

REACTIONS OF NITRILE OXIDES WITH NITROGEN OXIDES.

2.* REACTIONS WITH NITROGEN MONOXIDE AND NITROGEN SESQUIOXIDE

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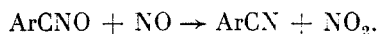
UDC 542.91:547.582.4-
31:546.172.6-31

We have studied the reactions of aromatic nitrile oxides with nitrogen monoxide and nitrogen sesquioxide. It was shown that nitrogen monoxide removes an oxygen atom from the nitrile oxide with formation of the corresponding nitrile and nitrogen dioxide. The reaction products with nitrogen sesquioxide are formed as a result of reactions of the nitrile oxide with nitrogen monoxide and nitrogen tetroxide.

Earlier [1] we published on the reaction of nitrile oxides with nitrogen tetroxide, which leads to aryltrinitromethanes in the case of aromatic nitrile oxides and to nitrolic acids or nitrofucoxans in the case of aliphatic nitrile oxides.

In continuation of that work we have studied the reactions of aromatic nitrile oxides with nitrogen monoxide (NO) and nitrogen sesquioxide (N₂O₃). As nitrile oxides we selected benzonitrile oxide and its o-, m-, and p-nitro derivatives.

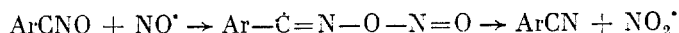
It was shown that nitrogen monoxide removes an oxygen atom from o-, m-, and p-nitrobenzonitrile oxide with formation of nitrogen dioxide and the corresponding nitrile.



Such a reaction of nitrile oxides is not described in the literature.

The capacity of nitrogen monoxide to eliminate an oxygen atom from inorganic compounds, such as molecular oxygen or hydrogen peroxide, is known [2]. On the other hand there are data on the capacity of valency-unsaturated compounds of carbon(II) [cobalt octacarbonyl, Co₂(CO)₈] [3] and phosphorus(III) (Alk₃P, Ph₃P) [4, 5] to eliminate an oxygen atom from nitrile oxides and to form the corresponding nitriles.

Apparently, the reaction of benzonitrile oxides with nitrogen monoxide proceeds via addition of the radical-like molecule NO to the oxygen atom of the nitrile oxide with subsequent splitting off of an NO₂ molecule.



The reaction of nitrile oxides with nitrogen monoxide proceeds slowly and therefore the nitrile oxide, on the one hand, has time to dimerize partly to the furoxan and, on the other hand, to react with the nitrogen dioxide formed in the reaction to the aryltrinitromethane [1]. Thus, p- and m-nitrobenzonitrile oxide give the corresponding nitriles, furoxans, and the trinitromethyl compounds, and o-nitrobenzonitrile oxide forms, in addition to o-nitrobenzonitrile and bis(2-nitrophenyl)furoxan, instead of o-nitrophenyltrinitromethane the degradation product of the nitrile oxide, o-nitrobenzoic acid.

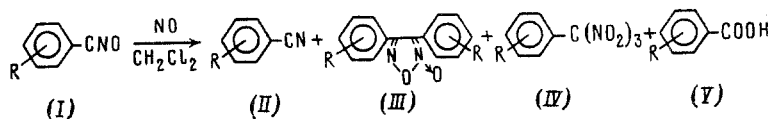
The most unstable of the aromatic nitrile oxides that we have studied, benzonitrile oxide, practically does not succeed in reacting with nitrogen monoxide; the main product isolated is the dimerization product of benzonitrile oxide, diphenylfuroxan. Benzonitrile and phenyltrinitromethane are present in the reaction mixture in trace amounts.

*For previous communication, see [1].

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. 1623-1625, July, 1990. Original article submitted August 2, 1989.

