

## The Photochemical Reaction of $\alpha$ -Diketones

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(Received July 5, 1971)

The relative photochemical reactivity of  $\alpha$ -diketones, in particular, 9,10-phenanthraquinone, 1,2-naphthoquinone, acenaphthoquinone, benzil, 4,4'-dimethylbenzil, 2,4,6-trimethylbenzil, 2,5,2',5'-tetramethylbenzil, 2,3,5,6-tetramethylbenzil, 2,4,6,2',4',6'-hexamethylbenzil, phenylglyoxal, 2,5-dimethylphenylglyoxal, and 2,4,6-trimethylphenylglyoxal was investigated in hydrogen donating solvents. Type of the product and relative reactivity differ widely according to the structure of  $\alpha$ -diketones. Whereas 9,10-phenanthraquinone gives 1,4-adduct (V) in a hydrogen donating solvent (THF), 2,5,2',5'-tetramethylbenzil gives 2-hydroxy-2-(2',5'-dimethylphenyl)indanone (VII) *via* intramolecular hydrogen abstraction in nearly quantitative yield. No photochemical reaction of 2,4,6-trimethylbenzil or 2,3,5,6-tetramethylbenzil could be observed in the same solvent even under a long irradiation.

The photochemical reaction of  $\alpha$ -diketones has been studied under various reaction conditions since Klinger.<sup>1)</sup> Vapor phase photolysis of biacetyl or hexafluorobiacetyl yields products formed by cleavage of the carbon-carbon bond between two carbonyl groups. However, when *o*-quinones are irradiated in solution in the presence of a hydrogen donor, the resulting products can almost invariably be rationalized taking consideration the mechanistic pathway involving the initial hydrogen abstraction by photo-excited *o*-quinone *via*  $n \rightarrow \pi^*$  excitation. As an example, camphorquinone<sup>2)</sup> in methanol and 2-propanol gives products derived from initial hydrogen abstraction from the solvent, and 9,10-phenanthraquinone yields 1,2-adduct or 1,4-adduct corresponding to the structure of the solvent when it is irradiated in solution.<sup>3)</sup> On the contrary, benzil in cyclohexane gives benzaldehyde formed by cleavage of the carbon-carbon bond between the two carbonyl groups. The present study was undertaken with the aim of elucidating the relationship between reactivity and the structure of  $\alpha$ -diketones. 9,10-Phenanthraquinone, 1,2-naphthoquinone, acenaphthoquinone, benzil, methyl substituted benzils and methyl substituted glyoxals have been studied.

### Results and Discussion

**Reaction Products.** Irradiation of 1,2-naphthoquinone in 2-propanol in the absence of oxygen led to an unstable white product identified to be naphthalene-1,2-diol (I). Similarly irradiation of acenaphthoquinone in tetrahydrofuran (THF) in the absence of oxygen give a white product (II) formed by photo-addition. However, in the presence of oxygen, acenaphthoquinone in THF gave naphthalene-1,8-dicarboxylic acid anhydride (III), when it was irradiated. Presumably the first step for the production of this anhydride may be hydrogen abstraction from the solvent resulting in the formation of semiquinone radical, which may react with oxygen to give III according to Scheme 2. Rubin and Zwitkowitz reported on the photochemical reaction

of phenanthraquinone in some hydrogen donating solvents.<sup>3)</sup> They stated that phenanthraquinone reacted with solvents produced 1,2-adduct or 1,4-adduct in the absence of oxygen. Irradiation of phenanthraquinone in mesitylene and in THF gave the corresponding 1,2-adduct (IV) and 1,4-adduct (V), respectively. Relative hydrogen abstraction rate of photo-excited phenanthraquinone in several hydrogen donating solvents have been reported.<sup>4)</sup> Recently the reactions have been extensively reinvestigated and their radical nature was confirmed using CIDNP technique.<sup>5)</sup> The *o*-quinones unexceptionally abstract hydrogen from the solvent in the first stage of the reaction. The photochemical behavior of benzil, however, differs from that of the *o*-quinones and the principal products in cyclohexane are benzoic acid, benzaldehyde, phenyl cyclohexyl ketone and benzoin.<sup>6)</sup>

