

FREE RADICAL REACTIVITY OF NITRILOXIDES. 1,3-ADDITION.

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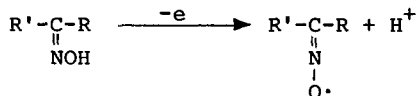
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Until now nothing has been recorded on the reactivity of free radicals with nitriloxides, if one excludes the hypothesis of Firestone¹, which was refuted by Huisgen², according to which the cycloaddition of this versatile class of compounds involves a spin-paired diradical intermediate.

The study of the radical reactivity of the nitriloxides is interesting for two other reasons :

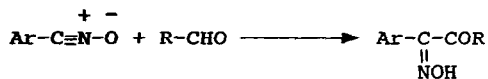
- a) The addition of a free radical to the nitriloxide group could be easy, as relatively stable radicals are formed, the same as those which are obtained by the oxidation of oximes³, and which were recently studied by e.s.r.



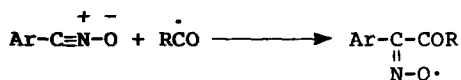
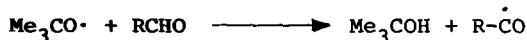
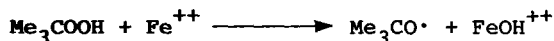
- b) The effect of the polar character of the radicals on the reactivity, so that a high reactivity of the nucleophilic radicals on the carbonium of the nitriloxide group could be predicted.

On the basis of this interest we carried out the following synthesis by the addition of nucleophilic radicals to nitriloxides :

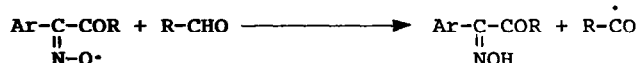
Addition of aldehydes. The reaction leads to the mono-oximes of α -diketones according to the following equation :



The reaction was carried out in the presence of the t-butylhydroperoxide ferrous salt redox system, and proceeds through the following steps :



It is not likely that the following chain reaction occurs in the final step



due either to the relative stability of the iminoxy radicals and because the reaction requires stoichiometric quantities rather than catalytic amounts of the hydroperoxide and ferrous salt.

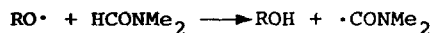
In the reaction system both electrophilic ($\text{Me}_3\text{CO}\cdot$) and nucleophilic ($\text{RCO}\cdot$) radicals are present, but only the latter reacts additively to the nitriloxide group.

The nucleophilic character of the acyl radicals was well demonstrated recently⁴.

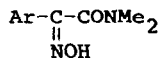
The contribution of polar forms in the transition state probably plays an important role on the reactivity :



Addition of dimethylformamide. The reaction is analogous to that described above; the alkoxy radical causes the abstraction of the hydrogen from the dimethylformamide,

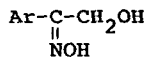


The product of the reaction has the following structure :

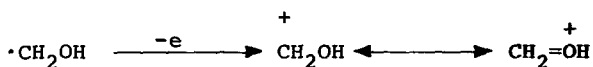


Also the carbamoyl radical has a net nucleophilic character⁵.

Addition of methanol. The redox system is the same as that used in the preceding cases and causes the formation of the radical $\cdot\text{CH}_2\text{OH}$ so that the product of the reaction has the following structure :

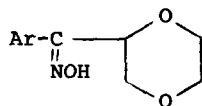


The nucleophilic character of the $\cdot\text{CH}_2\text{OH}$ radical is related to the stability of the corresponding cation :



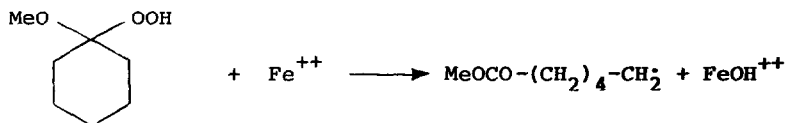
Addition of ethers. The hydrogen abstraction from ethers gives rise to nucleophilic radicals for the same reason indicated for methanol.

With dioxane products having the following structure are formed :

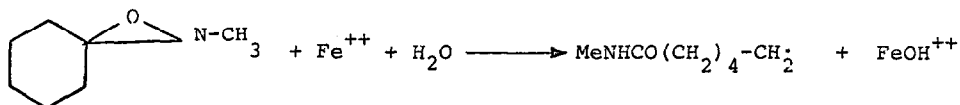


Addition of alkyl radicals from peroxides and oxaziranes. Also the alkyl radicals have a prevalent, although less pronounced, nucleophilic character, especially in solvents such as water and alcohols that solvate and stabilize the corresponding cations⁶.

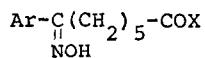
Two sources of alkyl radicals have been successfully employed : the 1-methoxy-cyclohexylhydroperoxide



and N-methylpentamethyleneoxazirane



The Products of the reaction have in these cases the following structure:



X = OMe or NHMe

The yields of these reactions are closely related to the stability of the nitriloxides, because, under the experimental conditions till now used, the radicals are generated in the space of 10-20 minutes.

For example with p-chlorobenzonitriloxide yields of 30-40% are obtained in all cases.

Quantitative data and experimental details will be published in an Italian journal.

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