Nitroformonitrile oxide
2.* Generation of nitroformonitrile oxide as an intermediate for the preparation of dinitrofuroxan

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Two methods for the generation of nitroformonitrile oxide (NFNO) were proposed, namely, by dehydration of dinitromethane and by nitration of 2-methyl-1-nitro-1-propene. NFNO was identified as its cyclodimerization product, dinitrofuroxan.

Key words: dinitromethane, dehydration; nitroformonitrile oxide, acetylmethanenitrolic acid, 2-methyl-1-nitro-1-propene, nitration; dinitrofuroxan.

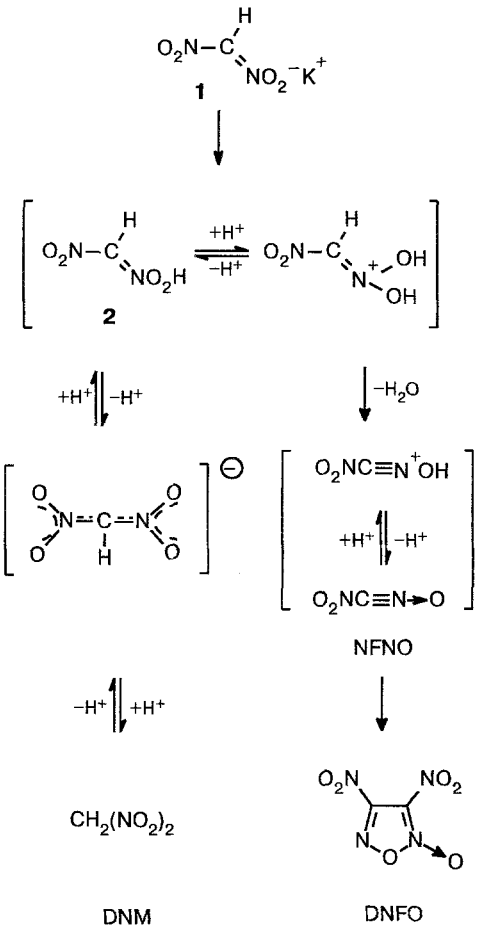
Previously,[2,3] we suggested a new method for generating nitrile oxides by reactions of N_2O_4 with salts of substituted dinitromethanes. However, this method was found to be unsuitable for obtaining nitroformonitrile oxide (NFNO) from the K-salt of trinitromethane (TNM). Several attempts at generating NFNO have been reported. For example, its intermediate formation was suggested in theoretical considerations of the thermal decomposition of dinitromethane (DNM)[4] and of the trimethylsilylation of methylnitroacetate, DNM,[6] and TNM.[7] However, no experimental evidence of NFNO formation was obtained in any of the cases.

In the present work we studied the possibility of generating NFNO by other methods, namely, by dehydration of DNM and by nitration of acetylmethanenitrolic acid and 2-methyl-1-nitro-1-propene.

The dehydration of primary nitro compounds is a rather popular method for synthesizing nitrile oxides. Of the reagents used previously for this purpose,[8] we chose concentrated H_2SO_4 and oleum, since this allowed us to use the more readily accessible and convenient K-salt of DNM (**1**) rather than free DNM. Treatment of salt **1** with H_2SO_4 gives the aci-form of DNM **2** (Scheme 1), which, according to the literature data,[9] can undergo dehydration to give NFNO. In addition, it is known[10] that concentrated H_2SO_4 can stabilize the aci-form of polynitroalkanes for a short period of time.

Thus, one could expect that the interaction of compound **1** with concentrated H_2SO_4 or oleum should give NFNO due to dehydration of **2** and free DNM due to a tautomeric transformation of **2**. Since the rate of

Scheme 1



† Deceased.

* For Part 1, see Ref. 1.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 722—726, April, 1995.

