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Synthesis of 1-aryl-2-nitrodiazene 1-*N*-oxides

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1-Aryl-2-nitrodiazene 1-*N*-oxides were synthesized for the first time by nitration of the appropriate 2-acetyldiazene 1-*N*-oxides with nitronium salts; their structure was confirmed by an X-ray diffraction study.

1-Aryldiazene 1-*N*-oxides, Ar–N(O)=N–X, in which the N(2) atom is connected to a functional group can be synthesized by formation of the N=N bond of a diazene oxide fragment or by oxidation of appropriate diazenes.[1] This method is probably not suitable for the preparation of 2-nitrodiazene 1-oxides (NDO) (X = NO_2). Here we suggest a convenient route for the preparation of these compounds, in the course of which the N(2)–X bond is formed. 2-Acetyldiazene 1-oxides **2**, which were prepared by Kovacic's method[2] from nitroso compounds and *N*,*N*-dibromoacetamide[3] and were involved *in situ* in the nitration,[†] were used as a starting material.

$(NO_2)_2SiF_6$ turned to be the most convenient nitrating reagent for the preparation of **3a**–**f** (see Table 1).[‡] N_2O_5 can only be used in those cases where the benzene ring does not contain electron-withdrawing substituents (*e.g.* **3a**). The employment of NO_2BF_4 was effective for the synthesis of heterocyclic NDO **3g**,**h**. When using this reagent for the synthesis of **3a**–**f**, the yield of NDO did not exceed 50% due to decomposition of the starting compound **2** by BF_3, which was

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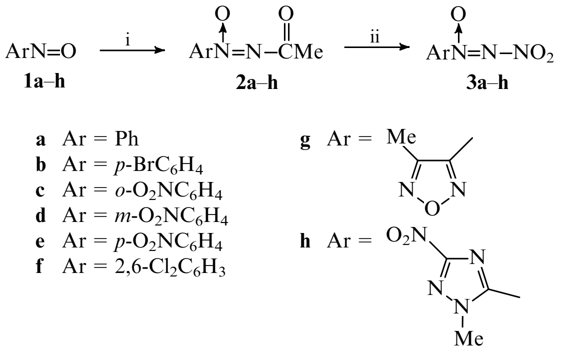
[†] Acetyldiazene oxides **2** can be isolated if necessary.

2a: oil; IR (NaCl plates): ν/cm^{-1} 1335, 1490 [N(O)=N], 1755, 1770 (C=O); NMR in CD_2Cl_2; ^{1}H NMR δ 2.38 (3H, s, COMe), 7.5 (3H, m, Ph, H-*m* and H-*p*), 8.15 (2H, d, *J* = 8.0 Hz, Ph, H-*o*); ^{13}C NMR δ 186 (C=O); ^{14}N NMR (δ, standard $MeNO_2$) −38 ($\Delta\nu_{1/2}$ = 370 Hz, N→O).

[‡] Nitroso compounds **1a**–**g** were prepared according to literature procedures; **1h** was obtained by oxidation of the appropriate hydroxyamine[4] with dibromoisocyanuric acid in MeCN, yield 77%, mp 82–85 °C.

General procedure for NDO. To a stirred solution of *N*,*N*-dibromoacetamide (5 mmol) in CH_2Cl_2 (10 ml) was added a solution of the appropriate nitroso compound (5 mmol) in CH_2Cl_2 (10 ml). After 1 h at 20 °C (2 h in the case of **1f**) the solvent was removed *in vacuo* to yield the corresponding compound **2**, which was dissolved in dry MeCN (5 ml) and, under stirring at −20 °C, 2.5 mmol of $(NO_2)_2SiF_6$ (procedure A) or 5 mmol of NO_2BF_4 (procedure B) were added. The evolution of gas was observed. The mixture was warmed to 20 °C and stirred for an additional hour. Subsequently, the solvent was removed *in vacuo*, the residue was washed with water and an aqueous solution of $NaHCO_3$ and purified by crystallization or chromatography (silica gel, $CHCl_3$ or CCl_4) if necessary. All NDOs **3** gave satisfactory analytical and spectroscopic data.