We have studied in detail the photochemical reaction of benzil and its methyl substituted derivatives, *viz.* 2,5,2',5'-tetramethylbenzil, 2,4,6-trimethylbenzil, 2,3,5,6-tetramethylbenzil, 2,4,6-trimethylphenylglyoxal, 2,4,6,2',4',6'-hexamethylbenzil, and 4,4'-dimethylbenzil. The reaction products are shown in Scheme 1. Irradiation of benzil in THF (in the absence of oxygen) gave a mixture of products containing benzaldehyde, a small amount of benzoin and unidentified products. 2,5,2',5'-Tetramethylbenzil gave a white product (VII) 2-hydroxy-2-(2',5'-dimethylphenyl)indanone, *via* intramolecular hydrogen abstraction accompanying 2,5-dimethylbenzaldehyde (VI) when it was irradiated in THF in the absence of oxygen (Scheme 3). In benzene, carbon tetrachloride, or cumene no 2,5-dimethylbenzaldehyde was obtained but product (VII) was exclusively obtained in a nearly quantitative yield. Both 2,4,6,2',4',6'-hexamethylbenzil and 2,4,6-trimethylphenylglyoxal dissolved in THF gave 2,4,6-trimethylbenzoic acid as the main product when they were irradiated. Possibly, this acid is formed by the autoxidation of the

4) K. Maruyama, K. Ono, and J. Osugi, *This Bulletin*, **42**, 3357 (1969).

5) K. Maruyama, H. Shindo, and T. Maruyama, *ibid.*, **44**, 585 (1971); K. Maruyama, H. Shindo, T. Otsuki, and T. Maruyama, *ibid.*, **44**, 2756 (1971); H. Shindo, K. Maruyama, T. Otsuki, and T. Maruyama, *ibid.*, **44**, 2789 (1971); K. Maruyama, T. Otsuki, H. Shindo, and T. Maruyama, *ibid.*, **44**, 2000 (1971).

6) D. L. Bunburg and C. T. Wang, *Can. J. Chem.*, **46**, 1473 (1968).

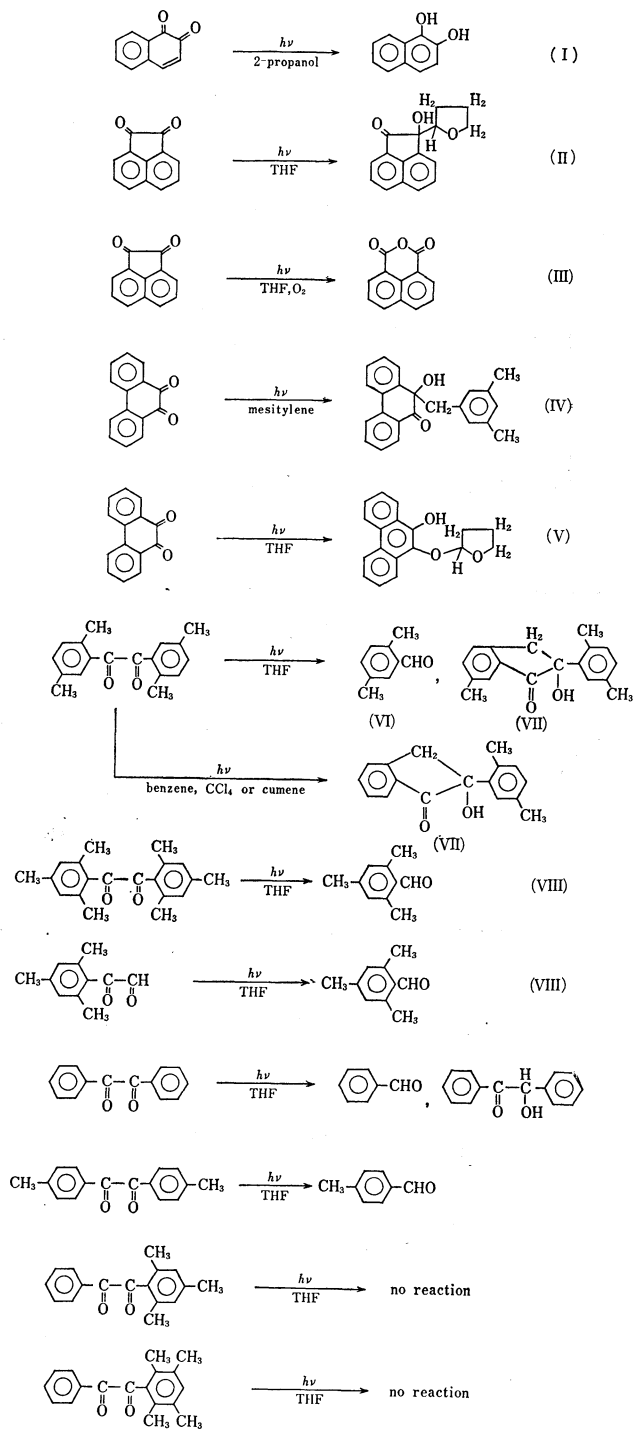
1) H. Klinger, *Ber.*, **19**, 1862 (1886).

