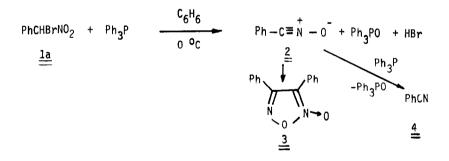
THE REACTION OF TRIPHENYLPHOSPHINE WITH ARYLBROMONITROMETHANES. FORMATION OF ARYLNITRILOXIDES. E. Coutouli-Argyropoulou Department of Chemistry, Lab. of Organic Chemistry University of Thessaloniki, Greece

ABSTRACT: Formation of furoxans and Δ^2 -isoxazolines confirms that arylnitriloxides are inter-mediates in the reaction of arylbromonitromethanes with triphenylphosphine.

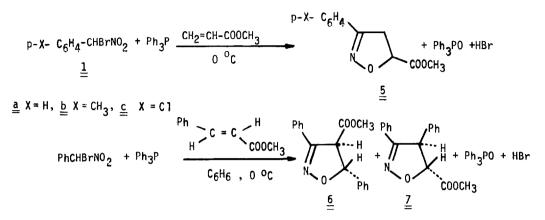
In connection with former studies^{1,2} on the possibility of aryInitrocarbenes generation from arylbromonitromethane and aryldinitromethane salts, the reaction of arylbromonitromethanes with triphenylphosphine has been examined. According to Trippett and Walker³ the reaction of 1-bromo-1-nitroalkanes with triphenylphosphine gave in very low yield or no phosphonium salts and mainly the corresponding nitriles. Nitriloxides were supposed to be intermediates but it was not possible to be detected although alkenes were used for their trapping.

A reinvestigation of the reaction of phenylbromonitromethane la and triphenylphosphine under several conditions (varying temperatures and solvents) gave no phosphonium salt, which could be used as a precursor for phenylnitrophosphonium ylide and subsequently phenylnitrocarbene. However, when the reaction was carried out with equimolecular amounts of triphenylphosphine and phenylbromonitromethane <u>la</u> at 0⁰C in dry benzene, diphenylfuroxan <u>3</u> was obtained in very good yield (80%). When the reaction was carried out with excess of triphenylphosphine besides the furoxan <u>3</u> benzonitrile <u>4</u> was also isolated according to Trippett's results³.



Since diphenylfuroxan $\underline{3}$ is the normal dimerization product of benzonitriloxide $\underline{2}^4$, its isolation may be taken as evidence for the formation of benzonitriloxide in the above reaction. Furthermore when the reaction of la,b,c with triphenylphosphine was carried out using methyl acrylate as solvent, the corresponding Δ^2 -isoxazolines 5a,b,c were isolated in good yields(50-80%), whereas in the presence of methyl cinnamate the two regionsomeric Δ^2 -isoxazolines <u>6</u> and <u>7</u> were isolated in a ratio 52:17 almost the same to that observed in the reaction of methyl cinnamate with benzonitriloxide (70:30).⁵ In all cases triphenylphosphine oxide was also

isolated in almost quantitative yields. All the isolated Δ^2 -isoxazolines were identified with authentic samples prepared by the reaction of the corresponding nitriloxides(from arylhydroxamoyl chlorides and triethylamine) and alkenes.



On the basis of the above evidence the formation of arylnitriloxides in the reaction of triphenylphosphine with arylbromonitromethanes is confirmed. A possible mechanistic scheme for the formation of arylnitriloxides is the following:

$$Ar - C = N + PPh_3 \longrightarrow Ar - C = N + O^- + PPh_3 \longrightarrow Ar - C = N + O^- + Ph_3PO + HBr$$

An analogous scheme is accepted by Trippett and Walker for the formation of nitriles in the same reaction, although they couldn't detect nitriloxides. The initial attact of triphenylphosphine at the oxygen of the nitro group has been suggested also in the reaction of triphenylphosphine with bromonitroalkenes⁶ and 1-halo-1-nitro-cycloalkanes⁷.

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