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A NOVEL PHOTOCYCLOADDITION OF o-DIBENZOYLBENZENE TO OLEFINS

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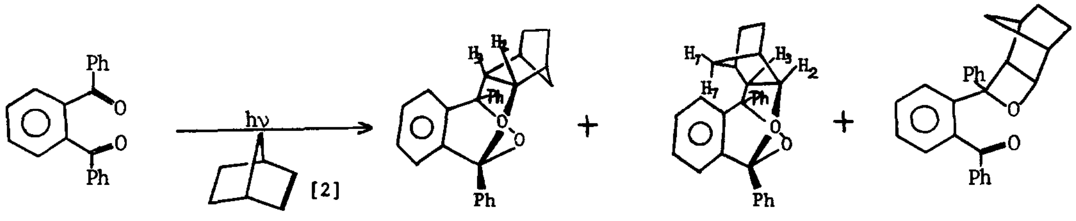
The photocycloaddition reactions of aromatic monoketones to olefins yielding oxetanes have received much attention.[1] On the other hand, those of aromatic diketones having adjacent carbonyl groups such as an o-diacylbenzene have not been reported, although such a diketone might be expected to undergo unique photochemical reactions due to interaction between the adjacent carbonyl groups. We wish to report herein our observation that o-dibenzoylbenzene [1] undergoes the hitherto unknown photocycloaddition to olefins such as norbornene [2], cyclooctene [5], and tetramethylethylene [8] to give novel 1,3-dioxane derivatives.

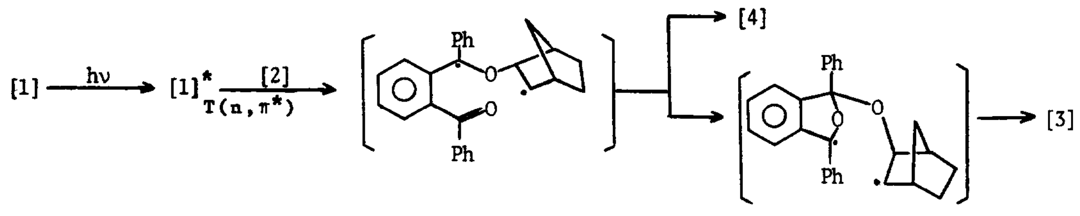
Irradiation of a benzene solution of [1] (7 mmole) and [2] (35 mmole) with a 500-W high pressure mercury lamp through a Pyrex filter gave two stereoisomeric 1,3-dioxane derivatives [3a] (m.p. 143–145.5°, 13%) and [3b] (m.p. 153–155°, 5%), together with *exo*-oxetanes [4] (m.p. 126–149°, 27%).[2]



[1] [3a] [3b] [4]

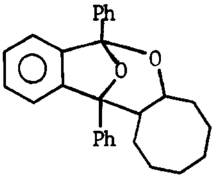
The nmr spectrum of [3a] showed H_2 as a doublet at δ 3.74 (J=7 Hz), and that of [3b] showed H_2 and H_3 as two doublets at δ 4.3 (J=7 Hz) and 2.6 (J=7 Hz), respectively. These data establish the stereochemistry of both isomers to be an *exo*-configuration. Furthermore, the signals for bridge protons H_7 of [3b] appeared as two broad doublets at considerable upfield (δ 0.34 and 0.74) due to anisotropy of benzene ring.

The phosphorescence emission of [1] strongly supports the concept that the lowest triplet state of [1] is n–π^* in nature.[3] In addition, it is generally accepted that benzophenone derivatives undergo intersystem crossing more rapidly than photochemical reaction from an excited singlet state. Consequently, it is not unreasonable to assume the n–π^* triplet state of [1] as a reactive species leading to the novel 1,3-dioxane formation.[4] The attack of the n–π^* triplet state of [1] on [2] to form a 1,4-diradical [I] may initiate this novel photocycloaddition. Namely, the 1,3-dioxanes may be formed through a 1,6-diradical [II] which can be derived from transannular C–O bonding of initially formed 1,4-diradical [I].

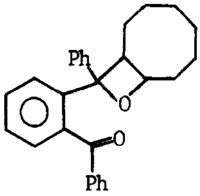


[I] [II]

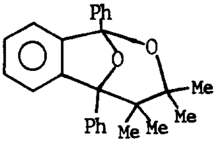
Similar irradiation of [1] with [5] or [8] also afforded novel 1,3-dioxane derivatives [6] (m.p. 220–221°, 5%) and [9] (m.p. 237–239°, 7%), in addition to oxetanes [7] (amorphous, 40%) and [10] (m.p. 119–121°, 11%), respectively.[5]



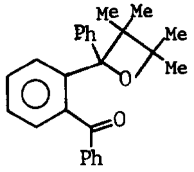
[6]



[7]



[9]



[10]

Further studies on the novel photocycloaddition of other diketones such as o-acetylbenzophenone and 1,8-dibenzoylnaphthalene are now in progress.

REFERENCES AND NOTES

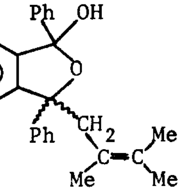
1 a) D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968). b) A. A. Lamola and N. J. Turro, "Energy Transfer and Organic Photochemistry," Wiley-Interscience, New York, N.Y., 1969, p 210.

2 The structures of products were confirmed on the basis of elemental analyses and spectral data

3 The phosphorescence emission spectrum of [1] was determined in an ethanol-methanol (4 1) glass at 77°K. From the location of the 0–0 band, the lowest triplet energy is estimated to be 69.4 Kcal/mole. The energy gap between the 0–0 and 0–1 bands is 1650 cm^{-1} . This value is coincident with carbonyl stretching frequency of [1].

4 The photoreduction of [1] in isopropyl alcohol has been reported to give isobenzofuran derivatives, but the mechanism for product formation is not cleancut At present we assume that the reaction may proceed *via* a ketyl radical formed by hydrogen abstraction by the $n-\pi^*$ triplet state of [1]· A. Schönberg, N. Latif, R. Moubasher, and W. I. Awad, *J. Chem. Soc* , **1950**, 374; P. Courtot and D. H. Sachs, *Bull. Soc. Chim. France*, **1965**, 2259.

5 In the case with [8], we isolated a hydroxylic compound in a 30% yield to which we tentatively assigned a phthalan [11] from spectral data. But the definitive structure has not been confirmed yet.



[11]