

REACTIONS OF NITRILE OXIDES WITH NITROGEN OXIDES.

1. REACTIONS WITH NITROGEN TETROXIDE

O. A. Rakitin, V. A. Ogurtsov, T. I. Godovikova,
and L. I. Khmel'nitskii

UDC 542.91:547.582.4-
31:546.174-31

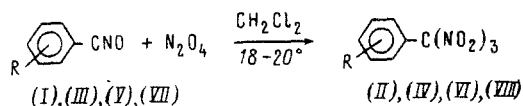
We have studied the reaction of nitrile oxides with nitrogen tetroxide. It was shown that the reaction is selective: acetonitrile oxide yields ethylnitrolic acid, α -oximinophenylacetonitrile oxide gives a mixture of isomers of phenylnitrofoxan, and aromatic nitrile oxides give aryltrinitromethanes.

Nitrile oxides form one of the most reactive classes of organic compounds [1]. The literature describes comprehensive studies of their isomerization to isocyanates, dimerization to furoxans, and reactions with unsaturated compounds, bases, and nucleophilic reagents. Reactions with oxides of nitrogen have not been described before.

Among the oxides of nitrogen, nitrogen tetroxide has broad spectrum of applications, which may manifest itself as oxidizing, nitrosating, and nitrating agent.

This article deals with the investigation of the reactions of aromatic and aliphatic nitrile oxides with nitrogen tetroxide.

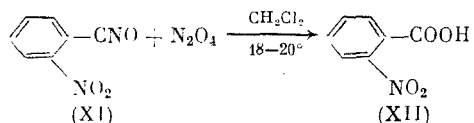
It was shown that the nature of the nitrile oxide influences the outcome of these reactions. Thus, aromatic nitrile oxides - benzonitrile oxide, p- and m-nitrobenzonitrile oxide, and p-bromobenzonitrile oxide - yield the corresponding aryltrinitromethanes when the reaction is carried out at room temperature.



R = H (I), (II); 4-NO₂ (III), (IV); 3-NO₂ (V), (VI); 4-Br (VII), (VIII).

In the cases of benzonitrile oxide and p-bromobenzonitrile oxide also degradation products of the nitrile oxide are formed: benzoic (IX) and p-bromobenzoic (X) acid in yields of 26 and 25%, respectively.

The main product of the reaction of o-nitrobenzonitrile oxide with nitrogen tetroxide is o-nitrobenzoic acid, which apparently is connected with steric hindrance. We failed to isolate the corresponding trinitromethyl derivative in this case.



As examples of other nitrile oxides we selected acetonitrile oxide (XIII) and α -oximinophenylacetonitrile oxide (XV).

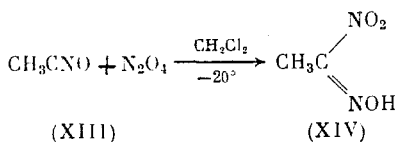
Acetonitrile oxide reacts with nitrogen tetroxide in methylene chloride with formation of ethylnitrolic acid.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 7, pp. 1620-1622, July, 1990. Original article submitted August 2, 1989.

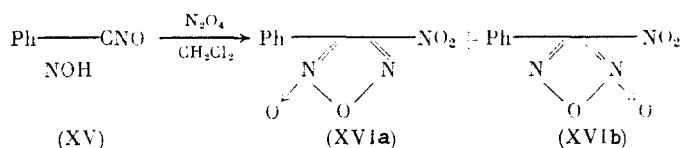
TABLE 1. Data on the Reactions of Nitrile Oxides with N₂O₄

Compound	Product	Yield, %	R _f	Mp, °C	²⁰ n _D
				(lit. data)	
(I) [4]	(II)	45	0.73		1,5385
	(IX)	26	—	120–121 (121,7 [6])	(1,5395 [5])
(III) [7]	(IV)	70	0.82	46–47 (46–47 [8])	
(V) [7]	(VI)	79	0.78	63–64 (63–64 [8])	
(VII) [7]	(VIII)	65	0.75		1,5694 *
	(X)	25	—	252–253 (251–253 [6])	
(XI) [7]	(XII)	18	—	148 (148,6 [6])	
(XIII) [9]	(XIV)	45	0.67	80–82 (81–82 [10])	
(XV) [11]	(XVIa) + (XVIb)	15	0.75	80 **	

*p-Bromophenyltrinitromethane was not described earlier. Found, %: C 27.69, H 1.32, Br 25.93. C₇H₄N₃O₆Br. Calculated, %: C 27.45, H 1.31, Br 26.14. IR spectrum, (ν, cm⁻¹): 1600 and 1300 (NO₂), 1500, 1410, 1085, 850 (Ph). **The IR spectra and melting point of a mixture of (XVIa) and (XVIb) coincide with the IR spectrum and melting point of a mixture of authentic 4-nitro-3-phenyl- and 3-nitro-4-phenylfuroxan, prepared according to [12].



The reaction of α-oximinophenylacetonitrile oxide with N₂O₄ yields a mixture of 4-nitro-3-phenyl- and 3-nitro-4-phenylfuroxans in the ratio of 1:1, with a total yield of 15%.