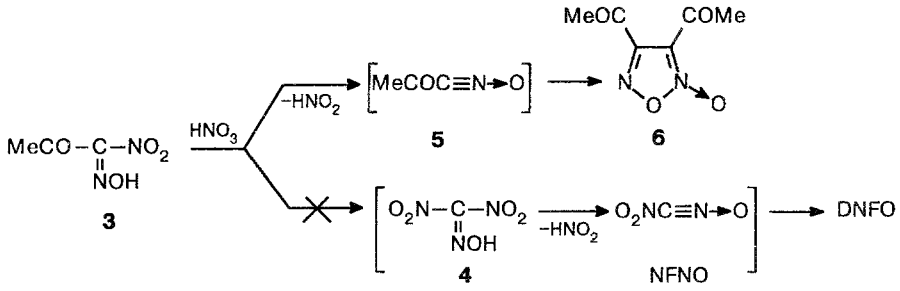
1066-5285/95/4404-0702 $12.50

Table 1. Dehydration of DNM

Entry	Starting compound	Dehydrating agent (DA)	Number of DA moles per mole of the starting compound	T/°C	t/min	Yield* (%)	
						DNFO	DNM
1	$KCH(NO_2)_2$	Oleum (30 % SO_3)	6	20	4	28	72
2	$KCH(NO_2)_2$	95 % H_2SO_4	26	20	4	12	88
3	$KCH(NO_2)_2$	95 % H_2SO_4	26	20	60	12	86
4	$KCH(NO_2)_2$	95 % H_2SO_4	26	20, 100	4, 60	34	—
5	DNM	Oleum (30 % SO_3)	6	20	4	—	99

* The DNFO : DNM ratio was determined from a plot of the dependence of n_D^{20} of the DNFO—DNM two-component mixture on its composition (see Fig. 1). The yield of DNM was also determined from ^1H NMR spectra (see Ref. 13) using 1,3,5-trinitro-1,3,5-triazacyclohexane as the internal standard. The yield of DNFO was determined from ^{14}N NMR spectra (see Ref. 12) using $C(NO_2)_4$ as the internal standard. The results are in good agreement with those relying on n_D^{20} of the mixtures.

Scheme 2



cyclodimerization of nitrile oxides into furoxans increases with the electron-withdrawing ability of the substituent,[11] we assumed that the main direction of NFNO transformation would involve its cyclodimerization into dinitrofuroxan (DNFO). We believe that detection of DNFO can serve as direct evidence that NFNO is generated. The results of dehydration by this procedure are presented in Table 1.

Indeed, the treatment of salt **1** with 95 % H_2SO_4 at 20 °C gave DNFO (see Ref. 12) and DNM (see Ref. 13) in a 1 : 14 molar ratio, and their overall yield corresponded to almost complete transformation of the starting salt **1** (see Scheme 1, Table 1, experiment *2*). Oleum (30 %) was found to be a better dehydrating agent at 20 °C, causing the formation of DNFO and DNM in a 1 : 5.3 molar ratio (experiment *1*), again in quantitative overall yield. Free DNM remains unchanged under these conditions (experiment *5*). Heating the reaction mixture obtained from salt **1** and 95 % H_2SO_4 at 100 °C gives DNFO in 34 % yield (experiment *4*). One can surmise that in this case the yield of the product decreases due to its partial decomposition under the reaction conditions, which was confirmed in a separate experiment by heating DNFO with H_2SO_4 at 100 °C. The increase in DNFO yield in experiment *4* compared to that in experiment *2* may suggest that DNM can be transformed into the aci-form when heated in concentrated H_2SO_4.

One of the methods for generating nitrile oxides involves elimination of HNO_2 from nitrolic acids.[14,15] We attempted to perform the substitutive nitration of acetylmethanenitrolic acid **3**. It was anticipated that the resulting dinitroformaldoxime **4** should eliminate HNO_2 to give NFNO. However, oxime **3** either does not undergo nitration under the conditions studied, or eliminates HNO_2 with subsequent cyclodimerization of the resulting acetylformonitrile oxide **5** to give diacetylfuroxan **6** (see Ref. 16) (Scheme 2).

