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Reaction of N_2O_4 with Substituted Dinitromethane Salts as a New Method for the Generation of Nitrile Oxides

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Nitrile oxides have been synthesized by the reaction of substituted dinitromethane salts **1** with N_2O_4; this reaction has been shown to proceed through a dinitronitrosomethylene intermediate, the further transformation of which has been investigated.

The reaction of N_2O_4 with aryldinitromethane salts is a known method for the preparation of aryltrinitromethanes.[1,2] We have shown that the reaction can be directed towards the formation of benzonitrile oxides, although formation of aryltrinitromethanes cannot be completely avoided. Nitrile oxides **3a–d** have been identified spectroscopically and also by their cyclodimerization to form furoxans **4a–d** (Scheme 1). The reaction of **1e–h** with N_2O_4 was also investigated.

2,4,6-Trinitrobenzonitrile oxide **3e** does not dimerize at 20 °C to form **4e**, apparently because of steric hindrance,[3,4] and it decomposes with increasing temperature. It undergoes, however, some reactions typical for nitrile oxides[5] (Scheme 2). Compound **2e** is not formed, even when the excess of N_2O_4 reacts with **1e** under the same conditions as in refs. 1 and 2.

In order to reveal the pathway of nitrile oxide formation in the reaction of **1** with N_2O_4 and its further reactions, the

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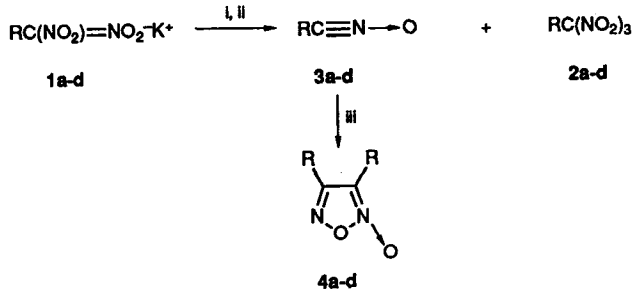
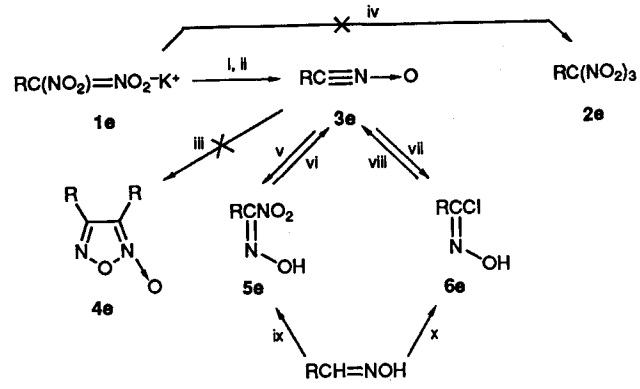


a; R = Ph
b; R = $C_6H_4NO_2$-3
c; R = $C_6H_3(NO_2)_2$-3,5
d; R = $C_6H_2(NO_2)_2$-3,5-OMe-4
e; R = $C_6H_2(NO_2)_3$-2,4,6
f; R = CO_2Et
g; R = Me
h; R = CO_2Me

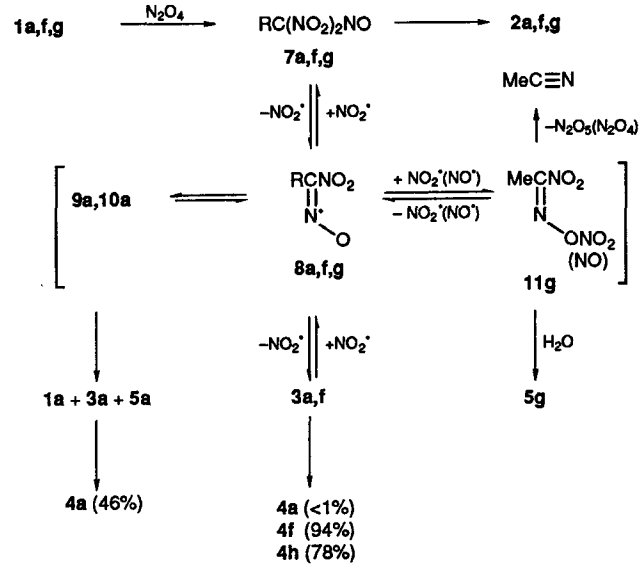
Scheme 1 *Reagents and conditions*: i, N_2O_4 (1 mol), $CHCl_3$, 0–10°C, 10–15 min; ii, 5% $NaHCO_3$; iii, $CHCl_3$, 20°C, 48 h