2) B. M. Monroe and S. A. Weiner, *J. Amer. Chem. Soc.*, **91**, 450 (1969).

3) M. B. Rubin, *J. Org. Chem.*, **28**, 1949 (1963); M. B. Rubin and P. Zwitkowitz, *ibid.*, **29**, 2362 (1964).

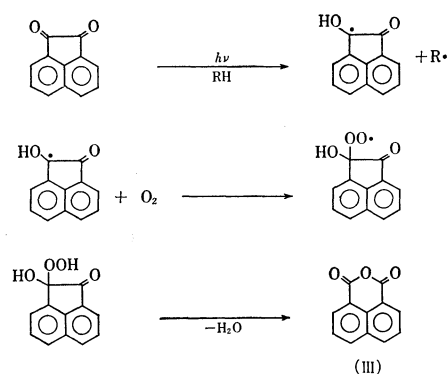
resulting 2,4,6-trimethylbenzaldehyde in the course of separating procedures.<sup>7)</sup> However, both 2,4,6-trimethylbenzil and 2,3,5,6-tetramethylbenzil were extremely photo-stable and did not change after being irradiated for over a week.

**Determination of Quantum Yields.** The quantum yields for the disappearance of  $\alpha$ -diketones are shown in Table 1. It has been reported that the quantum yield for the photo-reduction of camphorquinone is very low.<sup>2)</sup> On the other hand, the quantum yield of 1,2-naphtho-

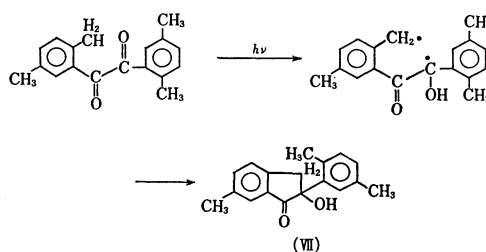


Scheme 1.

7) Methyl substituted benzaldehyde can be oxidised rapidly in the air.



Scheme 2.



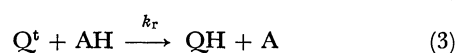
Scheme 3.

TABLE 1. QUANTUM YIELDS OF THE DISAPPEARANCE OF  $\alpha$ -DIKETONES IN THF (EXCITING LIGHT: 3640 Å, TEMPERATURE: 25°C)

| $\alpha$ -Diketone          | Quantum yield | Condition    |
|-----------------------------|---------------|--------------|
| 1,2-Naphthoquinone          | 1.00          | Degassed     |
| 9,10-Phenanthraquinone      | 0.86          | Degassed     |
| Acenaphthoquinone           | 0.75          | In the air   |
| Camphorquinone              | 0.057         | Degassed     |
|                             | 0.018         | (2-propanol) |
|                             | 0.018         | (methanol)   |
| Benzil                      | 0.85          | In the air   |
| 2,5,2',5'-Tetramethylbenzil | 1.30          | In the air   |
| 2,4,6-Trimethylbenzil       | <0.02         | In the air   |

Light intensity was determined by a potassium ferrioxalate actinometer.

quinone or 9,10-phenanthraquinone was nearly unity. These reactions are characteristic in that the photo-reduction with the solvent acts as a hydrogen donor. The reaction mechanism can be described by the following equations, where  $Q^s$  and  $Q^t$  are excited singlet and triplet states, respectively and AH the hydrogen donor.

