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The Photochemical Reaction of Diphenylacetylene with Enamines[1]

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The irradiation of a mixture of diphenylacetylene (I) and the enamine of the diethyl ketone (II) or of cyclopentanone (IV) gives two β,γ-unsaturated ketones, III and X respectively, in which the diphenylacetylene moiety is formally inserted into the respective enamine double bond under hydrogen migration. The reaction with the enamine of cyclohexanone (V) affords 2-(1,2-diphenylvinyl)cyclohexanone (XIII) as the major product in addition to the cycloadduct (XV). In each case, the formation of photodimers of I has been observed. The reaction is quenched by the addition of pyrene, is sensitized by triphenylene, and is supposed to proceed by way of a triplet path. The different routes of the enamine reactions can be explained by considering the geometry of the intermediate diradicals.

Little is known about photochemical reactions in which an enamine[2] is attacked by photochemically-excited species. Foote and Wei-Ping reported the oxidative fission of the enamine double bond by singlet oxygen photochemically produced.[3] We ourselves have been interested in the reaction of photoexcited benzophenone with enamines, in which the oxetane formation competes with the hydrogen abstraction at the allylic position,[4] and also in the photoreaction of diphenylacetylene with enaminoesters.[5]

In continuation of previous studies along this line, we have investigated the photoreaction of diphenylacetylene with several types of enamines; the results will be described in this paper.

TABLE 1. PHOTOREACTION OF I WITH ENAMINES IN ETHANOL AND ACETONITRILE

Enamine	solvent	Product (yield[9] in %)
II[6]	EtOH	dimers[7] of I (13), III (10)
	CH_3CN	dimers[7] of I (16), III (18)
IV[6]	EtOH	dimers[7] of I (10), X (15)
	CH_3CN	dimers[7] of I (6.2), X (20)
V[6]	EtOH	dimers[7] of I (10), XIII (11), XV[6] (2.3)
	CH_3CN	dimers[7] of I (15), XIII (15), XV[6] (3.1)

When a benzene or *n*-hexane solution of diphenylacetylene (I) and 3-morpholinopent-2-ene (II)[6] was irradiated, the photodimers of I as described by Büchi *et al.*[7] and Bryce-Smith and Lodge[8] were obtained in a 10% yield.[9] In addition to this, β,γ-unsaturated ketone (III) was isolated as a viscous liquid in a 16% yield[9] upon silica gel-column chromatography (Scheme 1). The assigned structure for III was consistent with the IR, NMR, and UV spectra (see Experimental Section), and the semicarbazone gave correct analyses.

A similar reaction with 1-morpholinocyclopentene (IV) gave a cyclic β,γ-unsaturated ketone (X) as an oil in a 23% yield,[9] along with the photodimers[7] of I (Scheme 2). The structure of X was consistent with the spectroscopic data and was further proven by an alternative chemical method. When X was treated upon activated alumina as has been described by Heap and Whitham,[10] isomerization to an α,β-unsaturated ketone, 2,3-diphenylcyclohept-2-enone (XI), took place readily. The structure of XI was confirmed by the spectra and especially by the NMR, in which the absence of the vinyl-proton signal strongly supported the assigned structure. The precursor of X must be dienamine, IX. The presence of IX in the crude reaction mixture was directly ascertained by observing a characteristic triplet at δ 6.70 ppm (vinyl proton)[11] upon the NMR analysis of the residue obtained by the removal of the unchanged enamine from the irradiation mixture *in vacuo*. It may be noted that the reactions of both II and IV possibly proceed *via* such cyclobutenes as VIII and the dienamines to afford β,γ-unsaturated ketones, III and X, in which the diphenylacetylene moiety has been incorporated formally at the enamine double-bond site under hydrogen migration. Thermal reactions in a similar sense have been recorded exclusively with electronegatively-substituted acetylenes.[12,13] The attempted reaction of I with enamines completely failed to occur thermally in the dark.

When the photochemical reaction of 1-morpholinocyclohexene (V)[6] was effected similarly, a cyclohexanone derivative (XIII) and a minor amount of the adduct (XV) were isolated in 17 and 3.1% yields[9] respectively (Scheme 2).

The structure of XIII was elucidated by studying its

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[1] A part of this work was presented at the 24th Annual Meeting of the Chemical Society of Japan (1971).

[2] For the pertinent references on enamine reactions, see J. Szmuszkovicz, "Advances in Organic Chemistry," Vol. 4, ed. by R. A. Raphael, E. C. Taylor, and H. Wynberg, Interscience, New York, (1963); A. G. Cook, "Enamines," Marcel Dekker, New York, (1969).

