J. Org. Chem. **1982**, *47*, 2353–2354

Photochemistry of Benzil Monobenzhydrylimine

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Received July 31, 1981

Irradiation of benzil monobenzhydrylimine (**1**) in benzene with UV light yields 1-benzhydryl-2,2,4,5-tetraphenyl-3-imidazoline (**2**), benzil (**3**), 1,1,3,4-tetraphenyl-*N*-oxo-2-azabutadiene (**4**), benzophenone (**5**), and benzonitrile (**6**). Irradiaiton of 2,2,4,5-tetraphenyl-3-oxazoline (E) affords products **4–6**, and irradiation of **4** gives **5** and **6**. The probable mechanistic route is discussed.

The photochemical reduction,[1] reductive dimerization,[2] reductive rearrangement,[3] and oxidation[4] of substituted imines have oily reported in literature. It was considered necessary to examine the photochemistry of a substrate having the imino function in conjugation with a carbonyl group, for which benzil monobenzhydrylimine (**1**) was selected as a model. The photocleavage of a carbon–carbon bond in **1** and dimerization of the radicals gives benzil (**3**) and possibly benzil dibenzhydrylimine (C) which on cyclization yields 1-benzhydryl 2,2,4,5-tetraphenyl-3-imidazoline (**2**). Photoenolization of **1** followed by ring closure to oxazoline derivative and subsequent photofragmentation leads to 1,1,3,4-tetraphenyl-*N*-oxo-2-azabutadiene (**4**), benzophenone (**5**), and benzonitrile (**6**).

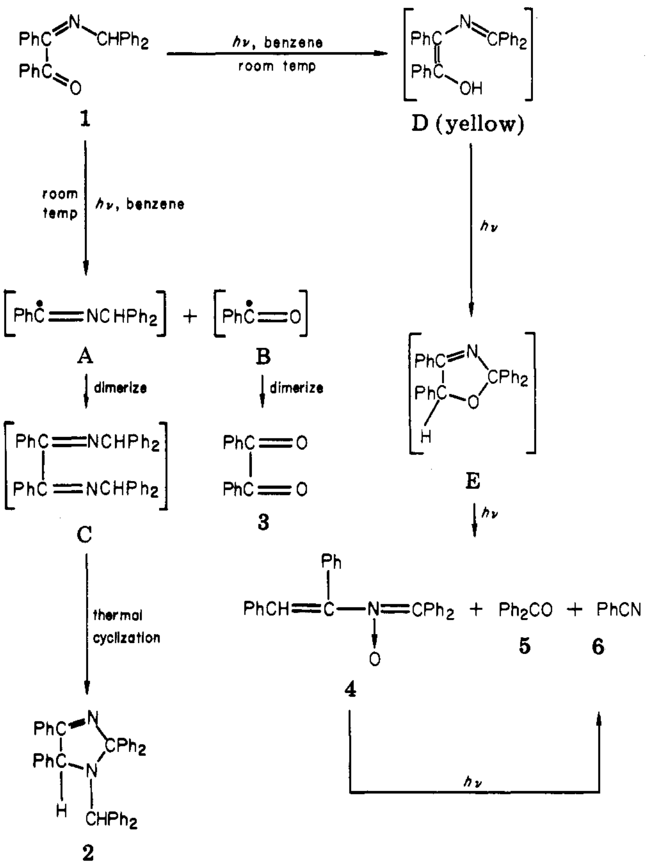
Irradiation of a solution of **1** in benzene with UV light gave an oily liquid. Trituration with ethanol gave a solid material which on fractional crystallization from propan-2-ol afforded 1-benzhydryl-2,2,4,5-tetraphenyl-3-imidazoline (**2**), benzil (**3**), and 1,1,3,4-tetraphenyl-*N*-oxo-2-azabutadiene (**4**). Chromatography on neutral alumina of the concentrated mother liquors gave benzophenone (**5**) and benzonitrile (**6**). The products have been characterized by analyses and spectral (UV, IR, NMR, and mass) data. The structural assignments of **5** and **6** have been confirmed by comparison (identical IR spectra) with authentic samples.

The photolysis of **1** leading to the above products is shown in Scheme I.