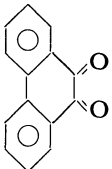
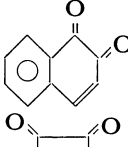
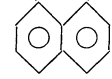
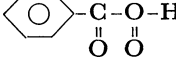
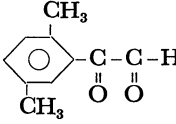
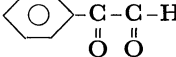
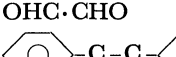
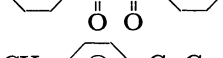
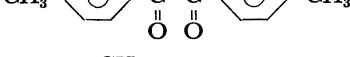
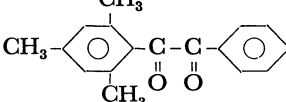
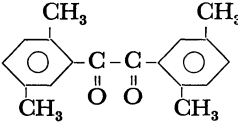
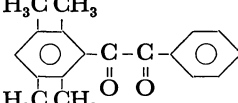
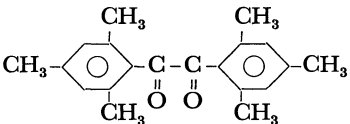
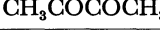


If the quantum yield for intersystem crossing is unity, the quantum yield for the disappearance of  $o$ -quinone is given by

$$\Phi = \frac{k_r[AH]}{k_r[AH] + k_d} \quad (6)$$

The quantum yield for intersystem crossing of camphorquinone is known to be nearly unity<sup>2)</sup> and the life time of its triplet state is similar to those of the other *o*-quinones.<sup>8)</sup> Therefore, the difference in the quantum yield of 1,2-naphthoquinone or 9,10-phenanthraquinone and camphorquinone seems to be caused by the difference in the nature of the triplet state. The radical oxygen atom

TABLE 2. ELECTRONIC SPECTRA OF  $\alpha$ -DIKETONES  
 $n \rightarrow \pi^*$  TRANSITION (SOLVENT: THF,  
ROOM TEMPERATURE)

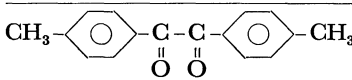
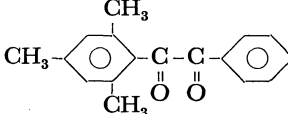
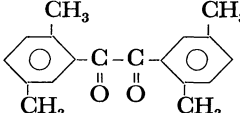
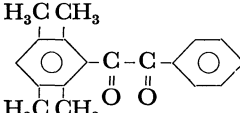
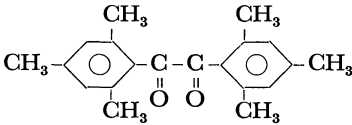
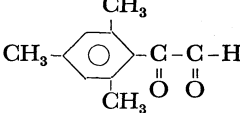
| $\alpha$ -Diketone                                                                  | $\lambda_{\max}$ (m $\mu$ ) |
|-------------------------------------------------------------------------------------|-----------------------------|
|    | 500                         |
|    | 520                         |
|    | 493                         |
|   | 420                         |
|  | 415                         |
|  | 440                         |
|  | 450                         |
|  | 370, 388                    |
|  | 364, 382                    |
|  | 410                         |
|  | 390 (Broad)                 |
|  | 420                         |
|  | 470, 498                    |
|  | 415—440                     |

of 1,2-naphthoquinone or 9,10-phenanthraquinone in the photo-excited  $n \rightarrow \pi^*$  triplet state should be more electrophilic than that of camphorquinone, for in the former the excited electron to  $\pi$ -orbital may be delocalized entirely on the rest of the molecule.<sup>4)</sup> Thus, the  $n \rightarrow \pi^*$  triplet state of the 1,2-naphthoquinone or 9,10-phenanthraquinone could be a better hydrogen abstractor.

