Nitrosamines from *N,N*-Disubstituted Hydrazines

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Photolysis of nitro hydrazones (from *N,N*-disubstituted hydrazines and tetranitromethane) gave nitrosamines.

We report a preparation of nitrosamines (**4**) by photolysis of nitro hydrazones (**2**). This step completes the first general 'oxidation' of a hydrazine to a nitrosamine since each hydrazone (**2**) was obtained from the corresponding hydrazine and tetranitromethane.[1] In a typical example the dimethylhydrazone (**2a**) in acetone was irradiated at 350 nm under argon for 72 h. Dimethylnitrosamine (**4a**) was isolated from an ethereal extraction of the reaction residue. Other nitrosamines were prepared by similar procedures (Table 1).[2]

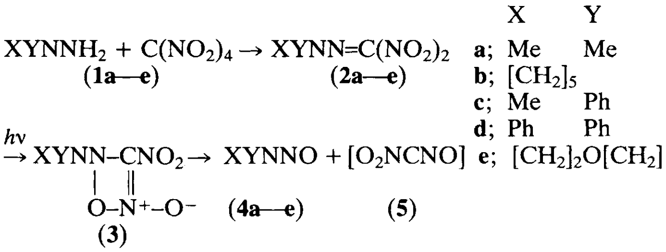
The nitrosamine is presumably formed by initial cyclization

Table 1. Nitrosamines (**4**) from hydrazines (**1**) *via* nitro hydrazones (**2**).

		XYNNO[d] (**4**)[c]	
(**1**)[a]	Yield (%) of (**2**)	Yield (%)	Ref.
(**1a**)	61	33	d
(**1b**)	74	61	e,f
(**1c**)	84	42	g
(**1d**)	43	23	h
(**1e**)	52[b]	26	i

[a] The hydrazines were commercially available. [b] The new compound (**2e**), m.p. 107—108 °C, showed i.r., ^1H n.m.r. (60 MHz), and mass spectra and elemental analysis consistent with the assigned structure. [c] Each nitrosamine was isolated by flash chromatography [silica gel; Merck grade 60, 60A; mixture (1 : 1) of dichloromethane and hexane] or by distillation, and identified by g.l.c. and i.r. comparison with authentic values. [d] H. H. Hatt, *Org. Syn. Coll.* Vol. II, 1943, p. 211. [e] Benzene was the solvent for photolysis. [f] W. D. Edmons, K. S. McCallum, and J. P. Freeman, *J. Org. Chem.*, 1954, **19**, 1472. [g] W. H. Hartman and L. J. Roll, *Org. Synth. Coli. Vol.*, II, 1943, p. 464. [h] B. Wexam, *Farm Chilena*, 1946, **20**, 299 (*Chem. Abstr.*, 1947, 405d). [i] G. Olah, L. Noszku, S. Kuhn, and M. Szelka, *Chem. Ber.*, 1956, **89**, 2374.

of the nitro hydrazone (**2**) to a 4-amino-3-nitro-1,2,4-oxadiazete 2-oxide (**3**), followed by ring cleavage (the comparable ring closure of a nitro-olefin to an oxazetone, sometimes isolated, followed by cleavage to a carbonyl compound, is known).[3,4] The undetected nitrilonitromethane oxide (**5**) was presumably a co-product; it may have dissociated to carbon dioxide and dinitrogen oxide.



$$\underset{\textbf{(1a—e)}}{XYNNH_2} + C(NO_2)_4 \rightarrow \underset{\textbf{(2a—e)}}{XYNN{=}C(NO_2)_2} \xrightarrow{h\nu} \underset{\textbf{(3)}}{\overset{}{XYNN\text{–}CNO_2}} \rightarrow \underset{\textbf{(4a—e)}}{XYNNO} + \underset{\textbf{(5)}}{[O_2NCNO]}$$

(**3**): ring O–N$^+$–O$^-$

	X	Y
a;	Me	Me
b;	$[CH_2]_5$	
c;	Me	Ph
d;	Ph	Ph
e;	$[CH_2]_2O[CH_2]$	

Heretofore, reports of 'oxidation' of a hydrazine to a nitrosamine were limited to the detection of diphenylnitrosamine and *N*-nitroso-*N*-methyltoluene-*p*-sulphonamide from an appropriate hydrazone and singlet oxygen.[5] Similar treatment of other hydrazones failed to produce nitrosamines.

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