Reaction of Triplet Aryl Nitrenes and Azides with Molecular Oxygen

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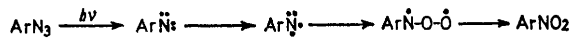
Summary Photolysis of aryl azides in the presence of oxygen gives nitro-compounds *via* a triplet nitrene and, in the case of *para*-substituted azides, also the azoxy-compound, probably *via* the nitroso-compound from the reaction of excited azide with oxygen, while triethyl phosphite deoxygenation of nitrosobenzene under oxygen also gave some nitrobenzene.

THERMAL and photochemical decomposition of aryl azides leads to nitrenes which can react either in their singlet or triplet states.[1] There is only one report of the *isolation* of the product formed by trapping the nitrene with oxygen: the formation of nitroferrocene by thermolysis or photolysis of ferrocenyl azide in the presence of oxygen.[2] We now report further evidence that nitro-aromatic compounds are formed by trapping triplet aryl nitrenes with triplet O_2, the addition of oxygen to photoexcited triplet azido-groups to give nitrosobenzenes, and evidence of the intermediacy of nitrenes in the deoxygenation of nitrosobenzenes. Support for the trapping of triplet ArN by $^3O_2$ has come from the recent direct e.s.r. observation of the formation of (**1**) and (**2**) in a frozen matrix.[3]



(1) (2)

Irradiation† of phenyl azide in acetonitrile or benzene solution under N_2 gave small amounts of azobenzene (**3**) and aniline (**4**), together with much tar, as had been previously observed.[4] Photolysis in a stream of oxygen gave nitrobenzene (5·9%) and tars, and only traces of (**3**) and (**4**).‡ Inclusion of singlet oxygen sensitisers (Rose Bengal or Methylene blue) or a singlet oxygen quencher (triethylamine) had no effect on this and other aryl azide photolyses, ruling out a singlet reaction; on the other hand, addition of triplet sensitisers (Me_2CO, PhCOMe) increased the yield of $PhNO_2$ to 11·3%. Addition of a triplet quencher (piperylene) resulted in a negligible yield of $PhNO_2$. Similar results were obtained with *para*-substituted aryl azides (Table); much less tar was produced, and the azoxy-compound was formed in addition to azo- and nitro-compounds. With a *p*-OMe group, the nitro-compound was the main product, while with *p*-NO_2 and *p*-CN the azoxy-compound predominated. Formation of *p*-dinitrobenzene from the photolysis of *p*-diazidobenzene or *p*-nitrophenyl azide in a solid matrix in the presence of oxygen has not been reported.[3]

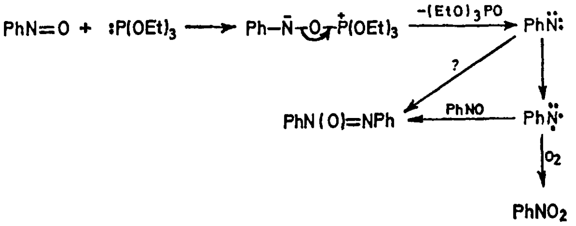
TABLE

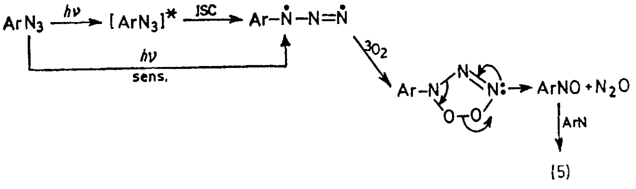
Photo-oxidation of $RC_6H_4N_3$ *at* 30° *for* 12 h.

R	Solvent	Additive	Product yield (%) $RC_6H_4NO_2$	ArNO=NAr	ArN=NAr	$ArNH_2$
H	MeCN	—	5·9	—	t	t
H	MeCN	PhCOMe	11·3	—	—	—
H	MeCN	Piperylene	0·2	—	—	t
p-MeO	MeCN	—	17·6	5·3	2·02	1·7
p-MeO	Me_2CO	—	19·8	1·3	4·0	a
p-MeO	MeCN	Piperylene	5·1	1·9	1·4	a
p-MeO	MeCN	Et_3N	18·0	2·2	3·1	a
p-CN	C_6H_6	—	5·3	13·9	—	10·5
p-CN	C_6H_6	PhCOMe	9·3	24·9	t	6·6
p-CN	C_6H_6	Piperylene	0	9·7	—	a
p-NO_2	MeCN	—	11·7	17·8	7·6	t
p-NO_2	Me_2CO	—	12·5	29·8	5·1	6·3
p-NO_2	MeCN	Piperylene	3·2	5·9	—	a
o-MeO[b]	MeCN	—	2	2	3	2
m-NO_2[b,c]	MeCN	—	15	6	t	2

t = trace.
[a] Not determined. [b] Carried out by Miss D. D. Daniels. [c] *o*-Nitrophenyl azide formed a polymer coating on the sides of the vessel which prevented further photolysis.

That nitrobenzene was derived from the nitrene was shown by deoxygenation of nitrosobenzene with triethyl phosphite in a stream of oxygen to give azoxybenzene (10·4%) and nitrobenzene (2·8%). In the absence of oxygen, only azoxybenzene (13·4%) was formed (see also ref. 5). Nitrosobenzene was not oxidised to nitrobenzene by oxygen under the same conditions. Thus, nitrobenzene appears to be formed at the expense of azoxybenzene in this deoxygenation, which suggests (a) that azoxybenzene is also formed *via* a nitrene reacting with nitrosobenzene, and not by deoxygenation of the nitroso-dimer,[6] in agreement with the conclusion of previous workers,[5] and (b) that azoxy-compounds are not formed by direct oxidation of ArN *via* ArNO. This raises the question of the origin of the azoxy-compounds in the aryl azide photo-oxidations. Since, as confirmed above, aryl nitrenes can be trapped by nitroso-





SCHEME

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† Using a medium-pressure mercury lamp.

‡ These are the expected triplet nitrene products.

compounds to give ArN(O)=NAr (**5**),[7] and photo-oxidation of the corresponding azobenzenes does not give (**5**) in significant amounts,[8] (**5**) must arise from ArN and ArNO, the latter not being formed from the former (see above). The alternative source of ArNO would be a direct oxidation of triplet aryl azide (Scheme). This possibility has been tested by condensing at −126° the gases evolved in the photo-oxidation of p-$NO_2C_6H_4N_3$. In addition to solvent and atmospheric gases, N_2O was found to be present both by gas chromatography and by mass spectrometry.

This work was supported by a grant from the National Science Foundation.

(*Received*, 25th *May* 1972; *Com.* 899.)

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[6] Nitrosobenzene is largely monomeric in acetonitrile and in benzene (deep green solution). See also R. Okazaki, T. Hosogai, E. Iwadare, M. Hashimoto, and N. Inamoto, *Bull. Chem. Soc. Japan*, 1969, **42**, 3611.

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