The successful attempt at generating NFNO involved nitration of 2-methyl-1-nitro-1-propene (**7**), the structural analog of β,β-dimethylacrylates, whose nitration with 100 % HNO_3 gives dialkyl furoxan-

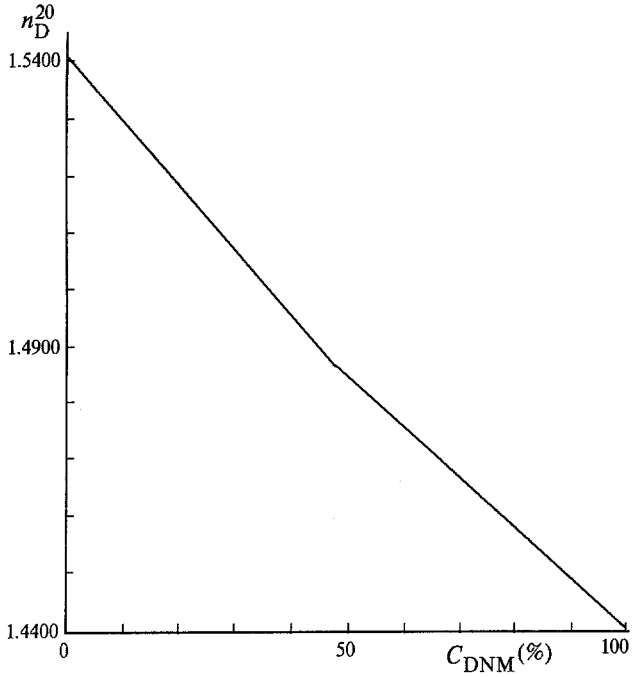


Fig. 1. Dependence of the refraction index, n_D^{20}, of a DNFO—DNM mixture on the content of DNM.

dicarboxylates.[17] We studied the following nitrating agents: HNO_3—H_2SO_4, 100 % and 90 % HNO_3, N_2O_5, and NO_2BF_4. The formation of DNFO was found to occur only in nitrating media based on 100 % HNO_3 [HNO_3—H_2SO_4, 100 % HNO_3, and N_2O_5—HNO_3, of which the latter was the best nitrating agent (Table 2)]. The reaction probably requires the nitrating agent to contain the NO_2^+ ion and to possess sufficient acidity to ensure efficient catalysis of the subsequent decomposition of adduct **9**. HNO_3 addition to the double bond of **7** occurs in parallel to give 2-methyl-1-nitro-2-propanol nitrate (**8**) (see Ref. 18) (Scheme 3). The latter was detected as a mixture with DNFO by ^1H NMR spectroscopy.

Experimental

IR spectra were obtained on a UR-10 spectrophotometer in thin films between NaCl glasses. ^1H NMR spectra were recorded on a Perkin-Elmer R-12 spectrometer. TLC was performed on Silufol UV-254. Preparative column chromatography was performed on silica gel L 5/40 μm. The plates were visualized under an UV lamp or by spraying with a 1 % ethanolic solution of diphenylamine.

Dehydration of dinitromethane. ***A.*** Pentane (10 mL) was added with stirring to 30 % oleum (5.8 mL; 41.7 mmol SO_3), and then the K-salt of DNM[13] (1.00 g, 6.95 mmol) was immediately added portion-wise over a period of 3 min with cooling in order to maintain the temperature at 20 °C. The mixture was stirred until the precipitate dissolved completely (~20 min), then 80 % H_2SO_4 (2.45 mL) was added with cooling over a period of 2 min, and the reaction mixture was poured into 50 mL of an ice—water mixture. The organic layer was separated, and the aqueous layer was extracted with ether (5 × 15 mL). The extract was dried with $MgSO_4$. According to TLC data (with $CHCl_3$ as the eluent), the solution contained a mixture of DNFO (R_f 0.58) and DNM (R_f 0.29). The solvent was removed on a rotary evaporator at 0 °C. Distillation at 10 Torr and then at 2 Torr gave 0.71 g of a liquid with n_D^{20} 1.4615, which (according to the plot in Fig. 1) corresponds to 24.2 % DNFO, *i.e.*, 28 % yield.