TABLE 1. Reactions of Benzonitrile Oxides with NO and N₂O₃

Com- pound	R	Reagent	Product	Yield, %	R _f	Mp, °C	Lit.
(Ia)	H	NO	(IIa)	traces	0.06	—	[8]
			(IIIa)	traces	0.23	—	[9]
			(IVa)	72	0.02	113–115	[10]
		N ₂ O ₃	(IIIa)	31	0.23	15385	[9]
(IVa)	37		0.02	113–115	[10]		
(Ib)	o-NO ₂	NO	(IIb)	20	0.09	113–114	[8]
			(IVb)	11	0.03	197–198	[10]
			(Vb)	35	—	147–148	[8]
		N ₂ O ₃	(Vb)	54	—	147–148	[8]
(Ic)	m-NO ₂	NO	(IIc)	23	0.07	116–117	[8]
			(IIIc)	27	0.26	63–64	[11]
			(IVc)	18	0.02	182–183	[10]
		N ₂ O ₃	(IIc)	10	0.07	116–117	[8]
			(IIIc)	38	0.26	63–64	[11]
			(IVc)	6	0.02	182–183	[10]
(Id)	p-NO ₂	NO	(IIId)	20	0.08	147–149	[8]
			(IIIId)	22	0.28	47–48	[11]
			(IVd)	27	0.02	203–204	[10]
		N ₂ O ₃	(IIId)	8	0.08	147–149	[8]
			(IIIId)	36	0.28	47–48	[11]
			(IVd)	9	0.02	203–204	[10]

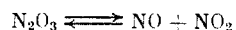


(I), (II), (III), (IV), (V): R = H (a), o-NO₂ (b), m-NO₂ (c), p-NO₂ (d).

Data on the reaction of nitrile oxides with NO are listed in Table 1.

Investigations of the reaction of aromatic nitrile oxides with nitrogen sesquioxide (N₂O₃) have shown that the compounds that are formed are products of reaction of the nitrile oxides with N₂O₄, viz., aryltrinitromethanes and the corresponding benzoic acids, and with NO, viz., aryl nitriles.

It is known [6] that in solvents N₂O₃ is in equilibrium with NO and NO₂.



Because the reaction with NO₂ proceeds considerably faster than that with NO, the products of the reaction with NO₂ (aryltrinitromethanes or o-nitrobenzoic acid) are formed in considerably larger amounts than those from the reaction with NO (arylnitriles). In some cases the products of the reaction with NO could not at all be isolated.

Data on the reaction of nitrile oxides with N₂O₃ are listed in Table 1.

Thus, reaction of aromatic nitrile oxides with NO leads to the corresponding nitriles. The products of the reaction with the sesquioxide are formed as a result of reactions of the nitrile oxide with NO and with N₂O₄.

EXPERIMENTAL

Reaction of Nitrile Oxides with NO (general method). Through a solution of 5 mmoles of nitrile oxide in 15 ml of abs. CH₂Cl₂ is bubbled at 20°C for 30 min a stream of dry NO, prepared according to [7]. The reaction mixture is allowed to stand overnight without access of air. The solvent is evaporated, the residue is treated with 10 ml of CCl₄, and the o-nitrobenzoic acid is filtered off. The mother liquor is evaporated and the residue is chromatographed over an SiO₂ (L 40/100 μ) column, eluent CHCl₃:CCl₄ 1:2.

Reaction of Nitrile Oxides with N_2O_3 (general method). To a solution of 5 mmoles of the nitrile oxide in 15 ml of abs. CH_2Cl_2 is added at 20°C a solution of 5 mmoles of N_2O_3 , prepared according to [6], in 1 ml of CH_2Cl_2 . The mixture was allowed to stand for 3 h, the nitrogen oxide and the solvent are evaporated, and the residue is worked up as described above.

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SULFYLIMINOFUROXANS: SYNTHESIS, STRUCTURE, AND OXIDATION TO NITRO AND NITROSO DERIVATIVES

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UDC 542.91:548.737:542.943:547.793.4

We have synthesized sulfolimines of the furoxan series. It was shown that by oxidation of 4-dimethylsulfoliminofuroxans both nitro and nitroso derivatives, the first examples of nitrososulfolimines, can be prepared. With x-ray structural analysis the main structural characteristics of the sulfoliminofuroxans were established.

In recent years the interest in methods to synthesize and to chemically convert aromatic and heterocyclic sulfolimines has grown considerably. Sulfolimines of the pyridine [1-3], pyrimidine [1, 4, 5], pyrazine [5-7], and furazan [8] series and of other heterocyclic compounds have been studied. Yet sulfoliminofuroxans have not been described.

The purpose of this work was to study the possibility of synthesizing 3- and 4-dimethylsulfoliminofuroxans, their structural characteristics, and their behavior in oxidation reactions.

For the synthesis of sulfoliminofuroxans we have investigated the reaction of aminofuroxans with the bis-triflate (I) and bis-trifluoroacetate (II) of dimethyl sulfide, which

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. 1625-1629, July, 1990. Original article submitted July 20, 1989.