BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 1737—1740 (1973)

Methylene Analogs of Cyclobutenedione. VII.[1] Photolysis of 2,3-Bis(diphenylmethylene)cyclobutanone and Its Derivatives

Fumio Toda, Hisao Nakaoka, Kentaro Yuwane, and Eishiro Todo
Department of Industrial Chemistry, Faculty of Engineering, Ehime University, Matsuyama 790

(Received July 29, 1972)

Photolysis of 2,2-dimethoxy-3,4-bis(diphenylmethylene)cyclobutanone (I), 2,3-bis(diphenylmethylene)cyclobutanone (XIV), and 3,4-bis(diphenylmethylene)cyclobutanedione (XXV) in methanol was investigated. Photolysis of I afforded tricyclic compound(II) and dimethyl cyclobutanedicarboxylate (III) in 48 and 35% yields, respectively. Photolysis of XIV and XXV afforded the dihydronaphthalene derivatives (XIX) (88% yield) and XXIV (72% yield), respectively. The mechanisms of these reactions were also studied.

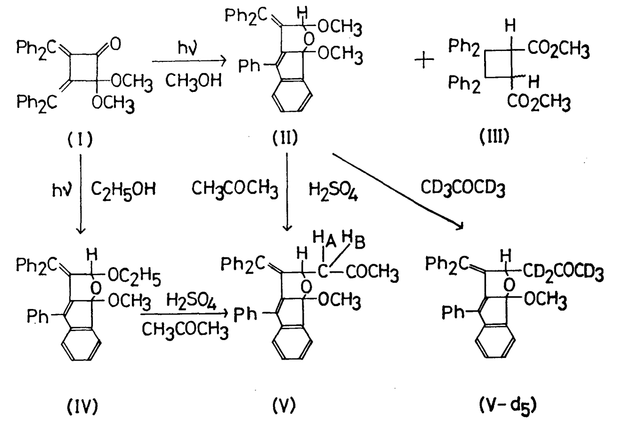
Two types of reaction for the photolysis of the four-membered ketones in alcohol, *viz.*, photo ring-expansion of cyclobutanone to tetrahydrofuran derivative *via* oxacarbene intermediate (1)[2-8] and the photo ring-cleavage of cyclobutenone to ester *via* ketene intermediate (2),[9-11] have been reported. However, no

(1)

(2)

photolysis of 2,3-dimethylenecyclobutanone derivative has yet been reported, although 2,4-dimethylenecyclobutanone has been shown to be inert to the photolysis in alcohol.[8] We have studied the photolysis of 2,3-bis(diphenylmethylene)cyclobutanone derivatives, I, XIV, and XXV in methanol, in order to confirm which type of reaction is appropriate. The photochemical reaction between the two over-crowded diphenylmethylene moieties of the cyclobutanones is also of interest.

Photolysis of I[12] in methanol under nitrogen at room temperature afforded methanol-insoluble colorless needles ($C_{32}H_{26}O_3$) and methanol-soluble colorless prisms ($C_{32}H_{28}O_4$). The former was identified to be II by means of spectral data and chemical reactions. The IR spectrum of II showed all the three oxygen atoms to be of ether linkage. The NMR spectrum showed the presence of the two magnetically nonequivalent methoxy group, in addition to one quite deshielded (3.95 τ) methine proton, and nineteen aromatic protons. However, the UV spectrum of II in ethanol, 294 nm (ε, 7900), differed from that of 1,4-diphenylbuta-1,3-diene in benzene, 334 nm (ε,



Scheme 1.

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[1] Part VI: F. Toda and N. Ooi, This Bulletin, **46**, 1733 (1973).

[2] H. U. Hostettler, *Helv. Chim. Acta*, **49**, 2417 (1966).

[3] G. Quinkert, G. Cimbollek, and G. Buhr, *Tetrahedron Lett.*, **1966**, 4573.

[4] R. F. C. Brown and R. K. Solly, *ibid.*, **1966**, 169.

[5] H. A. Staab and J. Ipaktschi, *ibid.*, **1966**, 583.

[6] H. A. Staab and J. Ipaktschi, *Chem. Ber.*, **101**, 1457 (1968).

[7] J. G. Pacifici and C. Diebert, *J. Amer. Chem. Soc.*, **91**, 4595 (1969).

[8] D. R. Morton, E. Lee-Ruff, R. M. Southam, and N. J. Turro, *ibid.*, **92**, 4349 (1970).