**Photochemical Behavior of Benzil Derivatives.** The photochemical behavior of benzil derivatives is more complicated than that of *o*-quinones. Both photodecomposition and photo-reduction take place at the same time, and in some cases photo-decomposition become the main reaction. Moreover, 2,4,6-trimethylated or 2,3,5,6-tetramethylated benzil derivatives are extremely photo-stable even in THF. We inspected the structural features using UV and PMR techniques and tried to discuss the relationship between the structure and the photochemical behavior of benzil derivatives. The wave lengths of maximum absorption of  $n \rightarrow \pi^*$  transition are shown in Table 2 and the chemical shifts of methyl protons of the derivatives in Table 3. Leonard and Blout<sup>9)</sup> concluded from the measurement of absorption spectra that non-substituted benzil had a skew structure as shown in Fig. 1 and 2,4,6,2',4',6'-hexamethylbenzil had a *trans* planar structure as shown in Fig. 2.

Thus, we can conclude reasonably that 2,5,2',5'-tetramethylbenzil or 4,4'-dimethylbenzil has twisted

TABLE 3. PMR CHEMICAL SHIFTS OF METHYL PROTONS OF  
BENZIL DERIVATIVES (ROOM TEMPERATURE)

| Benzil derivative                                                                    | $\tau$ -Values |              |              |
|--------------------------------------------------------------------------------------|----------------|--------------|--------------|
|                                                                                      | <i>o</i> -CH   | <i>m</i> -CH | <i>p</i> -CH |
|  |                |              | 7.59         |
|  | 7.68           |              | 7.62         |
|  | 7.24           | 7.53         |              |
|  | 7.85           | 7.69         |              |
|  | 7.87           |              | 7.75         |
|  | 7.86           |              | 7.71         |

60 MHz PMR spectrometer was used.

8) A. Kuboyama and S. Yabe, This Bulletin, **40**, 2475 (1967).

9) N. J. Leonard and E. R. Blout, *J. Amer. Chem. Soc.*, **72**, 484 (1950).

form around the carbon-carbon bond of the two carbonyl groups like that of non-substituted benzil. As shown in Table 3  $\tau$ -values of *meta* or *para* methyl protons (to carbonyl group) remain almost unchanged, but those of *ortho* methyl protons vary in the range  $\tau = 7.24-7.87$ . The differences seem to depend on the magnetic anisotropy of carbonyl group. The plane of the two carbonyl double bond and that of the mesityl ring of 2,4,6,2',4',6'-hexamethylbenzil would be perpendicular (Fig. 2), but in 2,5,2',5'-tetramethylbenzil the plane of the dimethylphenyl and the adjacent carbonyl might be nearly co-planar (Fig. 1). Thus, the *ortho* methyl protons of the former might be affected most effectively by the magnetic shielding effect of the carbonyl group. On the other hand, that of the latter is under the influence of the magnetic deshielding effect.

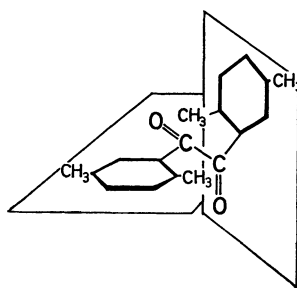


Fig. 1. Skew structure of benzil derivatives.

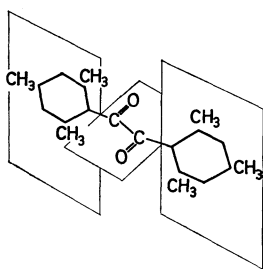


Fig. 2. Trans planar structure of benzil derivatives.

Whereas benzil, 2,5,2',5'-tetramethylbenzil and 4,4'-dimethylbenzil dissolved in THF react fast in the absence of oxygen, 2,4,6-trimethylbenzil or 2,3,5,6-tetramethylbenzil dissolved in THF remains almost unreacted after a long irradiation over a week. 2,4,6,2',4',6'-Hexamethylbenzil reacts slowly. The quantum yields for the photo-reaction of methylated benzils in the presence of oxygen are given in Table 1. We see that 2,4,6-trimethylbenzil or 2,3,5,6-tetramethylbenzil is very unreactive compared with benzil or 2,5,2',5'-tetramethylbenzil in the presence of oxygen as well as in the absence of oxygen.