[3] C. S. Foote and J. Wei-Ping, *Tetrahedron Lett.*, **1968**, 3267.

[4] M. Kawanisi, K. Kamogawa, T. Okada, and H. Nozaki, *Tetrahedron*, **24**, 6562 (1968).

[5] M. Kawanisi, K. Matsunaga, and N. Miyamoto, This Bulletin, **45**, 1240 (1972).

[6] *Y*=morpholino group.

[7] G. Büchi, C. W. Perry, and E. W. Robb, *J. Org. Chem.*, **27**, 4106 (1962).

[8] D. Bryce-Smith and J. E. Lodge, *J. Chem. Soc.*, **1963**, 695.

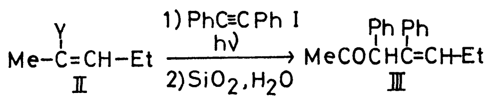
[9] The yields were based on the I used.

[10] N. Heap and G. H. Whitham, *J. Chem. Soc.*, *B*, **1966**, 164.

[11] The vinyl proton (triplet) of the IV enamine[6] appeared at δ 4.55 ppm.

[12] K. C. Brannock, R. D. Burpitt, V. W. Goodlet, and J. G. Thweat, *J. Org. Chem.*, **28**, 1464 (1963); **29**, 818 (1964).

[13] Recently similar reactions have been recorded with respect to the enamine-type double bond of indoles. See R. M. Acheson, J. N. Bridson, and T. M. Cameron, *J. Chem. Soc. Perkin Trans. I*, **1972**, 968.



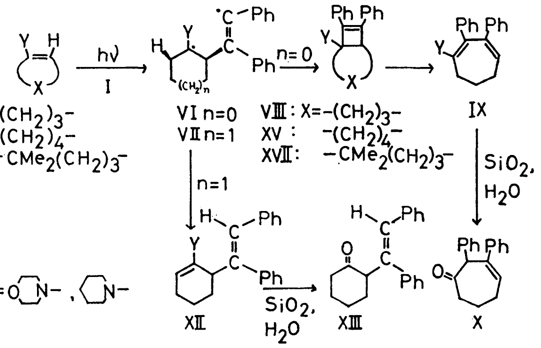
Scheme 1.

spectral data and by elemental analysis as well as by chemical degradation. The oxidation of XIII by Rudloff's method[14] gave 2-benzoylcyclohexanone (XIV), which was identical with the authentic specimen[15] prepared by the benzoylation of the enamine V.

Table 2. Photoreaction of I with piperidinoenamines in *n*-hexane

Enamine	Product (yield[9] in %)
II[16]	dimers[7] of I (8.2), III (20)
IV[16]	dimers[7] of I (10), X (25)
V[16]	dimers[7] of I (10), XIII (20), XV[16] (2.3)

The structure of the minor product, XV,[6] is mainly based on the spectral evidence. The UV showed the *cis*-stilbene chromophore, and the mass spectrum had eminent peaks at *m/e* 345 (M^+) and 167 (M^+-178). In addition, XV[6] remained unchanged upon chromatographic treatment.



Scheme 2.

The analogous reaction of an enamine[6] of 2,2-dimethylcyclohexanone (XVI) gave only a cycloadduct (XVII)[6] in a 2.0% yield[9] (Scheme 2). The structure was deduced from the spectral data.

Finally, the photoreaction of I with piperidinoenamines[16] of the diethyl ketone, cyclopentanone, and cyclohexanone proceeded much as with the corresponding morpholinoenamines (see Experimental Section).

Discussion

The photodimerization of I has been reported to proceed by way of a triplet path;[7] the same path was also assumed in the 2+2 photoaddition of I on 2,3-dihydropyran.[17] Ample evidence seems to support the idea that the π-π^* triplet pathway of I is important in the addition to enamines. Thus, the addition of pyrene[18] to a mixture of I[19] and enamines resulted in the complete suppression of either the cycloaddition or the dimerization of I.[20] Equimolar concentrations of I and pyrene were used. Since their molar extinction coefficients are approximately equal at the excitation wavelength (log ε=4.1 at 254 nm), the quenching effect of pyrene must be ascribed to the triplet energy transfer rather than to the absorption of the exciting light by itself. Meanwhile, the reaction conducted in a Pyrex vessel under irradiation with light filtered through aqueous 10% $CuSO_4$ was successfully sensitized by triphenylene (E_T=66.6 kcal/mol[18]). The photolysis in the absence of the sensitizer did not occur under the above conditions.

