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Mendeleev Commun., 1995, **5(6)**, 231–232

Mendeleev
Communications

Nitroformonitrile Oxide in the Reaction of 1,3-Dipolar Cycloaddition

Igor V. Ovchinnikov, Nikolai A. Popov, Nina N. Makhova,* Lenor I. Khmel'nitskii and Vladimir A. Shlyapochnikov

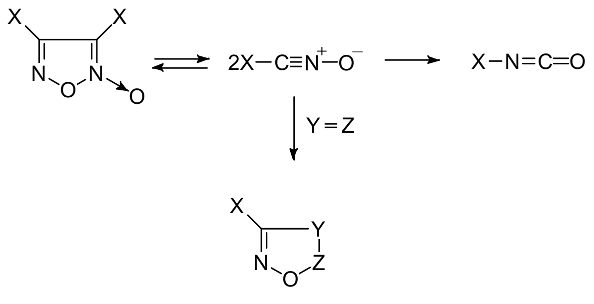
N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 117913 Moscow, Russian Federation.
Fax: +7 095 135 5328

A method for the generation of nitroformonitrile oxide (NFNO) by thermolysis of dinitrofuroxan (DNFO) has been proposed; the formation of NFNO was confirmed by IR spectroscopy and by synthesising cyclic adducts of NFNO with dipolarophiles.

Earlier[1] we proposed two methods for generating NFNO ($O_2N{-}C{\equiv}N^+{-}O^-$). The first one involved dehydration of dinitromethane and the second one was destructive nitration of 1-nitro-2-methylprop-1-ene. NFNO was detected as a product of its dimerization, DNFO. The reaction conditions[1] in this case were not suitable for studying the reaction of 1,3-dipolar cycloaddition of NFNO.

The present work studies the possibility of generating NFNO by thermolysis of DNFO and *in situ* introduction of the former into cycloaddition with different types of dipolarophiles.

The thermal decomposition of the furoxan[†] ring at the C–C and O(1)–N(2) bonds is a general method for *in situ* preparation of nitrile oxides and their subsequent transformation into cyclic adducts with dipolarophiles[2] (Scheme 1).



Scheme 1

[†] 1,2,5-Oxadiazole.

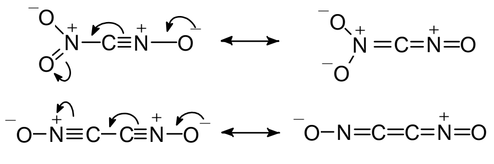
The temperature of thermolysis depends significantly on the nature of the substituents. The minimal temperature used for this purpose was 55 °C (thermolysis of cyclopentenefuroxans). The temperature of thermolysis ranges from 200 to 250 °C for alkyl- and arylfuroxans and from 110 to 140 °C for diacylfuroxans. The reaction is complicated by isomerization of nitrile oxides into isocyanates, whose fraction increases as the temperature increases.

The applicability of this method for the preparation of NFNO is doubtful since DNFO has low thermal stability and undergoes decomposition even at room temperature.[3]

To clarify the possibility of thermolysis of DNFO into NFNO, we used IR spectroscopy since the nitrile oxide fragment and other possible products of thermolysis have characteristic absorption bands (cm^{-1}): nitrile oxides 2315–2275 ($\nu_{C\equiv N}$) (broad intense band),[4] isocyanates 2280–2240 (broad intense band),[5–7] CO_2 (gas) 2350 (very intense band), N_2O (gas) 2224 ($\nu_{N\equiv N}$), NO (gas) 1900–1800 (doublet), NO_2 1620, N_2O_4 1740.[8]

A series of experiments on DNFO thermolysis in CCl_4 at several fixed temperatures within 25–75 °C was carried out. The process was performed directly in the thermostatically controlled cell of an IR spectrometer. First, IR spectra in CCl_4 were obtained: N_2O 2220 cm^{-1} ($\Delta 1/2 = 10\ \mathrm{cm}^{-1}$) (narrow intense band) and CO_2 2340 cm^{-1} (very intense band).

