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THE PHOTO-OXIDATION OF 2,4,6-TRIPHENYLPYRIDINE N-PHENYLIMINE AND RELATED COMPOUNDS

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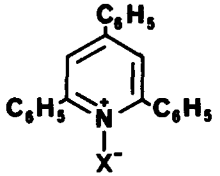
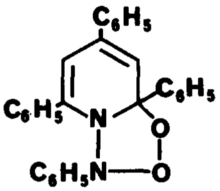
In an earlier communication[1] it was reported that photolysis of 1,2,4-triazole 4-p-nitrophenylimines under anaerobic conditions yields the corresponding triazoles and 4,4'-dinitroazobenzene. The latter product was replaced by the azoxy compound when oxygen was present during the photolysis. It was established that the azo compound was not being photo-oxidised to the azoxybenzene, and proposed that either intermediary p-nitrophenylnitrene or the ylid was being oxidised to p-nitronitrosobenzene. This could then intercept another nitrene with formation of the azoxy compound. However, concurrent papers[2] showed that triplet nitrenes normally combine with oxygen forming nitro compounds. Subsequently evidence was provided[3] that the nitroso precursors for azoxybenzene formation were derived by cycloaddition of oxygen to triplet aryl azide and ensuing fragmentation of the intermediary dioxatriazole.

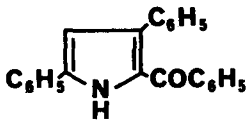


I X=NC_6H_5

II X=O



III



IV

Our inability to detect any other oxygenated products in the photooxidation of the triazole imines led us to investigate the behaviour of the pyridine N-phenylimine (I)[4], where breakdown of the species (III) should provide products such as (IV) already encountered[5] in the photochemical transformations of 2,4,6-triphenylpyridine N-oxide (II). Photolysis of oxygenated benzene solutions of (I) gave azoxybenzene (15%) and a minor amount of 2-benzoyl-3,5-diphenylpyrrole (IV)[6], in addition to aniline and 2,4,6-triphenylpyridine which are the major products[4] of anaerobic photolysis. However, when only a very limited amount of oxygen was present in the photolysis nitrosobenzene could be isolated but (IV) could not be detected. As comparable amounts of nitrosobenzene and (IV) would be expected to result from fragmentation of (III), this discordant observation cast doubt on its intermediary role.

An important clue to the true course of the reaction was obtained when the oxygen stream was conducted first through benzene in the photochemical reactor and then into a blacked-out benzene solution of the imine some two metres distant. The dark blue solution of the imine slowly assumed the characteristic apple green colouration of nitrosobenzene. Our deduction that the oxidant must be ozone was readily confirmed by passing a stream of conventionally generated ozonised oxygen through a benzene solution of the imine. The initially formed nitrosobenzene was further oxidised to nitrobenzene. In the light of previous observations[8] we were surprised to find that the accompanying 2,4,6-triphenylpyridine was slowly converted into its N-oxide, which gave (IV) under our normal photolysis conditions. In harmony with an earlier report[9] azobenzene was not converted into azoxybenzene by ozone, even under irradiation.

Thus we condlude that during photolysis of the imine (I) in the presence of oxygen concurrent production of ozone occurs. This either cleaves the imine producing nitrosobenzene, the precursor of azoxybenzene, or converts 2,4,6-triphenylpyridine to its N-oxide (II) which is then photochemically rearranged into the pyrrole (IV).

Ozonolytic cleavage of such N-imines has not been reported previously, although somewhat analogous cleavages have been observed for diazo compounds[10] and phosphoranes[11]. An initial survey shows that whereas 2,4-diphenyl-6-methylpyridine N-arylimines and 1,2,4-triazole 4-p-nitrophenylimines are also cleaved by ozone, no reaction occurs with 1,2,4-triazole 4-acylimines. Phenyl azide is alos ressistant to ozonolytic conversion to nitrosobenzene thus excluding an alternative interpretation of aforementioned conclusions[3]. The possible intervention of ozone in other photo-oxidations seems to have been frequently ignored. It is probably responsible for the photochemical conversion of α-diketones into carboxylic acid anhydrides previously observed[12] in these laboratories.

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