The mechanism of the cycloaddition of I to the IV enamine is considered to be as follows. The electrophilic nature of excited I has been demonstrated in the addition reaction to tetramethylethylene[21] and to 2,3-dihydropyran.[17] When the excited I in the triplet state is added to IV, the cycloadduct thus formed is the bicyclo[3.2.0]hept-6-ene derivative (VIII), which subsequently is isomerized to a cycloheptadiene, IX. The ring-opening of VIII might occur photochemically *via* a disrotatory mode,[22] but the true nature has not yet been determined.[23] The presence of the IX dienamine in the irradiation mixture, as evidenced by NMR spectroscopy, shows that the ring-opening proceeds prior to the hydrolysis upon silica gel.[24]

A priori, the formation of α-substituted cyclohexanone, XIII, may be explained in two ways. The first one is based on the hydrogen abstraction at the allylic position of the V enamine. The efficient abstraction of hydrogen has been observed both with the π-π^* excited state of olefins[25,26] as well as with that of acetylenes, as has been disclosed recently by Roberts *et al.*[27]

This route fails, however, to explain the fact that the reaction of II or of IV does not afford the products of a type such as XIII. Additionally, it should be noted that the hydrogen abstraction of cyclohexanone enamine occurs at the 3 position rather than at 6.[4]

An alternative mechanism (Scheme 2) is based on the facts that the reactive species is in the triplet state and that the reaction occurs independently of the

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14) L. Rudloff, *Can. J. Chem.*, **34**, 413 (1965).

15) R. D. Campbell, H. M. Gilow, and G. Stork, *J. Amer. Chem. Soc.*, **84**, 1440 (1963).

16) Y=piperidino group.

17) H. M. Rosenberg and P. Servé, *J. Org. Chem.*, **33**, 1653 (1968).

18) The E_T of pyrene is 48.7 kcal/mol; see W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537 (1964).

19) The E_T of I has been recorded to be 51 kcal/mol; see M. Beer, *J. Chem. Phys.*, **25**, 745 (1956).

20) Pyrene is an aromatic hydrocarbon useful as a triplet quencher; see A. A. Lamola, "Energy Transfer and Organic Photochemistry," Chap. I, Interscience, New York (1969).

21) O. L. Chapman and W. R. Adams, *J. Amer. Chem. Soc.*, **89**, 4243 (1967).

22) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim (1970).

23) J. S. McCanaghy and J. J. Bloomfield, *Tetrahedron Lett.*, **1969**, 3719, 3723: G. R. Branton, H. M. Frey, D. C. Montagne, and I. R. D. Stevens, *Trans. Farady Soc.*, **62**, 659 (1966).

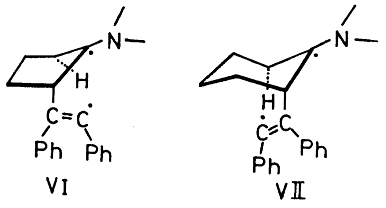
24) Silica gel contains 7% free water physically absorbed; see K. R. Lenge, *Chem. Ind.*, (London) **1968**, 441.

25) K. J. Crowly, *J. Amer. Chem. Soc.*, **85**, 1210 (1963).

26) H. M. Rosenberg and P. Servé, *ibid.*, **91**, 6185 (1969).

27) T. D. Roberts, L. Ardemagni, and H. Shechter, *ibid.*, **91**, 6185 (1969).

solvent polarity. The reaction of I with enamines in ethanol or acetonitrile gave results similar to those in *n*-hexane or benzene (see Experimental Section). We may reasonably assume that the attack of I on V proceeds step by step to give the diradical intermediate VII, first. Subsequent hydrogen abstraction takes place in VII through the six-membered transition state, thus producing an enamine, XII. The hydrogen abstraction caused by vinyl radicals has many precedents in the literature.[28] In sharp contrast, however, the cyclopentyl diradical, VI, gives the recombination product VIII predominantly, as has been stated previously. The difference may be explained as follows. Immediately after the attack of I on the π-bond in enamine, the stilbene moiety presumably occupies an axial position. Hydrogen abstraction takes place easily in such a conformation to give XII, while the less preferred radical recombination in VII forms XV in a far smaller yield. The corresponding intermediate diradical, VI, produced from the five-membered enamine, IV, must be less prone to hydrogen abstraction because of the disfavorable geometry. No hydrogen abstraction is observed, and the radical recombination product is formed exclusively (Scheme 3). The radical recombination was observed also with XVI, which has no removable hydrogen to afford the bicyclic product, XVII.[6]



Scheme 3.