Comparing the relative intensity of the phosphorescence of these benzils qualitatively, benzil or 2,5,2',5'-tetramethylbenzil shows intense phosphorescence in contrast to 2,4,6-trimethylbenzil, 2,3,5,6-tetramethylbenzil, or 2,4,6,2',4',6'-hexamethylbenzil, which shows extremely weak phosphorescence. The lifetime of triplet state of benzil and 2,5,2',5'-tetramethylbenzil in MMA plastic<sup>10</sup> are 0.20 msec and 0.65 msec, respectively, at room temperature, but in the case of 2,4,6-trimethylbenzil, 2,3,5,6-tetramethylbenzil, or 2,4,6,2',4',6'-hexamethylbenzil no T-T absorption of these benzils could be observed.

Thus, we might consider that the quantum yield for the intersystem crossing of 2,4,6-trimethylbenzil and 2,3,5,6-tetramethylbenzil are strikingly small. These benzil derivatives should be strongly photo-resistant.<sup>11</sup> However, there may be the other possibilities which are remained to be clarified in future. We next examined the solvent effects on the photochemical reactions. The

reaction rate of non-substituted benzil showed a remarkable solvent effect. In non-polar solvents such as benzene, toluene, or *n*-hexane, benzil, 4,4'-dimethylbenzil, and 2,4,6,2',4',6'-hexamethylbenzil were less reactive than in polar solvents such as THF, *N,N*-dimethylformamide, ether, or methanol, whereas 2,5,2',5'-tetramethylbenzil was equally reactive in the polar or non-polar solvents. Qualitative comparison of the relative reactivity of these benzils is given in Table 4.

TABLE 4. RELATIVE REACTIVITY OF  $\alpha$ -DIKETONES IN SEVERAL SOLVENTS (LIGHT SOURCE: 400W HIGH PRESSURE Hg LAMP, ROOM TEMPERATURE)

| $\alpha$ -Diketones              | Qualitative rates in several solvents                                           |
|----------------------------------|---------------------------------------------------------------------------------|
| Benzil                           | THF, methanol, benzene, toluene, DMF, ether $\gg$ <i>n</i> -hexane              |
| 4,4'-Tetramethylbenzil           | methanol $\gg$ benzene, <i>n</i> -hexane                                        |
| 2,4,6,2',4',6'-Tetramethylbenzil | THF $\gg$ benzene                                                               |
| 2,5,2',5'-Tetramethylbenzil      | THF, methanol, benzene, toluene, <i>n</i> -hexane (reacts fast in all solvents) |
| 2,4,6-Trimethylbenzil            | THF, methanol, benzene (does not react in all solvents)                         |

These phenomena seem to be ascribed to the cage effect of solvent for the carbonyl-carbonyl bond scission. However, 2,5,2',5'-tetramethylbenzil is reactive in non-polar as well as polar solvents. The carbonyl group and the *ortho* methyl proton of this benzil derivative should be positioned very close and nearly overlapping. Consequently VII might be produced *via* intramolecular hydrogen abstraction fairly easily even in the non-polar solvents. On the other hand, 2,4,6-trimethylbenzil and 2,3,5,6-tetramethylbenzil are unreactive in the polar or non-polar solvents. The cause of the low quantum yield for the intersystem crossing of these benzil derivatives remains to be explained. However, it does not seem incidental that these photochemically unreactive benzil derivatives are antisymmetric and the mean value of the dihedral angle between the two carbonyl groups are in the range 90–180°.