[9] J. D. Roberts and F. B. Mallory, *ibid.*, **83**, 393 (1961).

[10] J. E. Baldwin and M. C. McDaniel, *ibid.*, **89**, 1537 (1967).

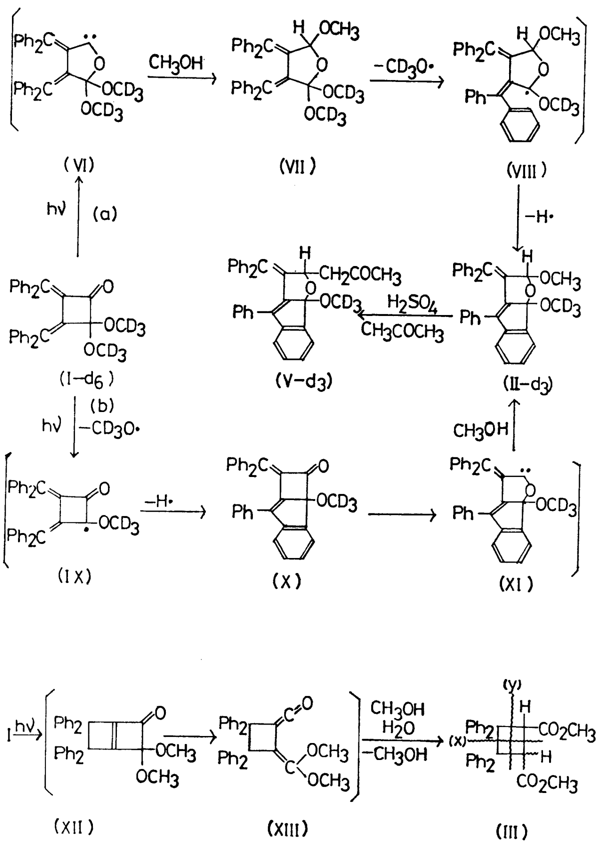
[11] J. E. Baldwin and M. C. McDaniel, *ibid.*, **90**, 6118 (1968).

[12] F. Toda and K. Akagi, *Tetrahedron*, **27**, 2801 (1971).

40000).[13] The difference is attributable to the noncoplanarity of II, since studies on a molecular model of II show that the indene and the diphenylmethylene chromophores are prevented from being arranged on a coplane.

In order to distinguish the two methoxy groups of II, II was allowed to react with acetone in the presence of concd sulfuric acid to afford the substitution reaction product (V). The NMR spectrum of V showed the methine proton signal as a quartet centered at 4.12 τ, and the methylene proton signal at 7.6—7.9 τ as a multiplet, in addition to the methoxy methyl and the acetyl methyl proton signals as a singlet at 6.99 and 8.10 τ, respectively. The multiplicity of the methine and methylene proton signals is probably due to the spin-spin coupling between the methine proton and the two magnetically nonequivalent methylene protons (H_A and H_B). The nonequivalency of the two methylene protons is probably due to an asymmetric effect. Direct evidence for the coupling was obtained by using V-d_5 which was prepared by the reaction of II and acetone-d_6. In the NMR spectrum of V-d_5, a methine proton signal appeared at 4.20 τ as a singlet in addition to a singlet signal of methoxy at 7.02 τ.

In order to determine the origin of the two methoxy groups of II, the photolysis of I in ethanol was carried out, and the ring-expanded product (IV) was obtained. The structure of IV was identified by its reaction with acetone to afford V. The magnetic nonequivalency of the two methylene protons of the ethoxy of IV is also probably due to an asymmetric effect. The production of IV in the above photolysis shows that the methoxy on the bridge-head and the other methoxy of II were derived from I and methanol, respectively. This was further supported by the photolysis of I-d_6 in methanol to afford II-d_3 (Scheme 2). The acid-catalyzed reaction of II-d_3 with acetone afforded V-d_3. The structures of II-d_3 and V-d_3 were determined by means of the spectral data.