B. DNM[13] (0.74 g, 6.95 mmol) was added at 20 °C to 30 % oleum (5.8 mL, 41.7 mmol SO_3), and the reaction mixture was stirred for 4 min. The mixture was then diluted and worked-up similarly to method ***A***. TLC data showed that the product was

Scheme 3

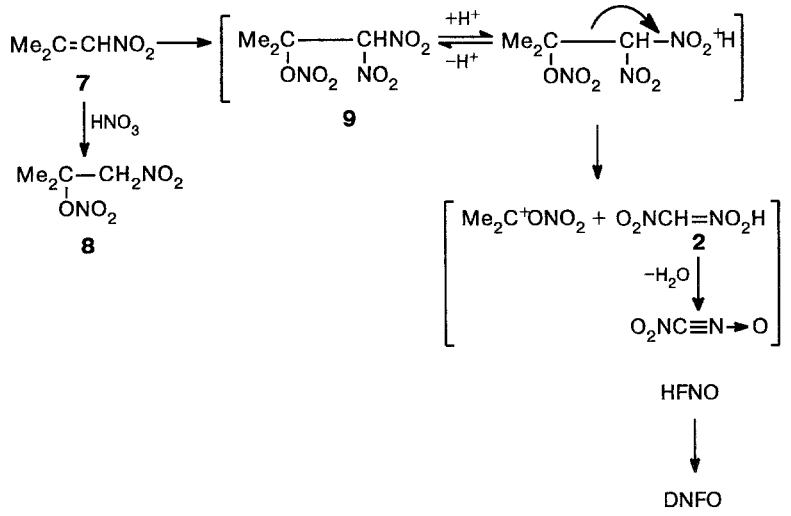


Table 2. Nitration of 2-methyl-1-nitro-1-propene with various nitrating agents

Entry	Nitrating agent (number of mols)	T/°C	t/min	Solvent	DNFO	
					n_D^{20}	Yield (%)
1	100 % HNO_3 + 95 % H_2SO_4, 1 : 2 v/v (4)	20	150	—	—	—*
2	100 % HNO_3 (12)	20	23	—	1.4973 1.5231	43.5 17**
3	90 % HNO_3 (12)	20	21	—	—	—
4	NO_2BF_4 (1)	20	90	Sulfolane	—	—
5	N_2O_5 (1)	20	20	CCl_4	—	—
6	N_2O_5 (1)	20	26	Sulfolane	—	—
7	N_2O_5 (1)	0, 20	48, 60	100 % HNO_3 (12 mol)	1.5091	50

* The presence of DNFO was demonstrated by TLC. ** Obtained after purification on a column with silica gel.

pure DNM (yield 0.73 g, 99 %) containing no DNFO admixture, n_D^{20} 1.4410 (*cf.* Ref. 13: n_D^{20} 1.4407).

C. The K-salt of DNM (1.00 g, 6.95 mmol) was added over 1.5 min at 20 °C with stirring and cooling to a mixture of 95 % H_2SO_4 (10.1 mL, 180.5 mmol) and pentane (10 mL). After the salt dissolved, the reaction mixture was kept for ~4 min and poured into 50 g of an ice—water mixture, then the mixture was worked-up similarly to method ***A*** to give 0.72 g of a liquid, n_D^{20} 1.4500, containing 10.6 % DNFO (yield 12 %). When the reaction time was increased to 60 min, the yield was 0.71 g, n_D^{20} 1.4502. The yield of DNFO was 12 % and that of DNM was 86 %.

