Gomberg–Bachman Reactions Using Primary Nitrosamines as Substrates

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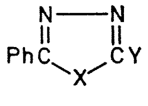
Summary Heating nitrosamino-oxadiazoles, -thiadiazoles, and -tetrazoles under reflux in benzene induces phenylation reactions, the NHNO function being replaced by Ph.

WE have recently reported[1] several new groups of primary nitrosamines, namely nitrosamino-oxadiazoles (I) and -tetrazoles (II). Spectroscopic evidence suggested their existence as the nitrosamines, RNHNO. We now report reactions in which the materials behave as the tautomeric diazohydroxides, RN=NOH.

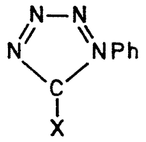
Heating 2-nitrosamino-5-phenyl-1,3,4-oxadiazole (I) in benzene solution under reflux for 30 min afforded 15% of 2-amino-5-phenyloxadiazole (III) (derived from N–NO bond cleavage), together with equivalent quantities of NO_2 (from the same bond-cleavage, NO being oxidised to NO_2) and 60% of the 2,5-diphenyloxadiazole (IV). This material was identical (mixed m.p., i.r.) with an authentic sample prepared unambiguously.[2] In addition to these materials a quantity of intractable red gum was formed. Photolysis of the nitrosamine (I) in benzene suspension (1g, 600 ml, Hanovia lamp, N_2 atmosphere, 25°) was less efficient than the thermolysis, 95% of (I) being recovered after 3 h irradiation, 2% of (IV) also being isolated.

The corresponding 2-nitrosamino-5-phenyl-1,3,4-thiadiazole (V), an example of a hitherto unreported group of primary nitrosamines,[3] similarly yields the corresponding 2,5-diphenyl derivative[4] (VI) in 50% yield after 30 min under reflux. Substantially less NO_2 and greater quantities of gum were formed and we could not detect any of the corresponding amine (VII).

Interestingly, 5-nitrosamino-1-phenyltetrazole (II) was much less labile towards thermolysis than compounds (I) and (V). After heating compound (II) under reflux in benzene for 30 min, 80% of unreacted material was recovered and also 10% of 2,5-diphenyltetrazole (VIII) (identical, mixed m.p., i.r., with a sample prepared unambiguously)[5] was obtained, together with trace quantities of NO_2 and gums. Running this experiment for 11 h yielded 62% of compound (VIII), together with substantial quantities of red gums. [In a blank run, heating compound (VIII) under reflux in benzene for 6 h afforded unchanged (VIII) in quantitative yield and no colour developed in the solution].



(I) X = O, Y = NHNO
(III) X = O, Y = NH_2
(IV) X = O, Y = Ph
(V) X = S, Y = NHNO
(VI) X = S, Y = Ph
(VII) X = S, Y = NH_2



(II) X = NHNO
(VIII) X = Ph

We regard these phenylation reactions as examples of Gomberg–Bachman processes,[6] involving homolysis of RN_2OH into R·, N_2 and ·OH. They are the first such reactions to derive from primary nitrosamine substrates. They should also occur with the nitrosaminotriazoles[7] and nitrosamino 1,2,4-thiadiazoles[8] reported by others.

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[1] (a) J. C. Tobin, R. N. Butler, and F. L. Scott, *Chem. Comm.*, 1970, 112; (b) R. N. Butler, T. Lambe, and F. L. Scott, *Chem. and Ind.*, 1970, 628.

[2] We thank Mr. P. A. Cashell for a generous supply of this material.

[3] J. Goerdeler and K. Deselaers, *Chem. Ber.*, 1958, **91**, 1025, have reported the synthesis of nitrosamino-1,2,4-*thiadiazoles*.

[4] B. Holmberg, *Arkiv Kemi, Mineral., Geol.*, 1944, **17**A, 1.

[5] G. Schroeter, *Ber.*, 1909, **42**, 3356; P. A. S. Smith and E. Leon, *J. Amer. Chem. Soc.*, 1958, **80**, 4647; J. Vaughan and P. A. S. Smith, *J. Org. Chem.*, 1958, **23**, 1909.

[6] W. E. Bachman and R. A. Hoffman, *Org. Reactions*, 1944, **2**, 224.

[7] H. Gehlen and J. Dost, *Annalen*, 1963, **665**, 144; J. Goerdeler and K. Deselaers, *Chem. Ber.*, 1958, **91**, 1025.

[8] Compare J. Goerdeler, K. Deselaers, and A. Ginsberg, *Chem. Ber.*, 1960, **93**, 963, for a minor example of the present reaction.