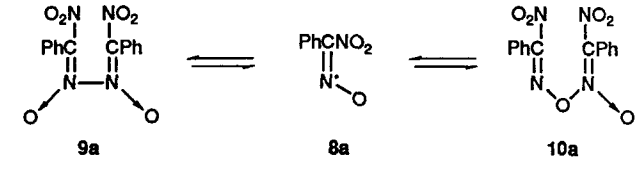
Scheme 2 *Reagents and conditions*: i, N_2O_4 (1 mol), $CHCl_3$, 0–10°C, 10–15 min; ii, 5% $NaHCO_3$; iii, $CHCl_3$, 20°C, 48 h, **3e** (68%); iv, N_2O_4 (5 mol), $CHCl_3$, 20°C, 3 h; v (analogous to iv), **5e** (46%); vi, CCl_4, 80°C, 1.5 h, **3e** (18%); vii, HCl, $CHCl_3$, 20°C, 15 h, **6** (90%); viii, 5% NaOH, CH_2Cl_2–H_2O, 0°C, **3e** (61%); ix, N_2O_4 (1 mol), CCl_4, 20°C, **5e** (50%); x, Cl_2, $CHCl_3$, 0°C, 1.5 h, **6** (83%)

interaction of N_2O_4 with **1a,f,g** has been studied by ^1H, ^{13}C and ^{14}N NMR spectroscopy.† The reaction was carried out in the temperature range from −40 to 20°C, recording NMR spectra as the reaction proceeded. In order to interpret the shape of the spectra observed the corresponding NMR spectra of **2a,g**, **3a**, **4a,f,g**, **5a,g**, phenyldinitromethane and N_2O_4 were recorded. Analysis of the dynamics of changes in the NMR spectra and the nature of the end products has shown that the first step of the interaction of **1a,f,g** with N_2O_4 is nitrosation of the dinitromethane anion to form dinitronitrosomethylene intermediates **7a,f,g**, irrespective of the substituent. Their structure has been confirmed spectroscopically and **7g** has been isolated. One of the routes for further transformation of **7a,f,g**, is their irreversible oxidation by N_2O_4 into **2a,f,g**. The other pathway for transformation of **7**, irrespective of the substituent, is most likely elimination of the NO_2 radical to produce radicals **8a,f,g**. Their further behaviour is determined by the character of substituent R. Possible transformation pathways for **8a,f,g** and the products obtained are given in Scheme 3.

Radical **8a** is most likely[6,7] to dimerize into an intermediate that can have the structure of either **9a** or **10a** (Scheme 4). If the reaction is not interrupted, it proceeds to form **2a** as a result of reversible transformations. At 20°C the formation of a small amount of **3a** is observed, possibly due to NO_2 radical elimination from **8a** (experiment 1). If the reaction is interrupted, the dimer is hydrolysed to form **3a**, **5a** and **1a** (experiment 2). In the case of **8f**, the NO_2 radical elimination becomes the prevalent reaction route; this may be associated with the stabilization of **3f** by conjugation in the nitrile oxide and ethoxycarbonyl fragments, and also with the high rate of cyclodimerization of **3f** to form furoxan **4f**.[8] No structures of type **9f** and **10f** have been found in this case. Radical **8g**, containing a methyl



Scheme 3 *Reagents and conditions*: **1a**: *experiment 1*, N_2O_4 (1 mol), $CDCl_3$, −40°C, 1 min (**7a** : **2a** = 10 : 1); −20°C, 30 min (**8a**, **9a** or **10a**, **7a**, **2a**); 20°C, 10 min (**7a** : **2a** = 1:10, **3a** < 1%); *experiment 2*, N_2O_4 (1 mol), $CDCl_3$, −10°C, 2 min, 5% $NaHCO_3$, 0°C, 5 min (**3a**, **5a**, **1a**). **1f**: N_2O_4 (1 mol), $CDCl_3$, −20°C, 1 min (**2f**, **3f**, **4f**, **7f**, N_2O_4). **1g**: N_2O_4 (1 mol), $CDCl_3$, −10°C, 2 min (**7g**), 15°C, 24 h (**2g**, MeCN, **5g**)



Scheme 4

† All new compounds have satisfactory spectroscopic characteristics. NMR spectra were run in $CDCl_3$, ^1H NMR at 250 MHz, ^{13}C NMR at 75.5 MHz ($SiMe_4$ as internal standard), ^{14}N NMR at 21.5 MHz ($MeNO_2$ as internal standard).