D. The K-salt of DNM (1.00 g, 6.95 mmol) was added over 1.5 min at 20 °C with stirring and cooling to a mixture of 95 % H_2SO_4 (10.1 mL, 180.5 mmol) and CH_2Cl_2 (10 mL). After the salt dissolved (~4 min), the reaction mixture was heated on a boiling water bath, and the CH_2Cl_2 was distilled off. The mixture was kept for 1 h, cooled, and worked-up similarly to method ***C***. The residue after solvent removal was mixed with $CHCl_3$ (15 mL), filtered off from insoluble admixtures, washed with water (5 mL), dried with $MgSO_4$, and concentrated at 20 °C (12 Torr) to give 0.21 g (34 %) of DNFO containing no admixtures (TLC data), n_D^{20} 1.5415 (*cf.* Ref. 12: n_D^{20} 1.5375). Method ***D*** can give a very pure product if the purification and isolation (starting with the stage of water washing) are carried out rapidly with cooling on an ice bath. This results in DNFO as colorless crystals with m.p. 14—15 °C, n_D^{23} 1.5390.

Heating of DNFO in 95 % H_2SO_4. A solution of DNFO (1.28 g) in 95 % H_2SO_4 (21.2 mL) was kept for 1 h on a boiling water bath, cooled, poured into an ice—water mixture (100 g), and extracted with ether (5 × 30 mL). The extract was dried with $MgSO_4$, and the solvent was distilled off *in vacuo* at 20 °C. $CHCl_3$ (30 mL) was added to the residue, and the solution was filtered through a paper filter, washed with water (10 mL), dried with $MgSO_4$, and concentrated *in vacuo* at 20 °C to give 0.47 g (37 %) of DNFO, n_D^{20} 1.5370.

Nitration of acetylmethanenitrolic acid 3. ***A.*** *Synthesis of acid 3* (see Ref. 16). N_2O_4 (3 mL) was added dropwise at 0 °C to a solution of acetone (30.6 mL) in CCl_4 (30.6 mL), and the mixture was stirred for 20 min at 0 °C and for 40 min at 20 °C. The excess acetone and CCl_4 were distilled off in the vacuum of a water-aspirator pump at a bath temperature not exceeding 25 °C to give 6.3 g (~100 %) of acid **3** as a reddish oil, R_f 0.43 (ether—benzene, 1 : 4).

B. *Nitration of acid 3 by the procedure reported previously.*[14] Acid **3** (0.5 g, 3.8 mmol) was added dropwise at 20 °C over a period of 6 min to 26 % HNO_3 (0.8 mL, 3.8 mmol), and the mixture was stirred for an additional 20 min. TLC showed only the presence of the starting compound **3**. Heating with stirring (30 min at 50 °C) resulted in gas evolution. TLC showed the presence of the starting **3** and diacetylfuroxan **6** (R_f 0.63, ether—benzene, 1 : 4). After heating for 10 min at 80 °C, TLC showed the presence of mostly furoxan **6** along with a small amount of acid **3**. The mixture was poured onto ice and extracted with $CHCl_3$ (2 × 20 mL). The extract was washed with 5 % $NaHCO_3$ and dried with $MgSO_4$, and the solvent was distilled off to give 0.30 g (93 %) of furoxan **6**. According to its IR spectrum, the sample was identical to an authentic sample.

C. *Nitration of 3 according to the known procedure.*[15] Acid **3** (0.50 g, 3.79 mmol) was added dropwise at 20 °C with stirring to a mixture of 100 % HNO_3 (1.58 mL, 37.9 mmol) and NH_4NO_3 (3.03 g, 37.9 mmol), and the mixture was stirred for an additional 2 h at 20 °C, poured onto ice, and extracted with $CHCl_3$. The extract was washed three times with water and dried with $MgSO_4$. The $CHCl_3$ was removed *in vacuo* at a bath temperature not higher than 25 °C to give 0.45 g (90 %) of a reddish oil identical to that obtained according to method ***A***.

