



N-Nitrohydrazines and their Salts

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The interaction of N_2O_5 with trimethylsilyl derivatives of functionally substituted hydrazines has for the first time resulted in the formation of nitrohydrazines; the relationship of the nitrohydrazone stability with the nature of the functional group and the molecular geometry is established.

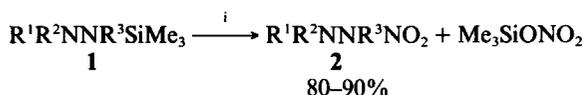
The problem of the connection between the structure and stability of polynitrous and polynitrogen–oxygen systems has not been sufficiently developed so far and was first discussed in ref. 1. Therefore the production of previously unknown structures containing nitrogen and oxygen atoms directly bonded with each other is now of great interest.

The absence of precise data on the synthesis of nitrohydrazines^{2–4} which are close analogues of the well-studied nitro-

amines might result either from a principal improbability of the existence of a nitro group and the amine function of one N atom, or from the instability of nitrohydrazines under the conditions of an ordinary acid nitration.

In order to minimize the possibility of nitrohydrazone decomposition during the reaction we applied our own method of substitute nitration of the N–Si bond which allows us to carry out reactions under mild conditions in a completely aprotic medium.

Thus for the first time nitrohydrazines have been obtained by the action of N_2O_5 on trimethylsilyl derivatives of functionally substituted hydrazines (Scheme 1).

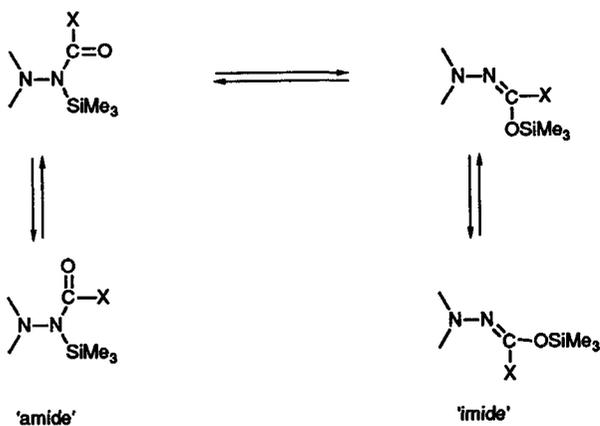


- a; $R^1 = Me, R^2 = R^3 = CO_2Me$
 b; $R^1 = Me, R^2 = R^3 = Ac$
 c; $R^1 = Me, R^2 = Ac, R^3 = CO_2Me$
 d; $R^1 = Me, R^2 = CO_2Et, R^3 = Ac$
 e; $R^1 = Ac, R^2 = R^3 = CO_2Me$
 f; $R^1 = R^2 = R^3 = Ac$
 g; $R^1 = SiMe_3, R^2 = R^3 = CO_2Me$
 h; $R^1 = NO_2, R^2 = R^3 = CO_2Me$
 i; $R^1 = SiMe_3, R^2 = R^3 = Ac$

Scheme 1 Reagents and conditions: i, $N_2O_5, CH_2Cl_2, -40 \rightarrow +20^\circ C$

The Me_3SiONO_2 formed during the course of the reaction is inert to the other components of the reaction mixture and is easily evaporated in vacuum. Quantitative observation of the reaction course was achieved using 1H NMR to detect the disappearance of a peak corresponding to the Me_3Si group in **1** and the appearance of a peak characteristic of Me_3SiONO_2 . The reaction proceeds smoothly at $20^\circ C$ and sharply accelerates when $SnCl_4$ is added.

It should be emphasized that each product obtained has the *N*-nitrohydrazone structure despite the fact that the original trimethylsilyl derivatives containing the NCO fragment exist in solution as mixtures of structural and spatial isomers, the distribution of which depends on the nature of the substituents^{5,6} (Scheme 2).



Scheme 2

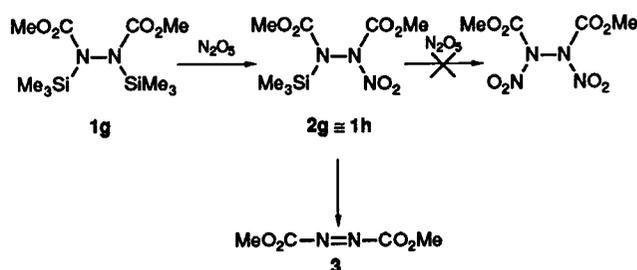
The structure of the *N*-nitrohydrazines was clearly detected by means of ^{15}N NMR spectroscopy using characteristic values of the N atom chemical shifts of the hydrazine fragment ($\delta - 80$ to -100 ppm for the 'imide' nitrogen) and of $J_{^{15}N^{15}NO_2}$.