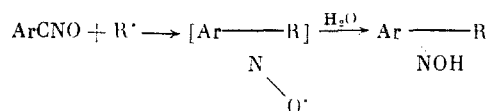


The nature of the reactions of nitrile oxides with nitrogen tetroxide may be explained by considering the character of N₂O₄.

It is known that N₂O₄ can dissociate with formation of both ionic particles and molecules of nitrogen dioxide [2].

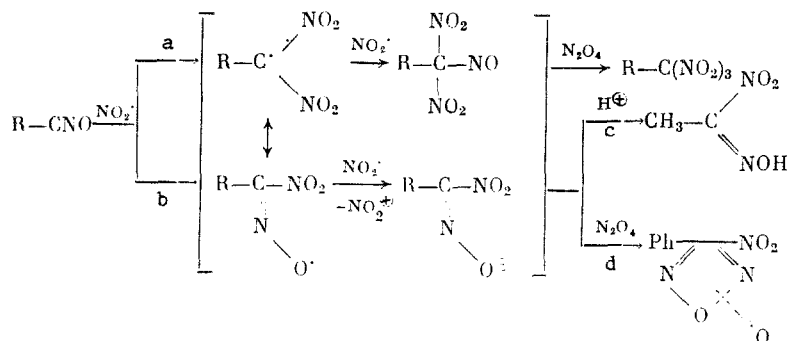


We have shown that aliphatic nitrile oxides react neither with nitrosonium-containing compounds (nitrosylfluoroborate, nitrosylsulfuric acid) nor with the nitrate anion (ammonium nitrate, nitric acid). Apparently, the attacking particle in the reactions of these nitrile oxides with N₂O₄ is the nitrogen dioxide molecule, which has, as is known, radical character. The reaction of nitrile oxides with radicals is described in the literature [3].



R = CH₃CO, CON(CH₃)₂, CH₂OH.

By analogy with these conversions it may be assumed that the first stage in the reaction of nitrile oxides with N₂O₄ is addition of the NO₂ radical to the carbon atom of the nitrile oxide group. Then, for aromatic nitrile oxides, addition of a second NO₂ molecule and oxidation to aryltrinitromethanes takes place, and for aliphatic nitrile oxides reduction of the nitroxyl radical to the oxime anion.



R = Ar (a), Alk (b), CH₃ (c), Ph-C- (d).
 NOH

Thus, the reaction of nitrile oxides with N₂O₄ is selective: from aliphatic nitrile oxides nitrolic acids or nitrofuraxans are formed, and from aromatic nitrile oxides aryltrinitromethanes.

EXPERIMENTAL

IR spectra were taken from KBr disks on a UR-20 spectrometer. Melting points were determined with a Boétius hot stage with a heating rate of 4°C/min near the melting point.

Reaction of Nitrile Oxides with N₂O₄ (general method). To a suspension or solution of 5 moles of the nitrile oxide in 15 ml of CH₂Cl₂ is added at ~20°C (in the case of acetonitrile oxide at -20°C) a solution of 1.22 ml (20 mmoles) of N₂O₄ in 2 ml of CH₂Cl₂. The mixture is kept at ~20°C for 3 h, the nitrogen oxide and the solvent are evaporated, 10 ml of CCl₄ is added, and the corresponding benzoic acid is filtered off. The mother liquor is evaporated and the residue is chromatographed over a column with SiO₂ (L 40/100 μ) with the eluent CHCl₃:(CH₃)₂CO, 20:1. The obtained results are summarized in Table 1.

LITERATURE CITED

1. C. Grundmann and P. Grunanger, *The Nitrile Oxides*, Springer Verlag, Berlin-Heidelberg-New York (1971).
2. P. Gray and A. D. Joffe, *Chem. Rev.*, **55**, 1069 (1955).
3. T. Caronna, A. Qiulico, and F. Minisci, *Tetrahedron Lett.*, 3633 (1970).
4. T. Mukaiyama and T. Hoshino, *J. Am. Chem. Soc.*, **82**, 5339 (1960).
5. A. I. Timov and V. V. Smirnov, *Dokl. Akad. Nauk SSSR*, **83**, 243 (1952).
6. A. A. Potekhina (ed.), *Properties of Organic Compounds (a Handbook)* [in Russian], Khimiya, Leningrad (1984).
7. A. Qiulico, *Isoxazoles and Related Compounds. The Chemistry of Heterocyclic Compounds*, A. Weissberger (ed.), Vol. 17, p. 21.
8. L. I. Khmel'nitskii, S. S. Novikov, and O. V. Lebedev, *Izv. Akad. Nauk SSSR, Otd. Khim.*, 2019 (1960).
9. E. Zinner and H. Guntner, *Angew. Chem.*, **76**, 440 (1964).
10. V. Meyer, *J. Liebigs Ann. Chem.*, **175**, 88 (1875).
11. G. Ponzio, *Gazz. Chim. Ital.*, **66**, 123 (1936).
12. N. N. Makhova, I. V. Ovchinnikov, B. N. Khasapov, and L. I. Khmel'nitskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 3, 646 (1982).