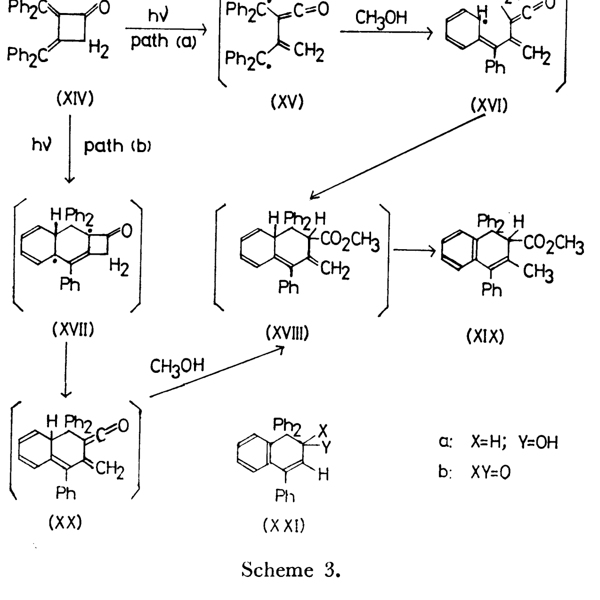


Scheme 2.

The photolysis of I to afford II corresponds to the type of reaction (1). The reaction might then proceed *via* an oxacarbene intermediate. Depending on whether or not the dihydrofuran-ring formation precedes the indene-ring formation, two reaction paths (a) and (b), and thereafter the oxacarbene intermediates, VI and XI, are applicable (Scheme 2). However, we could obtain no further evidence to distinguish the path.

The structure of the methanol-soluble compound accompanying II in the photolysis of I was identified by spectral data to be the cyclobutane derivative (III). The NMR data indicating that all the aromatic protons appear at a relatively higher field, 2.7—3.6 τ, agree with the structure of III, in which four phenyls are shielded each other. However, the geometry of the two carbomethoxy group could not be determined. The MS spectrum of III showed a fragment ion peak at *m/e* 238 which is just half of the mass of its parent ion. The data show that III undergoes ring-cleavage easily in the manner of (x) but not (y) (Scheme 2).

Formation of III can be interpreted by the photo ring-cleavage of XII initially produced by the photo ring-closure of I, to afford the ketene intermediate (XIII) and finally III. This type of photo reaction is analogous to (2). The conversion of XIII into III would proceed by the addition of methanol and water to the ketene and dimethoxyethylene moieties, respectively, followed by the elimination of methanol. Since II and III were obtained in 35 and 48% yields, respectively, when the photolysis of I was carried out in 95%



Scheme 3.

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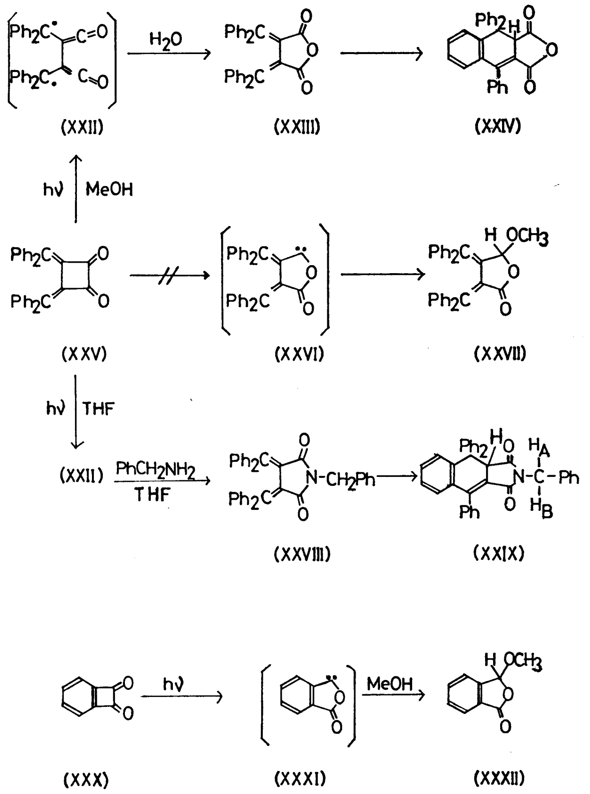
[13] K. W. Hausser, R. Kuhn, and A. Smakula, *Z. Phys. Chem.*, **B29**, 384 (1935).

methanol, it is clear that water is essential for the formation of III.

In order to clarify the special role of the methoxy group of I in its photolysis, the photolysis of XIV[12] was carried out, under the same conditions as those employed for I, and afforded the dihydronaphthalene derivative (XIX) as the sole product (85% yield). Its structure was identified by means of spectral data. The UV spectrum of XIX, 285 nm (ε, 6900), was comparable to that of the analogous compound (XXIa),[14] 288 nm (ε, 6000).