The obtained mononitrohydrazines containing the $N(R)COX$ fragment ($X = R = Me; X = OMe, R = Me, SiMe_3$) exist in solution as mixtures of conformers due to impeded rotation around the amide $N-CO$ bond. This impediment disappears with the introduction of acceptor substituents ($R = Ac, NO_2$) which readily conjugate a lone electron pair on the N atom.

The nature of the substituents directly bonded to the $NSiMe_3$ fragment determines the structure of the silylated derivatives and affects the nitration rate.

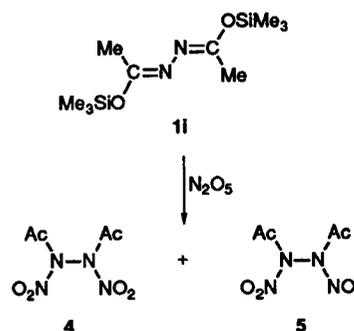
Silylated carbalkoxy-substituted hydrazines (Scheme 2, $X = OMe$) characterized by the 'amide' structure are more slowly nitrated than those ($X = Me$) which are inclined to the 'imide' form. This is obviously connected with the greater vulnerability of the 'imide' N atom to attack by an electrophilic reagent.

Substitution of the N atom next to the reaction site also affects the nitration rate. This is clearly seen in the cases of carbalkoxy derivatives. Thus the addition of electron acceptor substituents that lower hydrazine nucleophilicity hampers the interaction with N_2O_5 . Thus for a high product yield in the transition from (**1a**, $R^1 = Me$) to (**1e**, $R^1 = Ac$) it is necessary to apply stricter nitration conditions. In the first case of catalysis by $SnCl_4$ the reaction proceeds at $-20^\circ C$ for 50 min, in the second case at $0^\circ C$ for 90 min (**1h**, $R^1 = NO_2; R^2 = R^3 = CO_2Me$) nitration does not occur even at $+20^\circ$ and further heating leads to decomposition of the silylated nitrohydrazone, yielding **3**. Thus the first Me_3Si group of (**1g**, $R^1 = SiMe_3$) is smoothly nitrated ($-20^\circ C, 120$ min) though without yielding a dinitro derivative (Scheme 3).



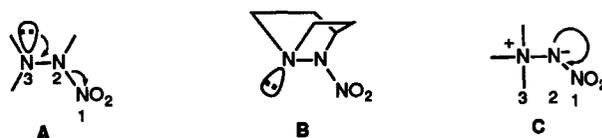
Scheme 3

We were able to synthesize a product containing an *N,N*-dinitrohydrazone fragment using a bis(trimethylsilyl) derivative of diacetylhydrazone (**1i**; $R^1 = SiMe_3, R^2 = R^3 = Ac$) which exists exceptionally in a readily nitrated 'imide' form⁵ as a starting compound. In the reaction, along with the expected **4**, nitronitrosohydrazone **5** is also formed. Its formation, as proved by special tests, is not connected with the presence of N_2O_4 in the nitrating agent.



Scheme 4

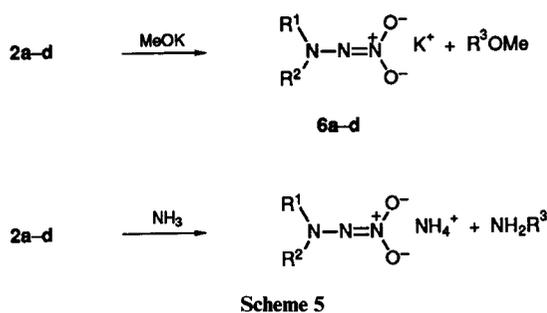
The nitrohydrazines obtained are in most cases thermally unstable, **2a-d** decompose almost completely after 24 h under normal conditions, **2e-f** are more stable and start to decompose only at $> 70^\circ C$. Therefore the introduction of electron acceptor substituents delocalizing a free electronic pair on the N atom into the molecule increases the relative stability of nitrohydrazines, thus confirming the course of the decomposition *via A*.