## Experimental

**Materials.** 1,2-Naphthoquinone (mp 121–122°C), acenaphthoquinone (decomp. 242°C), and 9,10-phenanthraquinone (mp 204°C) were prepared by the oxidation of 2-amino-1-naphthol, of acenaphthene, and of phenanthrene with suitable oxidizing agents. 2,5,2',5'-Tetramethylbenzil (mp 113–114°C), 2,4,6,2',4',6'-hexamethylbenzil (mp 120–121°C), 2,4,6-trimethylbenzil (mp 135°C) and 2,3,5,6-tetramethylbenzil (mp 62–63°C) were prepared by the air-oxidation of the corresponding benzoin<sup>12</sup> produced by the condensation of the corresponding glyoxals with suitable methylated benzenes.<sup>13</sup> Benzil (mp 94–95°C) and 4,4'-dimethylbenzil (mp 104–105°C) were prepared by the oxidation of the corresponding benzoin<sup>12</sup> produced by the benzoin condensation of benzaldehyde and *p*-tolualdehyde.

**Irradiation of  $\alpha$ -Diketones.** A typical photo-reaction was performed as follows. A known amount of  $\alpha$ -diketone

10) methyl metacrylate

11) 2,4,6,2',4',6'-Hexamethylbenzil reacts very slowly.

12) "Organic Syntheses," Coll. Vol. II, p. 509 (1948); "Organic Reaction," Vol. 4, p. 269.

13) "Organic Syntheses," Coll. Vol. I, p. 87 (1948).

(usually 1/100—1/1000 mol) dissolved (or suspended) in a solvent (20—100 ml) was irradiated in an ordinary glass tube through 5 cm thick of water layer from a light source (400W high-pressure Hg-lamp). Change of the substrate was followed spectroscopically. A reaction vessel fitted with a cell for spectroscopic measurement was used for the experiments under degassed conditions.

*Analyses of Photochemical Products.* **1,2-Dihydroxynaphthalene(I):** After the characteristic orange color of 1,2-naphthoquinone dissolved in 2-propanol faded to pale yellow, 2-propanol was evaporated under reduced pressure. The resulting dark orange colored solid was extracted with *n*-hexane. Removal of *n*-hexane left unstable white crystal which changes easily to the corresponding quinhydrone in the air, mp 59—60°C, IR:  $\nu_{OH}$  = 3340—3360  $\text{cm}^{-1}$ .

**1-Hydroxy-1- $\alpha$ -tetrahydrofuran- $\beta$ -8-oxoacenaphthene(II):** 1,8-Acenaphthoquinone dissolved in THF was irradiated in the absence of oxygen. After two days irradiation the solvent was removed under reduced pressure, and the resulting reddish oil was extracted with petrol ether, and then colorless crystal was obtained, mp 217—223°C (decomp), (yield 80%). Elemental analysis:  $\text{C}_{16}\text{H}_{14}\text{O}_3$ ; Found, C: 75.61%, H: 5.53%; Calculated, C: 75.57%, H: 5.56%.

**1,8-Dinaphthoic acid anhydride(III):** After the orange yellow color of acenaphthoquinone faded to pale yellow, removal of THF as solvent left a pale yellow solid which was recrystallized from ether. Colorless crystal, mp 273—276°C,  $\nu_{C=O}$ : 1730, 1770  $\text{cm}^{-1}$ . Elemental analysis; Found, C: 72.79%, H: 3.07%, Calculated,  $\text{C}_{18}\text{H}_8\text{O}_3$ , C: 72.75%, H: 3.13%.

**9-Hydroxy-9-(3',5'-dimethylbenzyl)-10-oxo-9,10-dihydrophenanthrene(IV):** After 9,10-phenanthraquinone suspended in mesitylene was irradiated for two days, the unreacted mesitylene was removed under reduced pressure. The resulting viscous oil was rinsed with petrol benzene several times, and then yellow crystals were crystallized out, mp 125—126°C,  $\nu_{OH}$ : 3470  $\text{cm}^{-1}$ ,  $\nu_{C=O}$ : 1690  $\text{cm}^{-1}$ ,  $\tau_{m-CH_3}$ : 7.83,  $\tau_{CH_3-}$ : 7.15,  $\tau_{OH}$ : 6.20, (yield: 75%). Elemental analysis; Found, C: 82.20%, H: 6.21%, Calculated,  $\text{C}_{23}\text{H}_{17}\text{O}_2$ , C: 84.93%, H: 5.26%.

