BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (5), 1445—1446 (1976)

The Photoreduction of *o*-Methoxycarbonylbenzophenone

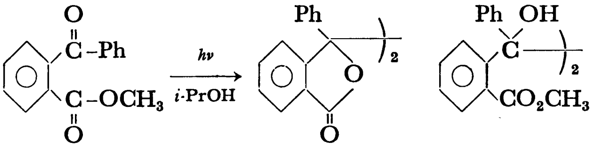
Yuji Tsujimoto, Yasuo Shigemitsu, Takuji Miyamoto, and Yoshinobu Odaira
Department of Petroleum Chemistry, Faculty of Engineering, Osaka University, Suita-shi, Osaka 565

(Received October 27, 1975)

Synopsis. The photoreduction of *o*-methoxycarbonylbenzophenone (I) in a hydrogen-donating solvent, such as isopropyl alcohol and toluene, was shown to give diphthalidyl (II) or/and a coupling product (IV).

Recently we have studied the photoreactions of several aromatic compounds with the same carbonyl groups, such as tetramethyl pyromellitate[1] and *o*-dibenzoylbenzene.[2] In such a system, an interesting interaction between two carbonyls has been pointed out.[1-3] As an extension of these studies, we now wish to report the photoreduction of benzophenones substituted with an ester at the *ortho* position.

The irradiation of *o*-methoxycarbonylbenzophenone (I) in isopropyl alcohol through a Pyrex filter afforded diphthalidyl (II) in a good yield, together with an appreciable amount of methanol. However, no pinacol (III) was found at all.



(I) (II) (III)

Moreover, the photoreaction of I with toluene gave benzyl-phthalide (IV), along with II and bibenzyl, whereas with a non-hydrogen-donating solvent such as acetonitrile, I was recovered almost quantitatively and the formation of II was negligible.

A ketyl radical (V), formed by the hydrogen abstraction of the n-π^* excited triplet of I from a solvent, such as isopropyl alcohol or toluene, may give (III) or/and (VI). III and VI subsequently undergo the lactonization, accompanied by the elimination of methanol, to give II and IV respectively.

In order to obtain information about the photoexcited state of I, the phosphorescence spectrum of I was measured and photocycloaddition to norbornene was examined.

In the phosphorescence spectrum, the entire shape of I resembles that of benzophenone, though fine structures do not appear clearly. In addition, the photocycloaddition of I to norbornene gave oxetane (VII) as a major product. These observations strongly suggest that I has the lowest n-π^* triplet level of benzoyl carbonyl.

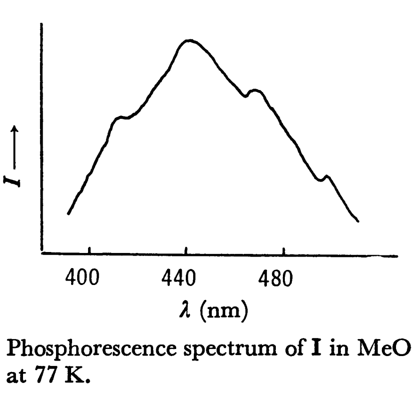
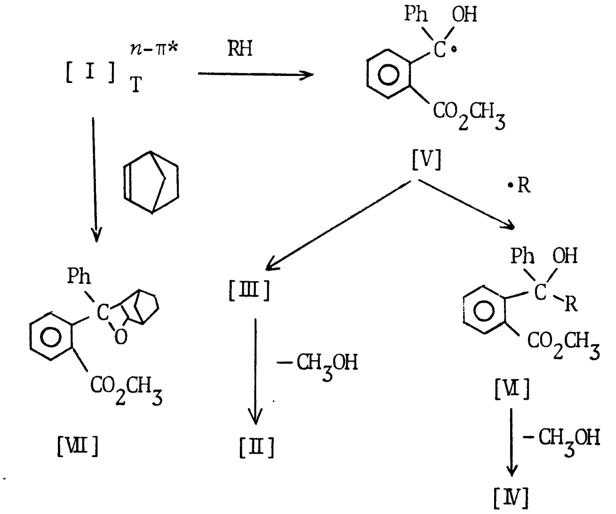
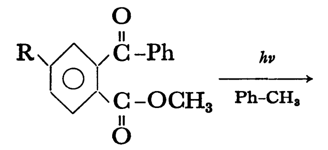


Fig. 1. Phosphorescence spectrum of I in MeOH-EtOH (1:3) at 77 K.

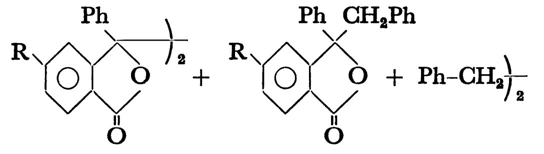
The following scheme may rationalize the above results:



Furthermore, the photoreduction of 2,5-dimethoxycarbonylbenzophenone (VIII) (bichromophoric system)[4] was examined. The irradiation of VIII in toluene afforded diphthalidyl (IX) and benzyl-phthalide (X).



