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THE FORMATION OF AZOBENZENES BY PHOTOLYSIS OF AZOXYBENZENES IN THE PRESENCE OF BENZOPHENONE

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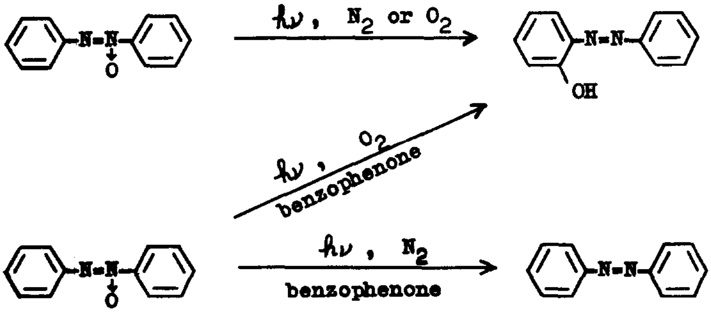
The photochemical rearrangement of azoxybenzenes to o-hydroxyazobenzenes was first reported by Knipscheer (1), and Badger and Buttery postulated an intramolecular pathway (2), which was confirmed by means of tracer methods (3, 4).

Now we wish to report that the photochemical reaction of azoxybenzenes takes a completely different course in the presence of triplet photosensitizers such as benzophenone, that is, azobenzenes are obtained as major products.

In a typical run, a solution of azoxybenzene (3×10^{-5} mole) in 99 % ethanol (3 ml.) was irradiated at $25.0 \pm 0.1^{\circ}$ C for 90 minutes with a mercury arc lamp (Halos, 100-w) with continuous bubbling of nitrogen. Thin-layer chromatography

(TLC) analysis on silica gel revealed that only two products, o-hydroxyazobenzene and cis-azoxybenzene, had been formed, but not azobenzene. The ratio of azoxybenzene (trans and cis) to o-hydroxyazobenzene was 11 to 89, and same even when oxygen was used instead of nitrogen.

On the other hand, when a solution of azoxybenzene (3×10^{-5} mole) and benzophenone (3×10^{-5} mole) in ethanol (3 ml.) was irradiated for 90 minutes, TLC of the crude reaction product separated it into azoxybenzene (trans and cis), o-hydroxyazobenzene and azobenzene (trans and cis) in 15 : 10 : 75 ratio. The product ratio, however, changed to 23 : 76 : 1 when oxygen was used as a quencher.



Since azobenzene is never obtained by photolysis of o-hydroxyazobenzene in the presence of benzophenone, the formation of azobenzene indicates a loss of oxygen from azoxybenzene, which is similar to photochemical deoxygenation of pyridine N-oxide through a triplet state (5).

In the lamp we used, the emission of the lines above 3000 A is more intensive than that at 2537 A, but has no effect on the photosensitization reaction of benzophenone, presumedly because the absorption of azoxybenzene is much stronger than that of benzophenone in the region above 3000 A.

From these results, it is tempting to assume that a triplet state of benzophenone is derived from its $\pi \rightarrow \pi^*$ excitation, and a photosensitized state of azoxybenzene, expected to be a triplet state, is a possible intermediate to azobenzene, but not to o-hydroxyazobenzene.

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

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