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New Aspects of Nitrile Oxides Chemistry

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Abstract: Reactivity of nitrile oxides (1) towards both dimerization and cycloaddition with dipolarophiles can be inhibited by catalytic amount of tris-(4-bromophenyl)-aminium hexachloroantimonate and subsequently restored.

Nitrile oxides are amongst the most important and most studied of 1,3-dipolar compounds.[1] Many of them are unstable, and it is generally not possible to isolate them meaning that they must be generated in situ in order to react with a dipolarophile.

Unstable nitrile oxides, in the absence of a catalyst, either undergo rapid dimerization to furoxans or irreversible isomerization to isocyanates.[2] Up to now, techniques for stabilizing nitrile oxides at room temperature are unknown. We observed that nitrile oxides **1** (**a**: R = Phenyl; **b**: R = 2-Chlorophenyl; **c**: R = 2,6-Dichlorophenyl), in the presence of tris-(4-bromophenyl)aminium hexachloroantimonate **2**, become unreactive towards both dimerization and cycloaddition reactions with dipolarophiles (Scheme 1).

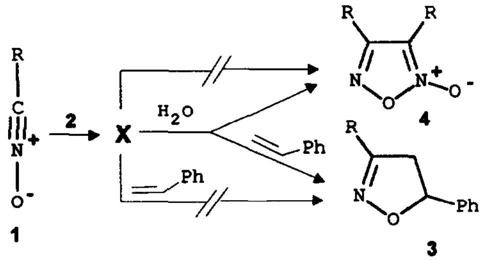
We report here the procedure used to inhibit the reactivity of benzonitrile oxide **1a**: tris-(4-bromophenyl)aminium hexachloroantimonate **2** was added to a 0.1 M solution of the nitrile oxide **1** in anhydrous dichloromethane at -20 °C. The resulting stirred suspension was allowed to reach room temperature. After 72 hours the resulting solution does not exhibit any reactivity, even following filtration and concentration. The data concerning the behavior of **1a**, both in the presence and absence of **2**, are reported in Table1.

Table 1

N°		% of 1a dimerized initially	 15 h	 72 h
i	solution 0.1 M of 1a	0.9	44.0	93.8
ii	mixture 0.1 M of **1a** and 0.02 equivalents of **2**	0.9	6.0	6.1

		% of cycloadduct **3a**
iii	solution entry (i) and styrene	97.0
iv	mixture entry (ii) and, after 72 h, styrene	0.0

Scheme 1



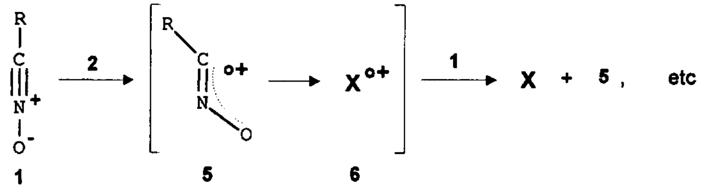
After 72 hours, the nitrile oxide, in the absence of the radical cation **2**, has almost totally dimerized, whilst in the presence of **2**, dimerization is inhibited. Analogous inhibition was observed for the cycloaddition reaction: in fact, upon addition of styrene to the unreactive mixture no 3,5-diphenyl-isoxazoline is formed (Table 1, entry iv), whilst under the identical reaction conditions, benzonitrile oxide and styrene yield the isoxazoline quantitatively. The usual reactivity of the nitrile oxide **1** can be observed upon addition of water. In fact, from mixture reported in Table1 entry iv, after addition of water the isoxazoline **3a** (R = Ph) is formed (~60% yield by GC and HPLC analises). HPLC and GC show the presence, in variable amount, of isocyanate and its usual derivatives.

Because of the unusual nature of these reactions, a plausible explanation for them should be desirable. Unfortunately all attempts to isolate a pure sample of unreactive intermediate **X** failed. However, when using a catalytic amount of **2** in the reaction mixture, **X** is virtually the only species present in solution. It was therefore possible to obtain some significant spectroscopic data on species **X**. For example, the data for **Xc** (obtained from nitrile oxide **1c**) were as follows: ^{13}C NMR ($CDCl_3$) δ 128.2, 131.3, 134.1, 135.3, 153.00* (the signal * is uncertain because of the signal noise ratio and because the intensity of the signal is significantly less than the others). MS spectra of **Xc**, obtained with various techniques (EI, CI, negative ions), always revealed a mass value of 187 for $C_7H_5Cl_2NO$, consistent with an isomeric structure of **1c**. IR spectroscopy did not show any peaks in the region 1700-3000 cm^{-1} (characteristic absorptions for triple or cumulated double bonds as $C\equiv N$ or $N=C=O$).

All known dimers and isomers can be excluded as possible structures since they are known compounds and their ^{13}C, IR and MS spectra are very different to that of **X**.

The observation that catalytic quantity of **2** leads to the formation of **X** in high yields, excludes the possibility that **X** is a radical species. A radical cation chain mechanism (Scheme 2) for the isomerization can be postulated.

Scheme 2



In this scheme the radical cation **5**, obtained by electron transfer from **1**, rearranges to the radical cation **6**. The electron transfer between **6** and **1** yields **X** and reforms the radical cation **5**.

Further studies on the scope of this reaction, the identification of **X** and the verification of the proposed mechanism of these reactions will be reported in due course.

References

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2. Grundmann, Ch.; Grünanger, P. *The Nitrile Oxides*; Springer-Verlag: Berlin. 1971; pp 75-84.

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