

THE REACTION OF TRIPHENYLPHOSPHINE WITH ARYLBROMONITROMETHANES. FORMATION OF ARYLNITRILOXIDES.

E. Coutouli-Argyropoulou

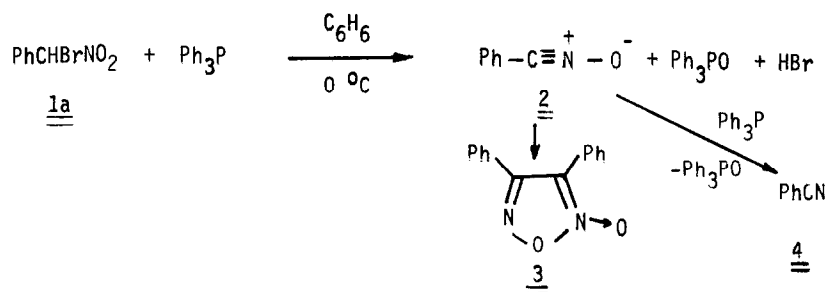
Department of Chemistry, Lab. of Organic Chemistry

University of Thessaloniki, Greece

ABSTRACT: Formation of furoxans and Δ^2 -isoxazolines confirms that aryl nitriloxides are intermediates in the reaction of aryl bromonitromethanes with triphenylphosphine.

In connection with former studies^{1,2} on the possibility of aryl nitrocarbenes generation from aryl bromonitromethane and aryl dinitromethane salts, the reaction of aryl bromonitromethanes 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 phenyl bromonitromethane 1a and triphenylphosphine under several conditions (varying temperatures and solvents) gave no phosphonium salt, which could be used as a precursor for phenyl nitro phosphonium ylide and subsequently phenyl nitro carbene. However, when the reaction was carried out with equimolecular amounts of triphenylphosphine and phenyl bromonitromethane 1a at 0°C in dry benzene, diphenylfuroxan 3 was obtained in very good yield (80%). When the reaction was carried out with excess of triphenylphosphine besides the furoxan 3 benzonitrile 4 was also isolated according to Trippett's results³.



Since diphenylfuroxan 3 is the normal dimerization product of benzonitriloxide 2⁴, its isolation may be taken as evidence for the formation of benzonitriloxide in the above reaction. Furthermore when the reaction of 1a,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 regioisomeric Δ^2 -isoxazolines 6 and 7 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