7a: ^{13}C NMR δ 130.3 (C_α), 123.7, 133.1, 128.5, 129.5 (*i*, *p*, *o*, *m*-H in Ph); ^{14}N NMR (Δ 1/2 Hz) δ −23.5 (46.6, NO_2), 401.5 (1870, NO); decomposes completely in 2 min at −10°C. **7f**: ^{13}C NMR δ 130.1 (C_α), 66.6 (q, CH_2), 13.6 (t, Me), 152.5 (CO); ^{14}N NMR (Δ 1/2 Hz) δ −33.3 (24, NO_2), 364.0 (NO); decomposes completely in 10 min at −10°C. **7g**: blue liquid, 71% yield, decomposes completely in 7 days at 15°C; UV λ_{max}/nm (n-C_6H_{14}) 630; IR ($CHCl_3$) ν/cm^{-1} 1588, 1558 (NO_2 as), 1440 (NO), 1382, 1360 (NO_2 s); ^1H NMR δ 2.34 (s, Me); ^{13}C NMR δ 133.5 (C_α); 16.6 (Me); ^{14}N NMR (Δ 1/2 Hz) δ −23.0 (29.5, NO_2); 410 (366, NO).

^{14}N NMR (Δ 1/2 Hz) δ: **2a**: −29.1 (24.7 NO_2); **2f**: −28.2 (25.0, NO_2); **2g**: −29.2 (NO_2).

3a: IR ν/cm^{-1} 2310 (C≡N); ^{14}N NMR (Δ 1/2 Hz) δ −182.0 (N→O). **3b**: IR ν/cm^{-1} 2300 (C≡N). **3c,d**: IR ν/cm^{-1} 2315 (C≡N). **3e**: decomp. at 63.5°C, 68% yield; IR ν/cm^{-1} 2315 (C≡N), 1490, 1610 (Ph), 1540, 1555 (NO_2 as), 1345 (NO_2 s); ^1H NMR [$(CD_3)_2CO$] δ 9.38 (s, H in Ar); ^{13}C NMR (CD_3CN) δ 152.47, 148.09, 126.20 (^1J 179.74, ^3J 5.13 Hz), 111.99 (*o*, *p*, *m*, *i*-H in Ar), 28.93 (C≡N); ^{14}N NMR [$(CD_3)_2CO$, Δ 1/2 Hz] δ −22.75 (71.5, NO_2), −161.21 (30.9, N→O).

4c: m.p. 236–237°C; ^1H NMR [$(CD_3)_2SO$] δ 8.71 (s, *o*-H in Ar), 8.90 (s, *p*-H in Ar); CIMS, *m*/*z* 418 (M^+, 20%), 402 (6), 388 (15), 372 (4), 358 (8), 342 (7), 312 (5), 266 (100), 220 (57), 209 (11), 174 (52). **4d**: m.p. 195–196°C; ^1H NMR (CD_3CN) δ 4.0 (s, Me), 8.25 (s, *o*-H in Ar); CIMS *m*/*z* 478 (M^+, 100%), 462 (11), 448 (2), 432 (16), 418 (89), 402 (5), 388 (7), 358 (5), 239 (10), 223 (5), 209 (7).

substituent incapable of conjugation, is probably stabilized, along with dimerization into **9g** or **10g**,[9] by reaction with NO_2 (or NO) radicals to produce the adduct **11g**, which can be decomposed by water to form **5g** and can eliminate nitrogen oxides to form acetonitrile. Thus, the reaction of **1** with N_2O_4 can serve as a method for preparing both trinitromethane derivatives **2** and nitrile oxides **3**. The latter can only be obtained from **1** if it has substituents capable of conjugation with the —C→N—O fragment, the preferential formation of **2** or **3** depending on the ratio of the rate of oxidation of **7** to **2** to that of cyclodimerization of **3** to **4**. In the case of rapidly dimerizing nitrile oxides one can expect high yields of furoxans.

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