Experimental

All the melting points and boiling points are uncorrected. The IR spectra were obtained on a Shimadzu IR-27-G spectrometer in a neat liquid film, unless stated otherwise. The NMR spectra were taken with a JEOL C-60-H spectrometer (60 MHz) with CCl_4 as the solvent, and the chemical shifts are recorded in δ values relative to TMS as the internal standard. The NMR data are given in the order of multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, and m=unresolved multiplet), integration, and assignment. The UV spectra were taken in EtOH on a Hitachi EPS-2 recording spectrophotometer. The MS spectra were obtained with a Hitachi RM-61 spectrometer at 80 eV. The column chromatography was carried out on Mallinckrodt silicic acid (100 mesh). Plates of silica gel G were used for the tlc, and the spots were visualized with iodine vapor.

Irradiation of Diphenylacetylene (I) in the Presence of 3-Morpholinopent-2-ene (II).[6] A solution of I (1.0 g, 5.6 mmol) and II[6] (1.7 g, 11 mmol) in *n*-hexane or benzene (40 ml) was placed in a quartz vessel and irradiated externally by means of 200 W high-pressure mercury arc under a nitrogen atmosphere at room temperature for 48 hr. The progress of the reaction was followed by tlc analyses of aliquots. The reaction mixture was then concentrated *in vacuo*, and the residue was chromatographed over a silica gel-column. Elution with *n*-hexane gave unchanged I (500 mg). Further elution with the same solvent gave 1,2,3-triphenylnaphthalene (the photodimer[7] of I reported by Büchi) (120 mg, 6.1%[9]), which was obtained as colorless crystals; mp 150—152 °C (lit,[7] 151—153 °C), M^+ (356). Later fractions contained a blue crystalline mass, 1,2,3-triphenylazulene (the photodimer[7] of I) (78 mg, 3.8%[9]); mp 216—217 °C (lit,[7] 216—217 °C), M^+ (356). Elution with benzene gave 3,4-diphenylhept-4-en-2-one (III, 220 mg, 16%[9]), which was obtained as a colorless and viscous oil. IR (neat): 3100—3000, 1715, 1600, 700, and 680 cm^{-1}. UV: λ_{max}=245 nm (log ε=4.13). NMR: δ 0.90 (t, 3H, $-CH_2C\underline{H}_3$), 1.55 (d, 3H, $=CH-C\underline{H}_3$), 2.35 (q, 2H, $-C\underline{H}_2CH_3$), 4.65 (s, 1H, $-CPh\underline{H}-$), 5.35 (q, 1H, $=C\underline{H}-CH_3$), and 7.00—7.36 ppm (m, 10H, aromatic). No suitable recrystallization solvent has been found for further purification. Elemental analysis was performed by converting III to its semicarbazone; mp 201—203 °C (benzene–petroleum ether (bp 60—70 °C) (1:1)). (Found: C, 74.5; H, 7.7%. Calcd for $C_{20}H_{23}N_3O$: C, 74.7; H, 7.2%).

Irradiation of I in the Presence of 1-Morpholinocyclopent-1-ene (V).[6] A solution of I (1.0 g, 5.6 mmol) and IV[6] (1.7 g, 11 mmol) in *n*-hexane or benzene (40 ml) was irradiated for 48 hr quite analogously to the above method. The subsequent concentration of the reaction mixture *in vacuo* and elution of the residue adsorbed on a silica gel-column with *n*-hexane gave the unchanged I (430 mg) and the photodimers[7] (160 mg, 7.9%[9]). Elution with benzene gave 2,3-diphenylcyclohept-3-enone (X, 340 mg, 23%[9]), which was obtained as a colorless and viscous oil. IR (neat): 3100—3000, 1705, 1600, 750, and 700 cm^{-1}. UV: λ_{max}=245 nm (log ε=4.18). NMR: δ 1.50—1.90 (m, 2H, CH_2 attached to both sp^3 carbons), 2.20—2.70 (m, 4H, CH_2 adjacent to sp^2 carbons), 6.82 (s, 1H, $-CPh\underline{H}-$), 6.30 (t, 1H, vinyl) and 7.00—7.30 ppm (m, 10H, aromatic). No suitable recrystallization solvent has been found for further purification. Elemental analysis was performed by converting X to its semicarbazone, mp 209—212 °C (benzene–petroleum ether (1:1)). (Found: C, 75.0; H, 6.6%. Calcd for $C_{20}H_{21}N_3O$: C, 75.2; H, 6.6%).