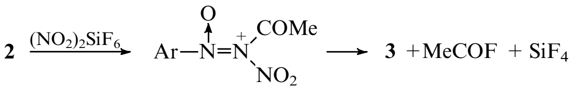
For **3a**: ^{1}H NMR δ 7.6 (3H, m, Ph, H-*m* and H-*p*), 8.06 (2H, d, *J* = 8.0 Hz, Ph, H-*o*); ^{14}N NMR (δ, standard $MeNO_2$) −32 ($\Delta\nu_{1/2}$ = 15 Hz, NO_2), −44 ($\Delta\nu_{1/2}$ = 50 Hz, N→O).



Scheme 1 *Reagents and conditions:* i, Br_2NCOMe, CH_2Cl_2; ii, $(NO_2)_2SiF_6$, MeCN (procedure A); NO_2BF_4, MeCN (procedure B).

released in the course of the reaction.

The reaction mechanism possibly involves the addition of an NO_2^+ cation onto the N(2) atom followed by loss of $MeCO^+$. It may be noted that this is the first reported case of functional group exchange at the N(2) atom of azoxy compounds by the action of electrophiles (for the intramolecular variant of the related reaction, in which benzo-1,2,3,4-tetrazine 1,3-di-*N*-oxides and benzo-1,2,3,4-tetrazine 1-*N*-oxides were formed, see refs. 5 and 6).



$$\mathbf{2} \xrightarrow{(NO_2)_2SiF_6} \mathrm{Ar{-}\overset{\overset{O}{\uparrow}}{N}{=}\overset{+}{N}}\begin{smallmatrix}\diagup COMe\\ \diagdown NO_2\end{smallmatrix} \longrightarrow \mathbf{3} + MeCOF + SiF_4$$

NDOs are a new type of functionalized azoxy compounds. Their structure was confirmed by IR[§] and NMR spectroscopy and X-ray diffraction[¶] investigations. IR spectra showed the absorption bands of an azoxy group (1312–1335 and 1480–1510 cm^{-1}) and those of a nitro group (1280–1295 and 1610–1650 cm^{-1}). In the ^{14}N NMR spectra there are narrow signals due to the N(1) atom of the azoxy group (δ −40 to −50 ppm, $\nu_{1/2}$ = 50–100 Hz) and the nitrogen atom of the nitro group (δ −30 to −35 ppm, $\nu_{1/2}$ = 15–25 Hz).

Table 1 1-Aryl-2-nitrodiazene 1-*N*-oxides **3a**–**h** from the corresponding nitroso compounds **1**.

Compound	Procedure	Yield[a] (%)	Mp/°C
3a	A	91	26–27 (hexane)
3b	A	73	74–76 (hexane)
3c	A	87	39–40 (hexane)
3d	A	86	53–54 (hexane)
3e	A	83	49–51 (CCl_4)
3f	A	68	54–56 (EtOH)
3g	B	79	oil
3h	B	80	99–100

[a] Isolated yield based on nitroso compound **1**.

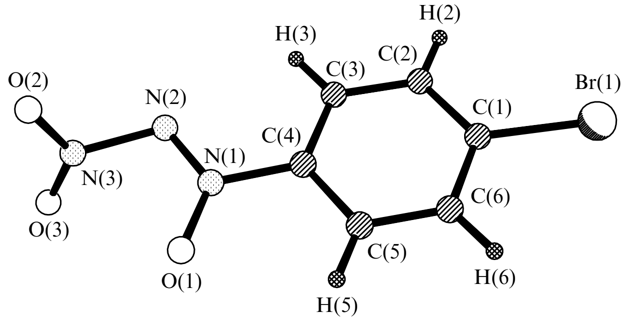


Figure 1 Molecular structure of **3b**. Selected bond lengths/Å: C(4)–N(1) 1.445(6), N(1)–O(1) 1.260(6), N(1)–N(2) 1.289(7), N(2)–N(3) 1.48(1), N(3)–O(2) 1.220(7), N(3)–O(3) 1.197(4). Torsion angles/°: O(3)–N(3)–N(2)–N(1) 88.6(5), O(2)–N(3)–N(2)–N(1) −99.1(5), N(3)–N(2)–N(1)–O(1) −0.7(7), N(3)–N(2)–N(1)–C(4) 175.4(9), N(2)–N(1)–C(4)–C(5) −179.0(1), O(1)–N(1)–C(4)–C(5) −2.2(8).

An X-ray diffraction study was performed on compounds **3b** and **3f** (Figures 1 and 2). The distinctive feature of both compounds is their rather long N–NO_2 bonds [1.48(1) and 1.475(3) Å, respectively]. It is interesting to note that in both compounds there is practically no conjugation between the π-system of the nitro group and that of the diazene oxide fragment, possibly due to steric hindrance. The dihedral angles between the plane of the NO_2 group and the O(1)N(1)N(2) planes are 83.7 and 85.9°, respectively.

