xrightarrow[25\ ^{\circ}C]{ether} \underset{\underline{2}}{XYNNO} + \underset{\underline{3}}{XYNN{=}C(NO_2)_2}$$

(a) $X = C_6H_5$, $Y = CH_3$; (b) $X = Y = C_6H_5$; (c) $XY = (CH_2)_5$

$$DBN + TNM \longrightarrow \underset{\underline{4}}{((CH_3)_3C)_2\overset{+}{N}{=}O\ [C(NO_2)_4]^{\dot{-}}}$$

$$\underline{1} \xrightarrow{\underline{4}} \underset{\underline{5}}{XY\overset{+}{N}{=}NH\ [C(NO_2)_4]^{\dot{-}}} \rightleftharpoons \underset{\underline{6}}{XYNNH\dot{O}N(O)C(NO_2)_3} \longrightarrow \underline{2}$$

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 dinitroformaldehyde 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, $XY = (CH_2)_2O(CH_2)_2$, and *N*–amino–*N'*– methylpiperazine 1e, $XY = (CH_2)_2N(CH_3)(CH_2)_2$, gave intractable mixtures on similar treatment with DNB and TNM.

Financial assistance was received from ONR.

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(Received December 12, 1990)