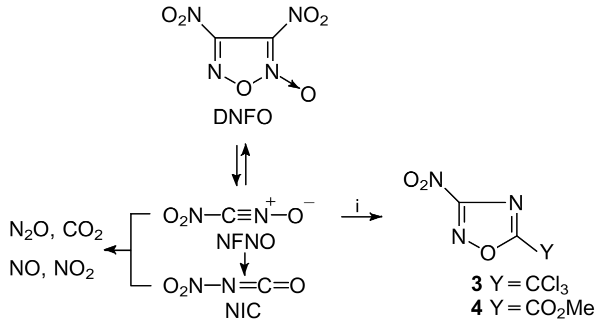
An analysis of IR spectra showed that two intense absorption bands appeared at moderate temperatures (25–35 °C), 2220 cm^{-1} ($\Delta 1/2 = 10\ \mathrm{cm}^{-1}$) and 2340 cm^{-1} which were attributed to N_2O and CO_2, respectively. Two absorption bands with low intensities at 2230 cm^{-1} ($\Delta 1/2 = 31\ \mathrm{cm}^{-1}$) and 2270 cm^{-1} were also observed, the increase in the intensity of the latter band being accompanied by a decrease in the intensity of the first band. It was reasonable to deduce that the latter absorption bands belong to NFNO and nitroisocyanate (NIC), respectively. However, their low intensity and low-frequency shift of $\nu_{C\equiv N}$ in the $–C\equiv N^+–O^-$ fragment were surprising. The low intensity of these absorption bands may result from the low relative concentrations of both compounds in solution. As for the low-frequency shift of $\nu_{C\equiv N}$ in NFNO, an example of the anomalous behaviour of this fragment in IR spectra is known for oxalodinitrile oxide, $O^-–N^+\equiv C–C\equiv N^+–O^-$ ($\nu_{C\equiv N}$ 2190 cm^{-1}),[4] which has found no explanation in the literature. Since the electronic structures of NFNO and oxalodinitrile oxide are similar (Scheme 2), one may propose that the shifts in the IR spectra are caused by the same reasons. The half width of the band at 2230 cm^{1} ($\Delta 1/2 = 31\ \mathrm{cm}^{-1}$) does not contradict its assignment to $\nu_{C\equiv N}$ in NFNO.



Scheme 2

As the temperature of thermolysis increases (40–75 °C), the absorption band of NFNO is not observed in the IR spectrum, but the absorption band of NIC is present, which may indicate the formation of NFNO quickly undergoing isomerization into NIC under these conditions. In addition to the absorption bands of N_2O and CO_2, absorption bands of NO (1880, 1830 doublet), NO_2 (1620) and N_2O_4 (1740 cm^{-1}) appear, which may result from a parallel pathway of DNFO decomposition. The complete decomposition of NIC at 75 °C occurs in 1 h, and decomposition of DNFO (disappearance of the absorption band at 1685 cm^{-1}) occurs in 1.5 h (Scheme 3).

The results obtained indicate that, if the absorption band at 2230 cm^{-1} belongs to NFNO, one should expect the formation of the target adducts as a result of interaction of DNFO with dipolarophiles. Obviously, the reaction should be carried out by treatment of NFNO with excess dipolarophile for a long period of time without heating. However, the presence of nitrogen oxides (NO, NO_2, N_2O_4) among the products of DNFO thermolysis may narrow the range of possible dipolarophiles due to their competitive reactions with these reactive compounds.



3 Y = CCl_3
4 Y = CO_2Me

Scheme 3 *Reagents and conditions*: i, $Cl_3CC\equiv N$ (**1**) or $MeO_2CC\equiv N$ (**2**), 7–10 mol/mol DNFO, $CHCl_3$, 20 °C, 7 days.

The reactions of DNFO with styrene, trichloroacetonitrile **1**, methylcyanoformate **2**, phenylacetylene, *trans*-stilbene and cyclohexene in $CHCl_3$ at room temperature were carried out. In the case of **1** and **2**, the required cyclic adducts, 3-nitro-5-trichloromethyl-1,2,4-oxadiazole **3** and 3-nitro-5-methoxycarbonyl-1,2,4-oxadiazole **4** were obtained (Scheme 3), which was further proof of the existence of NFNO. In other cases, we obtained complex mixtures of products which we failed to separate.

Hence, thermolysis of DNFO appears to proceed through the formation of NFNO according to the usual furoxan scheme. NFNO undergoes isomerization to the corresponding NIC and affords the products of 1,3-dipolar cycloaddition in the presence of active dipolarophiles, and the anomalously low (of those reported in the literature) thermolysis temperature should be noted.

The structure of the cycloadducts obtained was confirmed by IR, NMR and mass spectra. Compounds **3** and **4** were isolated by preparative column chromatography on SiO_2.[‡]

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Received: Moscow, 30th June 1995
Cambridge, 5th September 1995; Com. 5/04300J

[‡] *Compound* **3** (21%), m.p. 50–52 °C, R_f (Silufol UV-254, hexane): 0.35; ^{13}C NMR [$(CD_3)_2CO + CCl_4$]: 177.57 (C5), 159.03 (C3), 119.81 (CCl_3); ^{14}N NMR: −39.87 (NO_2, $\Delta 1/2 = 1.6$ Hz); mass spectrum (*m/z*): 237 $[M]^+$.

Compound **4** (23%), $n_D^{18.5}$ 1.4983; R_f (Silufol UV-254, $CCl_4/CHCl_3 = 1{:}1$): 0.34; ^{13}C NMR [$(CD_3)_2CO + CCl_4$]: 169.83 (C5), 159.30 (C3), 153.122 (C=O), 55.05 (CH_3O); ^{14}N NMR: −39.22 (NO_2); ^1H NMR: 4.15 s; mass spectrum (*m/z*): 171 $[M]^+$.