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PHOTOLYSIS OF 4-p-NITROPHENYLIMINO-1,2,4-TRIAZOLIUM YLIDS

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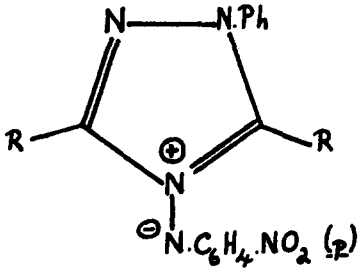
The 4-p-nitrophenylimino-ylids (Ia,b) of 3,5-dimethyl-1-phenyl and 1,3,5-triphenyl-1,2,4-triazoles may be prepared by deprotonation of the corresponding 4-p-nitrophenylamino-triazolium perchlorates[1]. The photolysis of these ylids in benzene, with the exclusion of oxygen, provides quantitative yields of 4,4'-dinitroazobenzene and the appropriate triazoles. By analogy with the photolysis of 4-acylimino-1,2,4-triazolium ylids[2] and ylids of other nitrogen heterocycles[3] we assume that the present ylids (Ia,b) dissociate yielding p-nitrophenyl nitrene, which either dimerises or attacks another molecule of ylid forming the observed azo compound. However, when our photolyses are repeated in the presence of oxygen the quantitatively formed products are 4,4'-dinitroazoxybenzene and the corresponding triazoles. Appropriate control experiments exclude the occurrence of direct photooxidation of 4,4'-dinitroazobenzene and, indeed, no such reaction appears to have been reported. It is not possible, however, to exclude photosensitisation of the reaction by the ylid.



I (a) R = Me
(b) R = Ph

An alternative explanation is suggested by the recent observation[4] of the interception of a nitrene by oxygen, as exemplified by the formation of nitroferrocene during the thermolysis or

photolysis of ferrocenyl azide in the presence of oxygen. If in the present case the intermediary p-nitrophenyl nitrene, or even the ylid, undergoes oxidation to p-nitronitrosobenzene then this could intercept another nitrene with formation of the azoxy compound. An intramolecular example of such a reaction is provided by the thermal or photolytic conversion of 2-azido-2'-nitrosobiphenyl to benzocinnoline N-oxide.

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