Isomerization of 2,3-Diphenylcyclohept-3-enone (X) to 2,3-Diphenylcyclohept-2-enone (XI). The method was based on the one reported by Whitham[10] in the isomerization of cyclooct-3-enone to cyclooct-2-enone. A benzene solution of 2,3-diphenylcyclohept-3-enone (X, 100 mg, 0.38 mmol) was treated with alumina (5.0 g, Woelm neutral activity I) in a column for 24 hr. Elution with benzene furnished recovered X (20 mg). Further elution with benzene–ether (1:1) afforded 2,3-diphenylcyclohept-2-enone (XI, 65 mg, 65%), which was obtained as white crystals; mp 103—105 °C (*n*-hexane). IR (KBr): 3100—3000, 1680, 1650, 1600, 760, and 700 cm^{-1}. UV: λ_{max}=222 (log ε=4.25), 272 nm (4.10). NMR: δ 1.50—1.90 (m, 4H, CH_2 attached to both sp^3 carbons), 2.20—2.75 (m, 4H, CH_2 adjacent to sp^2 carbons) and 7.00—7.28 ppm (m, 10H, aromatic). (Found: C, 87.3; H, 6.8%. Calcd for $C_{19}H_{18}O$: C, 87.0; H, 6.9%).

Irradiation of I in the Presence of 1-Morpholinocyclohexene (V).[6] A solution of I (1.0 g, 5.6 mmol) and V[6] (1.9 g, 11 mmol) in *n*-hexane or benzene (40 ml) was irradiated for 48 hr in a manner similar to that above. The subsequent concentration of the reaction mixture and elution of the residue adsorbed on a silica gel-column with *n*-hexane gave the unchanged I (390 mg) and the photodimers[7] (98 mg, 4.9%[9]). Elution with benzene afforded 2-(1,2-diphenylvinyl)cyclohexanone (XIII, 231 mg, 15%[9]) as colorless crystals; mp

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[28] O. Shimamura, "Topics in Stereochemistry," Vol. 4, ed. by E. L. Eliel and N. L. Allinger, Wiley-Interscience, New York (1969), p. 1.

86—87 °C (petroleum ether). IR (KBr): 3050—3000, 1710, 1600, 760, and 700 cm^{-1}. UV: λ_{max}=220 (log ε=4.23), 270 nm (4.11). NMR: δ 1.50—2.06 (m, 6H, β and γ methylenes of the cyclohexanone ring), 2.00—2.50 (m, 2H, $-CH_2-C=O$), 3.30 (t, 1H, methine), 6.30 (s, 1H, vinyl) and 7.00—7.30 ppm (m, 10H, aromatic). (Found: C, 86.4; H, 7.5%. Calcd for $C_{20}H_{20}O$: C, 86.9; H, 7.3%).

Further elution with ether gave 1-morpholino-7,8-diphenylbicyclo[4.2.0]oct-7-ene (XV,[6) 59 mg, 3.1%[9)), which was obtained as colorless crystals; mp 85—86 °C (petroleum ether). IR (KBr): 3100—3000, 1600, 1120, 760, and 700 cm^{-1}. UV: λ_{max}=219 (log ε=4.20), 268 nm (4.10). NMR: δ 1.10—1.80 (m, 4H, CH_2 of the cyclohexane ring), 2.25 (t, 1H, methine), 2.40 (t, 4H, CH_2-N), 3.50 (t, 4H, CH_2-O), and 6.95—7.20 (m, 10H, aromatic). MS: 345 (M$^+$), 167 (M$^+$—178). (Found: C, 83.0; H, 8.0%. Calcd for $C_{24}H_{27}NO$: C, 83.0; H, 7.9%).

Oxidative Degradation of 2-(1,2-Diphenylvinyl)cyclohexanone (XVIII) to 2-Benzoylcyclohexanone (XIV). The method was based on that reported by Rudloff.[14) The stock oxidant solution[29) was placed in a flask, and into this was added slowly with stirring XVIII (500 mg, 1.8 mmol) dissolved in *t*-butylalcohol (5.0 ml). The solution was stirred for 3 hr at room temperature, and then the reaction mixture was extracted twice with ether. The combined extracts were washed with brine and then dried (Na_2SO_4). The solvent was evaporated, and the residue was chromatographed over silica gel. Elution with benzene–ether (1: 1) afforded 2-benzoylcyclohexanone (XIV, 240 mg, 65%), which was obtained as colorless crystals; mp 88—89 °C (*n*-hexane–benzene (2: 1)) (lit,[15) 88—89 °C). The authentic sample of XIV was prepared by the benzoylation of the V enamine.[15) The IR spectrum of XIV was superimpossible on that of the authentic specimen.