**9-(10-Hydroxy)phenanthrenyl  $\alpha$ -tetrahydrofuran ether (V):** i.e., 1,4-adduct of 9,10-phenanthraquinone with THF; after 9,10-phenanthraquinone dissolved in THF was irradiated until it became colorless, removal of unreacted THF left crystals which were recrystallized from petrol ether, mp 110—112°C,  $\nu_{OH}$ : 3250  $\text{cm}^{-1}$ , (yield: 80%). Elemental analysis; Found, C: 81.90%, H: 4.48%, Calculated,  $\text{C}_{18}\text{H}_{16}\text{O}_3$ ; C: 81.79%, H: 4.57%.

**2-Hydroxy-2-(2',5'-dimethylphenyl)indanone (VII):** After 2,5-

2',5'-tetramethylbenzil dissolved in THF (or a suitable solvent) was irradiated for three days under degassed conditions, removal of THF under reduced pressure left heavy viscous oil, which was rinsed with petrol benzene several times. All of the oil then solidified, recrystallized from petrol benzene-benzene, pale yellow crystal, mp 153°C,  $\nu_{OH}$ : 3390  $\text{cm}^{-1}$ ,  $\nu_{C=O}$ : 1705  $\text{cm}^{-1}$ ,  $\tau_{CH_3}$ : 7.80, 7.77, 7.55,  $\tau_{OH}$ : 7.25,  $\tau_{CH_3-}$ : 6.63, (nearly quantitative yield). Elemental analysis; Found; C: 81.24%, H: 6.75%, Calculated,  $\text{C}_{18}\text{H}_{18}\text{O}_2$ , C: 81.19%, H: 6.81%. From the mother liquor 2,5-dimethylbenzaldehyde was isolated after it was treated with aqueous sodium bicarbonate and identified as semicarbazone, mp 217°C. After acidification of the bicarbonate solution a small amount of 2,5-dimethylbenzoic acid was separated, mp 132°C.

**2,4,6-Trimethylbenzaldehyde and 2,4,6-trimethylbenzoic acid:** After the solution of 2,4,6,2',4',6'-hexamethylbenzil in THF was irradiated for a week, the solution was concentrated and diluted with ether, and then treated with aqueous sodium bicarbonate. From the ethereal solution 2,4,6-trimethylbenzaldehyde was isolated and identified as semicarbazone, mp 184—187°C. After acidification of the sodium bicarbonate extract a fair amount of 2,4,6-trimethylbenzoic acid was isolated, recrystallized from ligroin, mp 153°C,  $\nu_{C=O}$ : 1690  $\text{cm}^{-1}$ ,  $\tau_{CH_3}$ : 7.70, 7.58,  $\tau_{CO_2H}$ : -2.10.

**Benzaldehyde:** After benzil dissolved in THF was irradiated under degassed conditions for three days, THF was removed under reduced pressure. The residue dissolved in ether was treated with aqueous sodium bicarbonate and concentrated to a small volume. It was treated with 2,4-dinitrophenylhydrazine hydrochloride solution and then reddish colored crystals were separated, mp 237°C. From a part of the ethereal solution, benzoin was isolated identified by the mp 137°C.

**p-Tolualdehyde:** After the usual treatment of irradiated solution of 4,4'-dimethylbenzil in THF *p*-tolualdehyde was identified to be its 2,4-dinitrophenylhydrazone, mp 232—232°C.

**Determination of Quantum Yields and Lifetime of Triplet State.** A known amount of an  $\alpha$ -diketone was dissolved in THF and irradiated with 400 W high-pressure Hg-lamp through a UV-cut filter (Toshiba VY-42) under the conditions indicated in Table 1. The light intensity was determined with a potassium ferrioxalate actinometer. The lifetime of triplet state of benzil derivatives was determined as follows. Benzil derivatives dissolved in MMA plastic were irradiated by flash method, and the decay of phosphorescence was followed oscillographically. T-T' absorption was also observed spectroscopically through the further activation of triplet state thus attained with a tungsten-lamp.