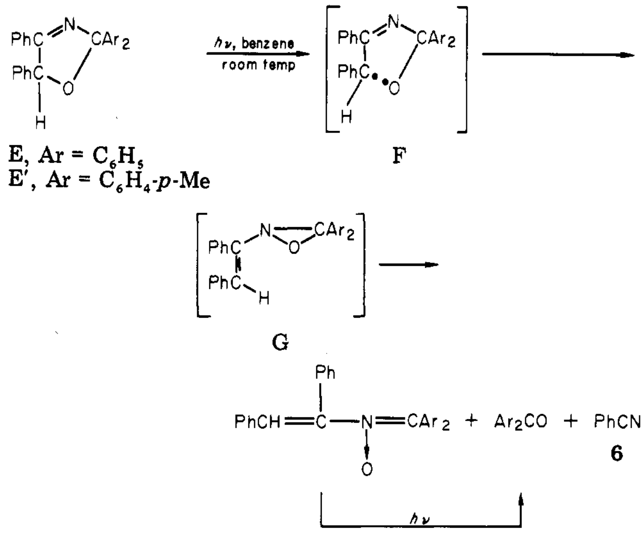
The formation of products **2** and **3** may involve the photofragmentation of the carbon–carbon bond of imine **1** to imino radical A and benzoyl radical B. The imino radical A dimerizes to the diimine C which on rearrangement and cyclization leads to **2**. The last step is thermal, which is supported by the reported[5] formation of **2** on heating C at 210 °C; moreover, irradiation of C in benzene does not form **2**. The radicals B dimerize to give benzil (**3**). Products **4–6** are formed from an intermediate oxazoline, E, which may arise from photoenol D, formed from **1** by intramolecular γ-hydrogen transfer from carbon to oxygen.[6] The oxazoline E was not isolated from the irradiated mixture.

However, oxazolines E and E′ have been obtained from the bis(acetylacetonato)copper(II)-catalyzed thermal decomposition of 2-diazo-1,2-diphenylethanone in presence of 1,1-diarylmethanimines.[7] Irradiation of a solution of E in benzene with UV light gave products **4–6** (Scheme II) which have also been obtained from **1** (Scheme I).

Scheme I



Scheme II



Irradiation of **4** led to the formation of **5** and **6**.

Similar irradiation of a solution of 2,2-di-*p*-tolyl-4,5-diphenyl-3-oxazoline (E′) gave 1,1-di-*p*-tolyl-3,4-di-

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phenyl-*N*-oxo-2-azabutadiene (**4′**), di-*p*-tolyl ketone (**5′**), and benzonitrile (**6**) as shown in Scheme II.

The formation of diradical F from oxazoline may occur by the photocleavage of a carbon–oxygen bond. A similar fragmentation of the carbon–sulfur bond in a thiazoline has been reported.[8] Rearrangement of F may give rise to the possible oxaaziridine G which may undergo a photochemical ring opening to form the *N*-oxoazabutadiene; subsequent photofragmentation would yield ketone and nitrile.

The photodecomposition of oxazolines E and E′ to *N*-oxoazabutadiene, diaryl ketone, and benzonitrile supports the intermediacy of E in the photolysis of benzil monobenzhydrylimine (**1**) to give products **4**–**6** (Scheme I).

Experimental Section

Melting points have been determined on a Büchi apparatus by the capillary method and are uncorrected. UV spectra were recorded on a Cary-14 spectrophotometer. IR spectra were determined on a Perkin-Elmer 621 spectrophotometer. ^{1}H NMR spectra were recorded by using a Varian A-60D spectrometer. Chemical shifts are reported in parts per million (δ) relative to Me_4Si as an internal standard. Microanalyses were performed by Coleman carbon, hydrogen, and nitrogen analyzers. Mass spectra were obtained on a CEC 110 double-focussing high-resolution mass spectrometer.

Irradiation of 1. A solution of **1** (0.5 g, 1.33 mmol) in 325 mL of benzene was irradiated with Pyrex-filtered light from a 450-W Hanovia lamp for 2 h under N_2. Two such runs were combined, and the solvent was evaporated under reduced pressure. The residual oily matter was triturated with propan-2-ol to give a solid which on repeated fractional crystallizations from propan-2-ol gave the following three products:

(i) 1-Benzhydryl-2,2,4,5-tetraphenyl-3-imidazoline (**2**): 0.25 g (35% yield); mp 206–207 °C; IR (Nujol) 1625 (s, C=N) cm^{-1}; NMR ($CDCl_3$) δ 5.20 (s, 1 H), 6.40–6.63 (m, 1 H), 6.90–7.50 (m, 26 H), 7.75–8.00 (m, 4 H); UV (EtOH) λ_{max} 250 nm; mass spectrum, *m/e* (relative intensity) 375 (8), 374 ($M^+ - Ph_2C$, 20), 358 (3), 271 ($PhCH{=}NCHPh_2$, 79), 270 ($PhCH{=}NCPh_2$, 100), 269 ($\overline{N{=}CPh{-}C}Ph_2$, 40), 254 (6), 253 (8), 244 (10), 193 (8), 192 (6), 190 (4), 167 (61), 166 (29), 165 (70), 139 (4), 104 (14), 103 (PhCN, 8), 91 (8), 90 (6), 89 (8). Anal. Calcd for $C_{40}H_{32}N_2$: C, 88.89; H, 5.92; N, 5.18. Found: C, 88.53; H, 6.12; N, 5.47.

(ii) Benzil (**3**): 0.05 g (18% yield); mp 95–96 °C.

