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PHOTOCHEMISTRY OF 2-HYDROXYBENZOPHENONES. I.
PHOTOREDUCTION IN HEXAMETHYLPHOSPHORIC TRIAMIDE

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Intramolecular hydrogen bonding in 2-hydroxybenzophenones facilitates singlet deactivation to such an extent that neither emission nor photoreduction is common (1). The precise mechanism of the deactivation process is considered to involve reversible intramolecular proton transfer to the carbonyl triplet or photoenolization (2). Rigid, polar solvents are able to disrupt the intramolecular hydrogen bond in these compounds and allow population of the low-lying triplet level (3). We wish to report here our observation that hexamethylphosphoric triamide (HPT) efficiently solvates 2-hydroxybenzophenone (I), allowing photoreduction to occur readily at ambient temperatures.

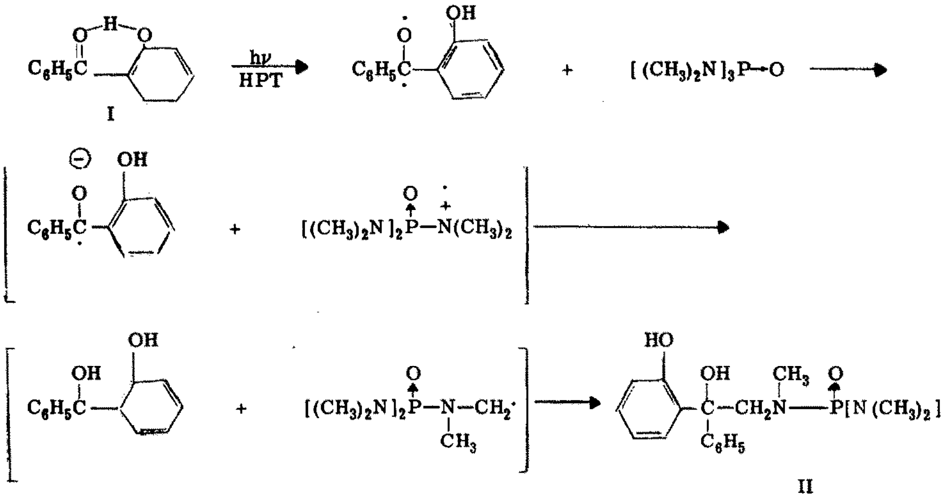
Solutions of the benzophenones in freshly distilled solvents were degassed thoroughly and then irradiated at 25-30° in Pyrex cells with light from a Hanovia 550-watt, medium-pressure, mercury arc in a "merry-go-round" apparatus. The incident light was restricted to the band between 280 and 410 nm by a combination of Pyrex glass and a Corning 9863 glass filter. The photolyses at 300 nm were performed similarly in a Rayonet photochemical reactor (4) equipped with fluorescent lamps having an emission maximum in the 300-nm region. Quantum yields were based on ferrioxalate actinometry. A Coleman-Hitachi Model 124 ultraviolet-visible spectrophotometer was used to follow the photodegradation of the benzophenones.

Quantum yields for the photodegradation of various benzophenones in amine solvents are shown in the following table:

Compound	Incident Light, nm	Solvent	ϕ
Benzophenone	-[a]	Butylamine	1.0 (6)[b]
"	-[a]	Triethylamine	0.19 (6)[b]
"	280-410	HPT	0.17
2-Hydroxybenzophenone	"	"	0.11
"	300	Triethylamine	1.6×10^{-3}
"	"	Butylamine	7.5×10^{-5}
2,4-Dihydroxybenzophenone	280-410	HPT	3.7×10^{-4}
2,4,4'-Trihydroxybenzophenone	"	"	7.5×10^{-4}

[a] Full mercury arc. [b] Quantum yields estimated from rate data in (6).

These data reflect the fact that solvation by HPT effectively disrupts intramolecular hydrogen bonding involving the 2-hydroxy substituent, allowing population of the reactive n,π * triplet. The large differences in quantum yields in HPT relative to those obtained in butylamine and triethylamine probably reflect the differences in the ability of the various solvents to solvate the hydroxybenzophenone, rather than differences in their electron-donating ability. Photoreduction in HPT then proceeds by electron transfer from a lone pair on an HPT nitrogen, followed by proton transfer and, in part, radical combination according to the following scheme:



The radical coupling product II (a pale yellow, viscous oil) was isolated from the photolysis mixture by preparative thin-layer chromatography (tlc) on silica gel. Elemental analysis indicated a 1:1 adduct of I and HPT, and nmr analysis confirmed the structure as II. Numerous other products were detected by tlc but were not identified.

The quantum yield of 7 × 10^{-3} for the photoreduction of I by direct irradiation in isopropyl alcohol (5) is much lower than the yield of 1.0 for the photoreduction of benzophenone, indicating the relative inefficiency of the alcohol in solvating I. The quantum yield for the photoreduction of I in HPT (0.11) is similar to that reported (6) for the reduction of benzophenone in triethylamine. Either HPT solvates I with very high efficiency or the electron-transfer process involves singlets of I and occurs in HPT at a rate which competes very favorably with singlet deactivation. The latter explanation is highly improbable.

The low quantum yields for benzophenones having 4-hydroxy substituents indicate that deactivation of the benzophenone singlet, by loss of a proton to HPT and formation of an unreactive charge-transfer state, competes favorably with intersystem crossing. The course of other photochemical reactions in HPT is being investigated.

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