Nitration of 2-methyl-1-nitro-1-propene (7). ***A.*** *Nitration with a sulfuric-nitric acid mixture.* Compound **7** (4.23 g, 41.9 mmol) (see Ref. 18) was added dropwise at −30 to −20 °C over a period of 4 min to a sulfuric-nitric acid mixture (21.5 mL, 2 : 1 v/v). The temperature was increased to 20 °C, and the mixture was stirred for 2.5 h at this temperature. This procedure gave a mixture of at least four compounds including DNFO (TLC with $CHCl_3$ as the eluent). However, we did not manage to isolate DNFO from the mixture by preparative column chromatography on silica gel due to the extreme instability of this compound under chromatographic conditions (exposure to silica gel resulted in strong self-heating and intense evolution of nitrogen oxides).

B. *Nitration with 100 % HNO_3.* Compound **7** (2.73 g, 25.9 mmol) was added dropwise at 0 °C with stirring over a period of 4 min to 100 % HNO_3 (13.65 mL). The reaction mixture was allowed to heat itself spontaneously to 20 °C, then it was stirred for 25 min, poured into an ice—water mixture (70 g), and extracted with CCl_4 (10 × 18 mL). The extract was concentrated *in vacuo* to a volume of ~30 mL, washed with water (2 × 10 mL), dried with $MgSO_4$, and concentrated *in vacuo* to give 0.99 g of a mixture of DNFO and nitrate **8**. The ^1H NMR spectrum, δ, HMDS, without a solvent [1.60 (s, 6 H, 2 CH_3); 4.84 (s, 2 H, CH_2)] coincides with the ^1H NMR

spectrum of compound **8** synthesized by the procedure described previously.[18] The IR spectrum contains absorption bands of both DNFO and compound **8**, n_D^{20} 1.4973 (*cf.* Ref. 18: **8**, n_D^{20} 1.448). According to TLC, the sample is homogeneous, R_f 0.58 ($CHCl_3$ as the eluent). We were unable to completely remove nitrate **8** from the sample of DNFO thus obtained even by preparative column chromatography on silica gel (CCl_4 as the eluent), which led to noticeable loss of DNFO (yield 17 %, n_D^{20} 1.5231).

C. Nitration with a N_2O_5—HNO_3 mixture. Compound **7** (3.98 g, 39.5 mmol) was added dropwise with stirring and cooling (0 °C) to a solution of N_2O_5 (4.26 g, 39.5 mmol) in 100 % HNO_3 (19.8 mmol). Stirring was continued for 50 min at 0 °C and for 1 h at 20 °C. The mixture was poured into an ice—water mixture (100 g) and extracted with CCl_4 (10 × 20 mL). The extract was concentrated *in vacuo* to a volume of ~50 mL (at a bath temperature not exceeding 30 °C), washed with water (2 × 20 mL), dried with $MgSO_4$, and concentrated *in vacuo* to give 1.74 g (50 %) of DNFO, n_D^{20} 1.5091.

D. Nitration with 90 % HNO_3. Compound **7** (0.39 g, 3.93 mmol) was added at 0 °C to 90 % HNO_3 (3 mL), and the mixture was stirred for 20 min at 0 °C and 20 min at 20 °C. Evolution of nitrogen oxides was observed, but DNFO formation was not detected.

E. Nitration with $NO_2^+BF_4^-$ in sulfolane. Compound **7** (1.75 g, 17.3 mmol) was added dropwise with cooling (0—10 °C) to a suspension of $NO_2^+BF_4^-$ (1.96 g, 17.3 mmol) in sulfolane (10 mL). The mixture was heated to 20 °C and stirred for 1.5 h. TLC detected no DNFO formation.

F. Nitration with N_2O_5 in CCl_4 (sulfolane). A solution of N_2O_5 (1.47 g, 12.5 mmol) in CCl_4 or sulfolane (10 mL) was added dropwise at 0—10 °C to a solution of compound **7** (1.26 g, 12.5 mmol) in 5 mL of the same solvent. The temperature was increased to 20 °C and the reaction mixture was stirred for 20 min. TLC detected no DNFO formation.

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Received October 17, 1994