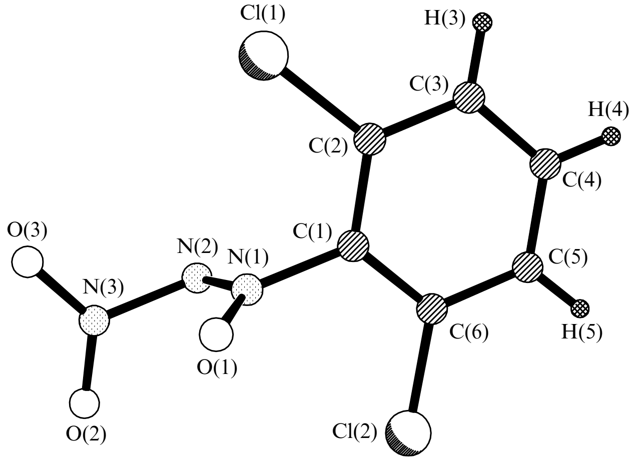
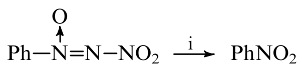


Figure 2 Molecular structure of **3f**. Selected bond lengths/Å: C(1)–N(1) 1.467(5), N(1)–O(1) 1.229(4), N(1)–N(2) 1.274(5), N(2)–N(3) 1.475(3), N(3)–O(2) 1.199(4), N(3)–O(3) 1.210(4). Torsion angles/°: O(3)–N(3)–N(2)–N(1) 87.8(5), O(2)–N(3)–N(2)–N(1) −97.1(5), N(3)–N(2)–N(1)–O(1) 0.8(4), N(3)–N(2)–N(1)–C(1) 178.3(4), N(2)–N(1)–C(1)–C(2) 86.0(4), O(1)–N(1)–C(1)–C(2) −93.1(5), N(1)–C(1)–C(2)–Cl(1) 0.5(2), N(1)–C(1)–C(6)–Cl(1) 0.6(2).

NDOs possess rather low thermal stability. Differential thermal analysis showed that the decomposition of **3a**–**f** begins within the range 85–110 °C. Compound **3f** turned out to be the most stable (*T* = 110 °C). The main product of **3a** decomposition is nitrobenzene (Scheme 2).



$$\mathrm{Ph{-}\overset{\overset{O}{\uparrow}}{N}{=}N{-}NO_2} \xrightarrow{i} PhNO_2$$

Scheme 2 *Reagents and conditions:* i, octane, 110 °C, 4.5 h (69%).

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[§] For the IR investigations of NDO, see ref. 7.

[¶] We are grateful to Dr. A. Espenbetov and Dr. V. S. Kuzmin for carrying out an X-ray diffraction study.

Crystal data for **3b**: $C_6H_4BrN_3O_3$, $M = 245$, monoclinic, space group $P2_1/n$, $a = 4.737(2)$, $b = 8.698(4)$, $c = 20.181(12)$ Å, $\beta = 94.95(6)°$, $Z = 4$, $D_{calc} = 1.973$ g cm^{-3}. The intensities of 1719 observed reflections were measured with a Syntex-P2$_1$ diffractometer (graphite monochromated Mo-Kα radiation, $\lambda = 0.71069$ Å, $\theta/2\theta$ scan technique, $2\theta \leqslant 52°$). The structure was solved by direct methods and refined by the full-matrix least-squares technique, anisotropically for the non-hydrogen atoms. The final discrepancy factors are $R = 0.079$ for 1719 reflections with $F_{hkl} \geqslant 2\sigma$.

Crystal data for **3f**: $C_6H_3Cl_2N_3O_3$, $M = 235$, rhombic, space group $P2_1ca$, $a = 7.302(2)$, $b = 7.590(3)$, $c = 16.819(6)$ Å, $Z = 4$, $D_{calc} = 1.682$ g cm^{-3}. The structure was solved and refined as **3b**. The final discrepancy factors are $R = 0.035$ for 868 reflections with $F_{hkl} \geqslant 3\sigma$. Atomic coordinates, bond lengths and bond angles for compounds **3b** and **3f** have been deposited at the Cambridge Crystallographic Data Centre (see Notice to Authors, *Mendeleev Commun.*, 1996, issue 1).

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