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THERMAL DECOMPOSITION OF ARYLBROMONITROMETHANE SALTS IN THE PRESENCE OF UNSATURATED SYSTEMS

N.Alexandrou, E.Coutouli[1] and A.Varvoglis

Laboratory of Organic Chemistry, University of Thessaloniki, Greece.

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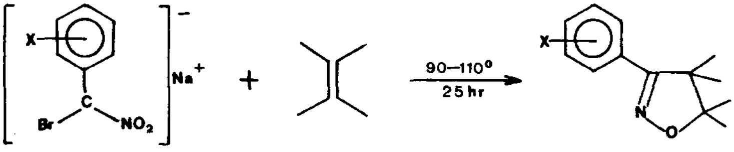
In connection with previous studies[2] on the reactions of phenylnitroacetonitrile salts, attempts have been made to detect the possible formation of arylnitrocarbenes by thermal decomposition of analogous salts. For this purpose, salts of type I were chosen as more suitable precursors and their thermal decomposition was carried out in the presence of alkenes to trap any carbenoid species that might have been formed. It has been found, however, that the reaction products are neither cyclopropane or insertion derivatives nor Δ^2-isoxazoline-N-oxides[3,4], but Δ^2-isoxazolines (II), identical with those obtained by 1,3-cycloaddition of the corresponding nitrile oxides and alkenes.



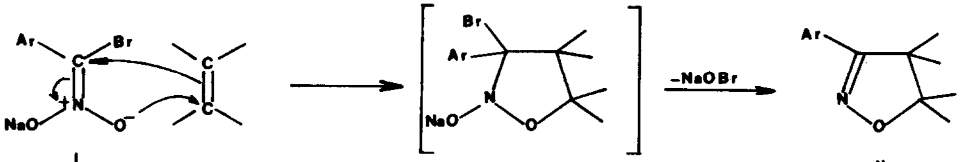
I (X = H, p-CH_3, p-Cl) II

The unsaturated systems used were cyclohexene, trans- stilbene and phenylacetylene and the yields of II ranged between 15-35%, calculated on the amount of starting salt and not on that which actually reacted. All new compounds have been characterised by elemental analysis and ir,nmr and mass spectra.

The orientation of the addition with phenylacetylene is the same to that observed with nitrile oxides[5] and so is the stereospecificity of the reaction, where trans-stilbene gives trans-isoxazoline[6]. Despite this evidence, formation of nitrile oxides as intermediates is ruled out on the following reasons: furoxans have never been isolated from the reaction products; also, when the decomposition of salts I is carried out in the presence of an inert solvent (benzene), substituted benzoic acids are obtained in the work-up, whereas with added primary amines benzamides are the reaction products and not the expected benzamidoximes, as if nitrile oxides had been formed[7].

On the other hand, formation of arylnitrocarbenes, which might have yielded Δ^2-isoxazoline-N-oxides, subsequently deoxygenated to II, is not considered probable, since 3,4,5-triphenyl-Δ^2-isoxazoline-N-oxide, independently prepared[8], did not give with cyclohexene any isoxazoline, under the experimental conditions.

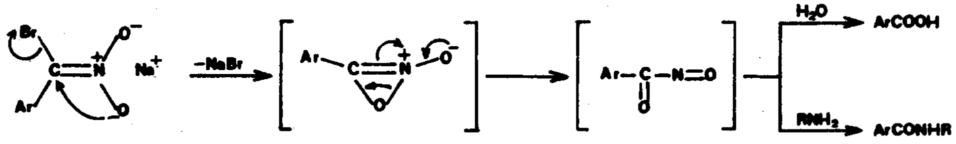
On the basis of the above evidence, a scheme may be envisaged, where the addition of the alkene takes place on the sodium nitronate form of I, with elimination of sodium hypobromite, which might occur by a free radical pathway. Indeed, in the presence of as little as 1% p-benzoquinone formation of II is greatly reduced.



I II

In agreement to this scheme various nitronic esters give isoxazolines by 1,3-cycloaddition with alkenes[9] and the in situ formed mixed anhydride $C_6H_5CH=N(O)OCOCH_3$ behaves like an 1,3-dipole, giving with dimethyl acetylendicarboxylate isoxazoles, under expulsion of acetate[10].

The decomposition of salts I in the absence of unsaturated systems probably occurs through an internal 1,3-nucleophilic displacement, analogously to an 1,5- displacement proposed for other bromonitro compounds[11]. The initial oxazirene-N-oxide III isomerizes to nitrosocarbonyl arene IV, which may give either benzoic acid or benzamides[12]:



I III IV

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