Two possible reaction paths (a) and (b) can be written for the formation of XIX (Scheme 3). The choice of path depends on whether the ring-cleavage of the cyclobutanone-ring or the reaction between the two diphenylmethylene moieties occurs initially.

Although it is difficult to define the real mechanistic pathway, it is clear that the photo reaction of XIV proceeds *via* a pathway analogous to (2). From a comparison of the photolysis of I to afford II with that of XIV to afford XIX, the special role of the methoxy group of I in its photolysis is clear. (b) is therefore the more plausible path of the photolysis of I to afford II (Scheme 2).



Scheme 4.

The photolysis of the diketone (XXV)[12] is of interest as regards the photolysis of benzocyclobutenedione (XXX) to afford the benzolactone (XXXII), the product of the type of reaction (1). The photolysis of XXV in 99% methanol afforded the acid anhydride (XXIV) in a 72% yield, but no detectable amount of lactone (XXVII). The structure of XXIV was identified by means of spectral data. The UV spectral bands of XXIV in chloroform, 242 (14000) and 315 nm (ε, 14000), were comparable to those of XXIb in ethanol, 240 sh (8100) and 316 nm (ε, 8900).[14] Since the photolysis of XXIII[12] under the same conditions as employed for XXV afforded XXIV in a 82% yield, XXIII is a probable intermediate of the photolysis of XXV. A possible precursor of XXIII is the bisketene (XXII) which is produced by ring-cleavage of XXV of type (2). The reaction of the bisketene (XXII) with water to afford the acid anhydride (XXIII) is reasonable, since the reaction of XXV with water in the presence of bromine to afford XXIII *via* XXII has been postulated,[15] and the photochemical reaction of XXV with benzylamine in dry tetrahydrofuran afforded XXIX *via* XXVIII. The intermediacy of XXVIII in the latter photolysis was defined by a separate photolysis of XXVIII prepared according to a modified procedure to afford XXIX.

The structure of XXIX was identified by means of spectral data. The magnetic nonequivalence of the two methylene protons of XXIX (H_A and H_B) gives further structural evidence for XXIX which has asymmetric center.

Experimental

All the melting points were uncorrected. Photolysis was carried out at room temperature under nitrogen atmosphere, with a 100-W high-pressure mercury lamp (Riko Kagaku Sangyo Co.). IR, UV, and NMR spectra were measured in Nujol mull, EtOH, and $CDCl_3$ respectively, unless otherwise stated. Mass spectra were measured with an ionization energy of 70 eV.

Photolysis of I in Methanol. A suspension of finely-powdered I (1.09 g) in 99% methanol (100 ml) was irradiated under stirring for 17 hr. The crude product precipitated was collected by filtration, and recrystallized from ethyl acetate to afford II as colorless needles; 0.52 g (48%); mp 180—181 °C. IR: 1120, 1010, and 990 cm^{-1} (C–O–C); λ_{max}: 237 (20200) and 294 nm (ε, 7900); NMR: 1.85—2.00 (m, Ph, 1H), 2.2—2.9 (m, Ph, 18 H), 3.95 (s, CH, 1H), 6.85 (s, OCH_3, 3H), and 7.03 τ (s, OCH_3, 3H); MS: *m/e* (rel intensity) 458.1917 (M^+ 458.1882, 2), 427 (40), 426 (100), 411 (90), 381 (15), 367 (20), and 278 (20).

Found: C, 84.01; H, 5.65%. Calcd for $C_{32}H_{26}O_3$: C, 83.82; H, 5.72%.

Concentration of the mother liquor remaining after the separation of crude II by filtration afforded crude crystals. Their recrystallization from ethyl acetate afforded III as colorless prisms; 0.38 g (35%); mp 172—174 °C. IR: 1740 and 1725 (C=O), and 1230 cm^{-1} (ester); λ_{max}: 262 (1100), 269 (1100), and 275 nm (ε, 700); NMR: 2.7—3.6 (m, Ph, 20 H), 5.03 (s, CH, 2H), and 6.63 τ (s, CO_2CH_3, 6H); MS: *m/e* (rel intensity) 238.0982 ($M^+/2$ 238.0992, 100), 237 (22), 207 (53), 179 (30), and 178 (25).

Found: C, 80.71; H, 5.73%; mol wt (benzene), 471. Calcd for $C_{32}H_{28}O_4$: C, 80.64; H, 5.92%; mol wt, 476.