(iii) 1,1,3,4-Tetraphenyl-*N*-oxo-2-azabutadiene (**4**): 0.10 g (10% yield); mp 126–127 °C; IR (Nujol) 1620 (s, C=N), 1580 (s, N→O) cm^{-1}; NMR ($CDCl_3$) δ 6.90–7.90 (m); UV (EtOH) λ_{max} 247 nm; mass spectrum, *m/e* (relative intensity) 375 (M^+, 5), 374 (13), 373 (2), 332 (5), 298 (5), 297 (5), 286 (7), 285 ($M^+ - PhCH$, 16), 272 (20), 271 (8), 270 (20), 269 ($\overline{N{=}CPh{-}C}Ph_2$, 39), 268 (50), 239 (15), 219 (3), 218 (15), 203 (17), 196 (Ph_2CNO, 10), 195 (6), 189 (8), 183 (15), 182 (Ph_2CO, 61), 181 (20), 180 (Ph_2CN, 9), 175 (12), 167 (21), 166 (Ph_2C, 50), 165 (63), 154 (15), 153 (11), 152 (19), 149 (16), 122 (19), 119 (6), 116 (10), 115 (16), 106 (25), 105 (PhCO, 100), 104 (25), 103 (PhCN, 61), 91 (16), 89 (10). Anal. Calcd for $C_{27}H_{21}NO$: C, 86.40; H, 5.60; N, 3.73. Found: C, 86.15; H, 5.78; N, 3.60.

The crude product obtained from concentration of the propan-2-ol mother liquor was chromatographed on an alumina column (1.8 cm × 25 cm, 65 g). The elution with *n*-hexane–benzene (4:1, 400 mL) gave 0.02 g (8% yield) of benzonitrile (**6**) and that with *n*-hexane–benzene (1:1, 500 mL) gave 0.04 g (9% yield) of benzophenone (**5**). The IR spectra of **5** and **6** were identical with those of authentic samples.

Irradiation of E. A solution of E (0.30 g, 0.80 mmol) in 325 mL of benzene was irradiated with UV light from a 200-W Hanovia lamp for 6 h. Two such runs were combined, and the solvent was evaporated under reduced pressure. The residue was treated with an *n*-hexane–benzene mixture. The solid material was filtered and crystallized from *n*-hexane–ethanol to give 0.24 g (40% yield) of **4**. The mother liquor was chromatographed as above to give 0.085 g (19% yield) of benzophenone (**5**) and 0.048 g (18% yield) of benzonitrile (**6**). When the irradiation of 0.10 g of E in 325 mL of benzene was done by using a 450-W Hanovia lamp with a Pyrex filter for 1.5 h, the yield of **4** was low.

Irradiation of E′. The irradiation of E′ in a similar manner as described above for E gave 1,1-di-*p*-tolyl-3,4-diphenyl-*N*-oxo-2-azabutadiene: 45% yield; mp 115–116 °C; IR (Nujol) 1620 (s, C=N), 1580 (s, N→O) cm^{-1}; NMR ($CDCl_3$) δ 2.36 (s, 6 H), 6.85–7.90 (m, 19 H); UV (EtOH) λ_{max} 245 nm; mass spectrum, *m/e* (relative intensity) 403 (M^+, 14), 377 (7), 313 ($M^+ - C_6H_5CH$, 9), 312 (7), 300 (14), 299 (11), 298 (27), 297, ($\overline{N{=}CPh{-}C}(C_6H_4\text{-}p\text{-}Me)_2$ 33), 286 (7), 285 (11), 279 (44), 266 (37), 255 (40), 224 ($(p\text{-}MeC_6H_4)_2CNO$, 14), 211 (59), 210 ($(p\text{-}MeC_6H_4)_2CO$, 74), 209 (44), 194 (70), 182 (27), 181 (41), 179 (40), 167 (35), 166 (35), 165 (65), 122 (63), 121 (68), 120 (65), 119 (74), 106 (65), 105 (100), 104 (65), 103 (PhCN, 60), 92 (59); 91 (80), 90 (61), 89 (63). Anal. Calcd for $C_{29}H_{25}NO$: C, 86. 35; H, 6.20; N, 3.47. Found: C, 86.58; H, 6.48; N, 3.57.

From the mother liquor concentrate *p*,*p*′-dimethylbenzophenone (19%, yield; mp 95–96 °C) and benzonitirle (19% yield) were obtained as described above. The IR spectra were identical with those of the authentic samples.

Acknowledgment. We thank Professor B. M. Shukla for helpful cooperation, Dr. G. P. Pandey for assistance in obtaining the mass spectral data, and the Council of Scientific and Industrial Research, New Delhi, for the award of a post-doctoral fellowship to B.P.G.

Registry No. **1**, 71690-10-3; **2**, 73219-54-2; **3**, 134-81-6; **4**, 81315-66-4; **4′**, 81315-67-5; **5**, 119-61-9; **5′**, 611-97-2; **6**, 100-47-0; E, 81315-68-6; E′, 81315-69-7.

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