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PHOTOCHEMICAL REARRANGEMENT OF 2-NITROPHENYL PHENYL SULFOXIDE TO 2-NITROSOPHENYL PHENYL SULFONE

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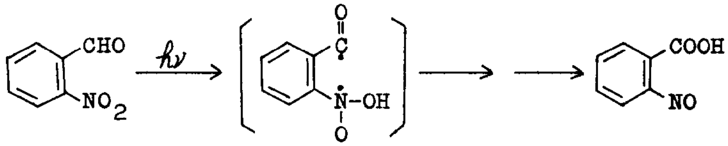
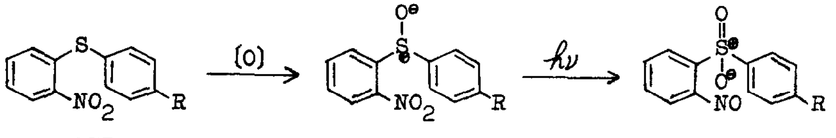
In aromatic nitro compounds a number of photochemical rearrangements are known, in which a transfer of an oxygen atom, originally attached to nitrogen, takes place. A possible mechanism for the rearrangements, for example, 2-nitrobenzaldehyde to 2-nitrosobenzoic acid, involves a hydrogen abstraction reaction by the nitro group followed by ring closure.[1)]



The photochemical oxygen transfer reactions are also found in other compounds such as azoxybenzene, N,α-diphenylnitrone and pyridine N-oxide, which are known to be stronger bases in the excited singlet state relative to the ground state,[2)] and to undergo the rearrangement via the excited singlet state[3-5)] without a hydrogen abstraction.[6)] On the other hand, nitrobenzene is also known to be a stronger base in the excited singlet state,[7,8)] so a nitro compound may be expected to undergo an oxygen transfer reaction from its excited singlet state, not involving a hydrogen abstraction reaction by the nitro group.

The principal objective of this communication is to report the new type of a photochemical oxygen transfer reaction, that is, the rearrangement of 2-nitrophenyl phenyl sulfoxide (I) to 2-nitrosophenyl phenyl sulfone (II).

I was prepared by oxidation of 2-nitrophenyl phenyl sulfide (III) with H_2O_2-acetic acid.



III I II

R = H a
CH_3 b
Cl c
CH_3CO d

A solution of 2-nitrophenyl phenyl sulfoxide (Ia) in benzene was irradiated with a high-pressure mercury lamp. Thin-layer chromatography (TLC) analysis on silica gel revealed that only one product had been formed. Chromatography on silica gel with chloroform gave a pale solid A: m.p. 140°C; $C_{12}H_9NO_3S$ (Found:C,58.58;H,3.66;N,5.59;S,12.85%. Calcd.:C,58.29;H,3.67;N,5.66; S,12.97%); $\nu_{max.}^{KBr}$ = 1320,1150 $cm^{-1}(SO_2)$; $\lambda_{max.}^{Benzene}$ = 783 nm (NO); positive in Liebermann nitroso test. Besides, oxidation of A with H_2O_2-acetic acid quantitatively gave 2-nitrophenyl phenyl sulfone. Therefore, A can be assigned to 2-nitrosophenyl phenyl sulfone (IIa).

Irradiation of other 2-nitrophenyl phenyl sulfoxides (IIb-d) gave similar results, which are shown in the following table.

		I	II			Yield(%)*	
	R	m.p.(°C)	m.p.(°C)	$\nu_{max.}^{KBr}$ (cm^{-1})	$\lambda_{max.}^{Benzene}$ (nm)	I	II
a	H	92	140	1320,1150	783	52	35
b	CH_3	140	200	1300,1150	785	68	22
c	Cl	118	169	1330,1160	790	59	35
d	CH_3CO	134	154	1320,1150	785	39	28

*A degassed solution (2×10^{-3}M, 2 ml) in benzene was irradiated at 30.0°C for 2 hours with a 100-W high-pressure mercury lamp (Halos PIH 100) using a Pyrex filter. The yield of each component was determined from the absorption intensity in an electronic spectrum after separation by TLC and extraction with chloroform.

2-Nitrophenyl 4-methylphenyl sulfoxide (Ib) afforded the corresponding sulfone (IIb) in a lower yield, and 2-nitrophenyl 4-methoxyphenyl sulfoxide (I, R=MeO) did not afford any 2-nitrosophenyl 4-methoxyphenyl sulfone. It is interesting to note that only starting material could be isolated after the prolonged irradiation of 2-nitrophenyl phenyl sulfide (III). These findings indicate that the migration of an oxygen atom probably requires the positive charge on a sulfur atom.

It cannot been determined what excitation is the first stage of the reaction, because no electronic spectrum of I has yet been assigned. The reaction, however, does not take place thermally, that is, II was not formed under reflux of I in diphenyl ether (b.p. 259°C) or triethylene glycol (b.p. 285°C). Irradiation of 2,4-dinitrophenyl phenyl sulfoxide or 2-nitrophenyl 4-nitrophenyl sulfoxide did not give any sulfone, presumably because the nitro group at the 4-position besides at the 2-position can be excited.

II was obtained in a slightly higher yield in a nonpolar solvent (n-hexane or benzene) than in a polar solvent (ethanol or acetonitrile), as found in the oxygen transfer reaction of nitrone.4) The rearrangement of I was not affected by the presence of oxygen at all, but it took a completely different cource in the presence of benzophenone, that is, II was not obtained during irradiation.

On the basis of these results, it is tempting to assume that in the excited singlet state of I an electron density increases on the oxygen atom and decreases on the sulfur atom, as in nitrobenzene7,8) and its derivatives,9) and the oxyanion attacks to the positive sulfur atom.

A detailed account of this investigation will be the subject of a forthcoming publication.

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