When the photolysis of I was carried out in 95% methanol, II and III were obtained in 35 and 48% yields, respectively.

Photolysis of I in Ethanol. A suspension of finely-powdered I (1.0 g) in 99% ethanol (100 ml) was irradiated

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[14] F. Toda and K. Akagi, *Tetrahedron*, **27**, 3795 (1969).

[15] F. Toda and J. Fujita, This Bulletin, **45**, 1928 (1972).

under stirring for 17 hr. The crude product precipitated was recrystallized from ethyl acetate to afford IV as colorless needles 0.68 g (68%); mp 176—177 °C. IR: 1110, 1010, and 995 cm^{-1} (C–O–C); NMR: 1.95—2.00 (m, Ph, 1H), 2.2—2.9 (m, Ph, 18H), 3.86 (s, CH, 1H), 6.2—6.9 (m, $\mathbf{OCH_2}CH_3$, 2H), and 7.02 (s, OCH_3, 3H), and 9.21 τ (t, $OCH_2\mathbf{CH_3}$, 3H).

Found: C, 84.10; H, 5.83%. Calcd for $C_{33}H_{28}O_3$: C, 83.87; H, 5.97%.

Photolysis of I-d_6 in Methanol. A suspension of finely-powdered I-d_6 (0.45 g), prepared from XXV and methanol-d_4 in 99% methanol (50 ml) was irradiated under stirring for 17 hr.[12] The crude product precipitated was recrystallized from ethyl acetate to afford I-d_3; 0.2 g (45%). IR: 2080 cm^{-1} (OCD_3) and 1110, 1005, and 990 cm^{-1} (C–O–C); NMR: 1.85—2.00 (m, Ph, 1H), 2.2—2.9 (m, Ph, 18H), 3.92 (s, CH, 1H), and 6.82 τ (s, OCH_3, 3H).

Acid-catalyzed Reactions of II, IV, and I-d_3 with Acetone. A solution of II (0.2 g) and three drops of concd sulfuric acid in acetone (10 ml) was heated under reflux for 20 min. The crude crystals obtained by the evaporation of the solvent to dryness were washed with water, dried and recrystallized from ethyl acetate to afford V as colorless needles; 0.15 g (71%); mp 243—244 °C. IR: 1720 (C=O), and 1060 and 995 cm^{-1}(C–O–C); λ_{max} ($CHCl_3$): 249 (28100) and 297 nm (ε, 10200); NMR: 1.8—2.0 (m, Ph, 1H), 2.2—2.9 (m, Ph, 18H), 4.12 (q, CH, 1H), 6.99 (s, OCH_3, 3H), 7.6—7.9 (m, CH_2, 2H), and 8.10 τ (s, $COCH_3$, 3H).

Found: C, 84.27; H, 5.54%. Calcd for $C_{34}H_{28}O_3$: C, 84.27; H, 5.82%.

The same treatment of IV with acetone as for II afforded V in a 65% yield.

The same treatment of II with acetone-d_6 as for II afforded V-d_5 in a 70% yield. IR: 1715 (C=O) and 1065 cm^{-1} (C–O–C); NMR: 1.85—2.05 (m, Ph, 1H), 2.3—3.0 (m, Ph, 18 H), 4.20 (s, CH, 1H), and 7.02 τ (s, OCH_3, 3H).

The same treatment of II-d_3 with acetone as for II afforded V-d_3 in a 50% yield. IR: 1720 (C=O) and 1060 cm^{-1} (C–O–C); NMR: 1.8—2.0 (m, Ph, 1H), 2.2—2.9 (m, Ph, 18H), 4.10 (q, CH, 1H), 7.5—7.8 (m, CH_2, 2H), and 8.11 τ (s, $COCH_3$, 3H).

Photolysis of XIV in Methanol. A suspension of finely-powdered XIV (1.03 g) in 99% methanol (100 ml) was irradiated under stirring for 17 hr. The crude crystals obtained by the evaporation of the solvent to dryness were recrystallized from ethyl acetate to afford XIX as colorless needles; 0.91 g (88%); mp 146—147 °C. IR: 1700 and 1720 (C=O), and 1225 cm^{-1} (ester); λ_{max}: 228 (18600) and 285 nm (ε, 6900); NMR: 2.5—3.1 (m, Ph, 18H), 3.25—3.45 (m, Ph, 1H), 6.03 (s, CH, 1H), 6.62 (s, CO_2CH_3, 3H), and 8.26 τ (s, CH_3 3H); MS: *m/e* (rel intensity) 430.1938 (M$^+$, 430.1932, 100), 398 (7), 371 (57), 356 (18), 293 (32), 279 (14), 278 (14), and 215 (13).