R: H (I)
R: CO_2CH_3 (VIII)



R: H (II) (IV)
R: CO_2CH_3 (IX) (X)

Experimental

Materials. *o*-Methoxycarbonylbenzophenone (I) (mp 48—50 °C, lit,[5] 51—51.6 °C) was prepared by the esterification of *o*-benzoylbenzoic acid (84%). 2,5-Dimethoxycarbonylbenzophenone ((VIII), mp 96—98 °C, lit,[6] 100—101 °C) was prepared by the following procedure: the Friedel-Crafts reaction[7] of *p*-xylene with benzoyl chloride gave 2,5-dimethylbenzophenone (91%), while the subsequent oxidation of 2,5-dimethylbenzophenone with potassium permanganate gave benzophenone-2,5-dicarboxylic acid (16%). Finally the esterification of the diacid afforded VIII (99%).

Irradiation Procedure. All the irradiations were carried out with a 500-W high-pressure mercury lamp through a Pyrex filter at room temperature. The solutions were flushed for 15 min with nitrogen prior to irradiation.

Photoreduction of I. In isopropyl alcohol: a solution of I (1.5 g, 6.25 mmol) in isopropyl alcohol (45 ml) was irradiated for 7 h. Then, the precipitated crystals were filtered off; subsequent recrystallization from ethyl acetate gave 3,3′-diphenyl-diphthalidyl (II) (990 mg, 76%); mp 252—254 °C, lit,[8] 269—270 °C. From the volatile parts, methanol was detected by GLC (20% PEG 20M on Celite 545). In toluene: a solution of I (1.5 g, 6.25 mmol) in toluene (63 ml) was irradiated for 11 h. After the solvent had been removed *in vacuo*, the residue was chromatographed using a silica gel column. The insoluble parts [(II), (400 mg, 28%)] of the residue in benzene were removed before chromatography. The eluent of benzene with petroleum ether (60%) gave 3-phenyl-3-benzyl-phthalide (IV) (950 mg, 54%), mp 100—100.7 °C, lit,[9] 103—105 °C.

Photocycloaddition of I to Norbornene. A solution of I (2.0 g, 8.3 mmol) and 2-norbornene (4.1 g, 43.6 mmol) in benzene (40 ml) was irradiated for 10 h. The subsequent evaporation of the solvent gave a residue (3.1 g), which was then chromatographed on silica gel. The eluent of benzene with petroleum ether (20%) gave VII[10] (688 mg, 39%); mp 148—151 °C; IR (KBr) 1720, 970 cm^{-1}; NMR ($CDCl_3$) δ, 0.4—2.2 (m, 8H), 2.7 (d, 1H, J=6.0 Hz), 3.6 (s, 3H), 5.9 (d, 1H, J=6.0 Hz), 7.0—7.4 (m, 9H). Found: C, 78.96; H, 6.66%. Calcd for $C_{22}H_{22}O_3$: C, 79.01; H, 6.63%.

Photoreduction of VIII in Toluene. A solution of VIII (800 mg, 2.68 mmol) in toluene (32 ml) was irradiated for 7 h. After the evaporation of the solvent, small amounts of benzene were added. The insoluble parts were removed, and then the soluble parts were chromatographed on silica gel. The recrystallization of insoluble parts from benzene gave 3,3′-diphenyl-5,5′-dimethoxycarbonyl-diphthalidyl (IX) (118 mg, 16%); mp 280—284 °C; IR (KBr) 1785, 1740 cm^{-1}. Found: C, 71.85; H, 4.07%. Calcd for $C_{32}H_{22}O_3$: C, 71.90; H, 4.15%. The eluent of benzene containing petroleum ether (30%) gave 3-phenyl-3-benzyl-5-methoxycarbonyl-phthalide (X) (276 mg, 29%); mp 154—155 °C; IR (KBr) 1775, 1725 cm^{-1}; NMR (CCl_4) δ, 3.5, 3.7 (AB quartet, 2H, J=14 Hz), 3.9 (s, 3H), 6.8—8.2 (m, 13H). Found: C, 77.38; H, 4.95%. Calcd for $C_{23}H_{18}O_4$: C, 77.08; H, 5.06%.

References and Footnotes

1) K. Fukui, K. Senda, Y. Shigemitsu, and Y. Odaira, *J. Org. Chem.*, **37**, 3176 (1972).

2) Y. Shigemitsu, S. Yamamoto, T. Miyamoto, and Y. Odaira, *Tetrahedron Lett.*, **1975**, 2819.

3) W. C. Agosta, *J. Am. Chem. Soc.*, **89**, 3505 (1967).

4) VIII is expected to have two excited sites, the one is benzophenone moiety, the other dimethylterephthalate moiety.[11]

5) M. S. Newman, H. G. Koivila, and A. B. Garrett, *J. Am. Chem. Soc.*, **67**, 704 (1945).

6) "Beilstein Handbuch der Organischen Chemie," Band 10, Haupt (1927), p. 881.

7) K. Elbs and E. Larsen, *Chem. Ber.*, **17**, 2847 (1884).

8) M. V. Bhatt, K M. Kamath, and M. Ravindranathan, *J. Chem. Soc., C*, **1971**, 3344.

9) C. R. Hauser, *J. Org. Chem.*, **23**, 861 (1958).

10) NMR datum shows that VII is an exo isomer.

11) See Ref. 1.