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This decomposition can only be realized with an antiperiplanar conformation of the nitrogen lone pair and the nitro group. In cases where the nitrohydrazine structure excludes an antiperiplanar conformation, as in 7-nitro-1,7-diazabicyclo[2.2.1]heptane,[†] which was specially synthesized for the purpose, the stability of the product increases markedly. Intensive decomposition starts only at 150 °C.[‡]

Compounds containing the NNNO₂ fragment have the highest stability since there is no lone electron pair on the N-3 atom§ and a stronger N—NO₂ bond owing to the interaction of the nitro group with the negative charge on the N-2 atom, similar to that in C. Stabilization due to the latter factor was also observed in nitrohydrazine salts obtained by the action of ammonia or alcoholic MeOK solution on **2a-d** (Scheme 5).



Salts **6a-d** gradually decompose in aqueous solutions, the corresponding tetrazenes being identified in the reaction products (Scheme 6).

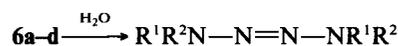
[†] For preparation of 1,7-diazabicyclo[2.2.1]heptane, see G. V. Shustov, N. B. Tavakalyon and R. G. Kostyanovskii, *Izv. Akad. Nauk, Ser. Khim.*, 1981, 1677.

NMR data for 7-nitro-1,7-diazabicyclo[2.2.1]heptane: ¹H NMR (300 MHz, CDCl₃, rel. Me₄Si) δ 1.58(m), 2.03(m, CH₂C), 2.8(m), 3.32(m, CH₂N), 4.98(t, CH); ¹³C NMR (75 MHz, CDCl₃, rel. Me₄Si) δ 25.0 (C-3, C-5), 49.3(C-2, C-6), 60.1(C-4); ¹⁴N NMR (22 MHz, CDCl₃, rel. MeNO₂) δ -23.5(NO₂).

[‡] This observation correlates well with the previously established sharp increase of stability in systems of type **D** in comparison with systems **E** in bicyclic heterocycles.⁷



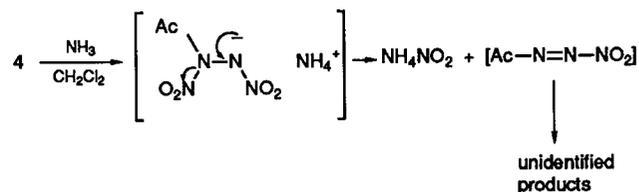
§ We have failed to detect any Me₂N—NMeNO₂ when the isomeric Me₃N⁺—NNO₂ is a stable compound with m.p. 212 °C.⁸



Scheme 6

Under the action of MeOK on **2f** the methoxide ion can attack both the NR³NO₂ and the NR¹R² fragments which contain two electron acceptor groups. As a result, after evaporation of the volatile compounds some complex mixtures are observed in the residue in which KNO₃, KNO₂ and AcOK can be identified.

During treatment of a solution containing **4** with ammonia instead of a diammonium salt, dinitrohydrazine NH₄NO₂ was obtained. This result can be accounted for by a scheme similar to that for the decomposition of **2** (Scheme 7).



Scheme 7

Therefore the specific character of compounds containing the nitrohydrazine fragment may be connected with both the presence of and the spatial arrangement of the lone electron pair and the N—NO₂ bond.

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References

- 1 F. G. Gal'perin, I. V. Stankevich, A. L. Chistyakov, V. B. Shur and M. E. Vol'pin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1675.
- 2 D. Harper and A. N. Lamberton, *J. Chem. Soc. (C)*, 1970, 1784.
- 3 R. N. Haszeldine and A. E. Tipping, *J. Chem. Soc. (C)*, 1966, 1236.
- 4 K. W. Cheung and M. G. Barlow, *J. Fluor. Chem.*, 1977, **10**, 191.
- 5 B. N. Khasapov, A. V. Kalinin, A. Ya. Shteinshneider, A. A. Blyumenfel'd, S. L. Ioffe and V. A. Tartakovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 1299.
- 6 I. D. Kalikhman, O. B. Bannikova, A. V. Kalinin, B. N. Khasapov, S. L. Ioffe, V. A. Tartakovskii and M. G. Voronkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 464.
- 7 I. E. Chlenov, I. M. Petrova, B. N. Khasapov, V. M. Shitkin, N. S. Morozova and V. A. Tartakovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 2613.
- 8 J. Epstein, A. R. Katritzky, E. Lunt, J. W. Mitchell and G. Roch, *J. Chem. Soc., Perkin Trans. 1*, 1973, 2622.