Found: C, 86.33; H, 5.88%. Calcd for $C_{31}H_{26}O_2$: C, 86.48; H, 6.09%.

Photolysis of XXV in Methanol. A suspension of finely-powdered XXV (1.0 g) in 99% methanol (100 ml) was irradiated under stirring for 17 hr. The crude crystals remaining after the evaporation of solvent were recrystallized from ethyl acetate to afford XXIV as colorless prisms; 0.73 g (72%); mp 225—226 °C. IR: 1760 and 1820 cm^{-1} (C=O); λ_{max}($CHCl_3$): 315 (12200) and 340 sh nm (ε, 7400); NMR: 2.5—3.2 (m, Ph, 18H), 3.2—3.4 (m, Ph, 1H), and 4.91 τ (s, CH, 1H); MS: *m/e* (rel intensity) 428.1437 (*M*$^+$ 428.1412, 100), 384 (98), 355 (56), 350 (86), 330 (98), 307 (75), 279 (98), and 278 (98).

Found: C, 84.36; H, 4.81%. Calcd for $C_{30}H_{20}O_3$: C, 84.09; H, 4.71%.

Photolysis of XXIII in Methanol. A suspension of finely-powdered XXIII (1.0 g) in 99% methanol (100 ml) was irradiated under stirring for 2 hr. The crude crystals remaining after the evaporation of solvent to dryness were recrystallized from ethyl acetate to afford XXIV; 0.82 g (82%). The IR spectral data were identical with those of an authentic sample prepared by the photolysis of XXV in methanol.

Photo Reaction of XXV with Benzylamine in Tetrahydrofuran. A solution of XXV (1.26 g) and benzylamine (3.2 g) in dry tetrahydrofuran (150 ml) was irradiated under stirring for 17hr. The residue remaining after the evaporation of the solvent was taken up in ether. The ether solution was washed successively with dil hydrochloric acid and water, and dried over sodium sulfate. The crude product obtained by the evaporation of solvent was chromatographed on alumina with carbon tetrachloride as a solvent. The elution with benzene afforded XXIX as colorless plates; 0.18 g (11%); mp 221—222.5 °C. IR: 1760 and 1690 (C=O), 1630 (C=C), and 1430 cm^{-1} (CH_2); λ_{max}($CHCl_3$): 310 (16800) and 340 sh nm (ε, 8800). NMR: 2.9—3.0 (m, Ph, 24H), 5.22 (s, CH, 1H), and 5.41 τ (q, CH_2, 2H); MS: *m/e* (rel intensity) 517.2015 (M$^+$ 517.2041, 100), 440 (28), 439 (55), 384 (17), 356 (65), and 307 (38).

Found: C, 85.54; H, 5.27%. Calcd for $C_{37}H_{27}O_2N$: C, 85.85; H, 5.26%.

Preparation of XXVIII. A mixture of XXV (3.9 g), bromine (2 g), benzylamine (10 g) and dry carbon tetrachloride (300 ml) was stirred at room temperature for 30 min. After removal of the amine salt formed as a result of filtration, the filtrate was evaporated to dryness to afford crude crystals. Recrystallization of the crude crystals from acetone afforded XXVIII as yellow plates; 2.2 g (45%); mp 227—228 °C. IR: 1750 and 1690 (C=O), and 1430 cm^{-1} (CH_2); λ_{max}: 252 (29000), 309 (21800), and 400 nm (ε, 11100). NMR: 2.4—3.2(m, Ph, 25H) and 5.31 τ (s, CH_2, 2H); MS: *m/e* (rel intensity) 517.2059 (M$^+$ 517.2041, 81), 384 (100), 356 (36), and 307 (36).

Found: C, 85.65; H, 5.32%. Calcd for $C_{37}H_{27}O_2N$: C, 85.85; H, 5.26%.

Photolysis of XXVIII in Tetrahydrofuran. A solution of XXVIII (1.12 g) in dry tetrahydrofuran (100 ml) was irradiated for 7 hr. The crude crystals obtained by the evaporation of solvent was recrystallized from ethyl acetate to afford XXIX as colorless plates; 0.50 g (45%). The IR spectral data were identical with those of an authentic sample prepared by the photo reaction of XXV with benzylamine.