Irradiation of I in the Presence of 6,6-Dimethyl-1-morpholinocyclohexene (XVI).[6) A solution of I (1.0 g, 5.6 mmol) and XVI[6) (2.1 g, 11 mmol) in *n*-hexane or benzene (40 ml) was irradiated for 48 hr much as above. The subsequent concentration of the reaction mixture and column chromatography afforded 2,2-dimethyl-1-morpholino-7,8-diphenylbicyclo[4.2.0]oct-7-ene (XVII, 41 mg, 2.0%[9)), besides unchanged I (360 mg) and the photodimers[7) (300 mg, 15%[9)). The bicyclic product, XVII,[6) was obtained as colorless crystals; mp 95—96 °C (petroleum ether). IR (neat): 3050—3000, 1600, 1120, 760, and 700 cm^{-1}. NMR: δ 1.12 (s, 6H, CH_3), 1.20—1.80 (m, 6H, CH_2 of the cyclohexane ring), 2.20 (t, 1H, methine), 2.40 (t, 4H, CH_2-N), 3.50 (t, 4H, CH_2-O) and 6.87—7.00 ppm (m, 10H, aromatic). MS: 373 (M$^+$), 195 (M$^+$—178). (Found: C, 83.3; H, 8.5%. Calcd for $C_{26}H_{31}NO$: C, 83.6; H, 8.4%).

Quenching Studies in the Presence of Pyrene. A solution of I (300 mg, 1.7 mmol), II[6) (530 mg, 3.4 mmol), and pyrene (200 mg, 1.7 mmol) in *n*-hexane (20 ml) was placed in a quartz vessel and irradiated for 48 hr in a manner similar to that above. Tlc analyses showed that both the photochemical reaction of I with II[6) and the formation of the photodimers[7) of I were completely suppressed. Column chromatography (silica gel) gave totally recovered I (290 mg). The reaction of I with IV[6) or V[6) was similarly quenched by pyrene.

Sensitization by Triphenylene. *(a)*: A solution of I (500 mg, 2.8 mmol), II[6) (870 mg, 5.6 mmol), and triphenylene (640 mg, 2.8 mmol) in benzene (20 ml) was irradiated externally for 48 hr with light filtered through aqueous 10% $CuSO_4$ (200 W high-pressure mercury arc). The subsequent concentration of the reaction mixture *in vacuo* and column chromatography (silica gel-column) afforded the photodimers[7) of I (140 mg, 14%[9)) and III (130 mg, 19%[9)) respectively.

(b): The photoreaction of I (500 mg, 2.8 mmol), IV[6) (860 mg, 5.6 mmol), and triphenylene (640 mg, 2.8 mmol) in benzene (20 ml) afforded the photodimers[7) of I (78 mg, 7.8%[9)) and X (73 mg, 10%[9)) under the same conditions as those described in (*a*).

(c): The photoreaction of I (500 mg, 2.8 mmol), V[6) (946 mg, 5.6 mmol), and triphenylene (640 mg, 2.8 mmol) in benzene (20 ml) afforded the photodimers[7) of I (130 mg, 13%[9)), XIII (130 mg, 17%[9)), and XV[6) (38 mg, 4.1%[9)) under the same conditions as in (*a*). In the absence of triphenylene, the reaction did not occur upon photolysis under the same conditions.

Photoreaction of I with Enamines[6) *in Other Solvents.* A solution of I (2.8 mmol) and an enamine[6) (5.6 mmol) in a solvent (20 ml) was irradiated in a quartz vessel for 48 hr (200 W high-pressure mercury arc). The results are summarized in Table 1.

Photoreaction of I with Piperidinoenamines.[16) A solution of I (2.8 mmol) and an enamine[16) (5.6 mmol) in *n*-hexane (20 ml) was irradiated for 48 hr much as above. The results are summarized in Table 2.

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29) The stock oxidant solution consisted of sodium metaperiodate (20 g, 97 mmol) and potassium permanganate (390 mg, 2.5 mmol) in water (1 l).