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Photochemical Behavior of 1,2-Diphenylcyclobutene in Protic Solvents. Addition of Secondary Amines

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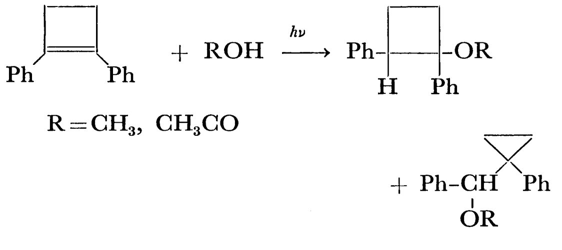
Irradiation of 1,2-diphenylcyclobutene (**1**) and diethylamine in hexane with light of longer wavelengths than 300 nm affords *N,N*-diethyl-1,2-diphenylcyclobutanamine (**2a**), 1,2-diphenylcyclobutane (**3**), and 1,1′,2,2′-tetraphenylbicyclobutyl (**4**). Upon similar irradiation, **1** and morpholine afford *N*-(1,2-diphenylcyclobutyl)morpholine **3** and **4**. A mechanism involving a charge-transfer complex is proposed on the basis of the observations that the amines quenched the olefin fluorescence at a rate close to the diffusion limit in hexane, and that when diethylamine-*N-d* was used as an additive the deuterium was retained in the methine groups of compounds **2a**, **3**, and **4**.

Amines interact with excited states, singlets and triplets of many molecules, including aromatic hydrocarbons and ketones. This interaction is believed to be of the charge-transfer type, which always results in deactivation of the excited state, and often in photoreactions.[1] In the photoreaction of aromatic hydrocarbons with tertiary amines an α-hydrogen atom of the amines is transferred to hydrocarbon anion radicals, resulting in reduction and addition products.[1] With primary and secondary amines an amino hydrogen atom can be transferred more easily than the α-hydrogen atom, generating a radical pair containing an aminyl radical. Only a few reports have appeared on the amino hydrogen transfer.[1–5] For example, 2-propanamine has been shown to react with 1-phenylcyclohexene, affording a mixture of the C-adduct and the N-adduct in the proportion of 58 : 37.[2] Piperidine and cyclohexanamine react with benzene to afford 1,4-addition products, 2,5-cyclohexadienamine derivatives.[3] Recently, a report was given on the photoinduced exchange of the nuclear hydrogen of benzonitrile with an amino hydrogen of diethylamine and with water in the presence of triethylamine.[4]

In an investigation of the photochemical behavior of 1,2-diphenylcyclobutene (**1**) in protic solvents,[6] it was shown that this cyclobutene is photoprotonated in methanol and acetic acid to give 1,2-diphenyl-1-methoxycyclobutane and 1-(α-methoxybenzyl)-1-phenylcyclopropane, and the corresponding acetates, respectively, and that the polar addition proceeds from the excited singlet state of the cyclobutene on the basis of quenching experiments of the olefin fluorescence.



R = CH_3, CH_3CO

We wish to report on an extended study of the photochemical behavior of the four-membered cyclic olefin with amines. The excited singlet state of the cyclobutene was quenched efficiently by secondary and tertiary amines, among which diethylamine and morpholine gave addition products, the corresponding cyclobutanamine derivatives.

Results and Discussion

Fluorescence quenching experiments of 1,2-diphenylcyclobutene (**1**) by amines were carried out under aerated conditions in hexane. No change was found in the fluorescence maximum and in the shape of fluorescence spectrum of **1** upon the addition of amines in various concentrations. Plots of the reciprocals of the relative fluorescence intensities against the concentrations of the amines are linear, fitting the Stern-Volmer equation,

$$I_0/I = 1 + k_q\tau_0[Q],$$

where I_0 and I denote the intensities of the fluorescence of **1** in the absence and in the presence of the quencher in the concentration [Q], respectively, k_q is the rate constant of the bimolecular quenching process, and τ_0 denotes the average lifetime of the excited singlet state of **1** in the absence of the quencher. The slopes of the Stern-Volmer plots ($k_q\tau_0$) are shown in Table 1 together with ionization potentials of the amines. Since the lifetime of the excited singlet state of **1** (τ_0)

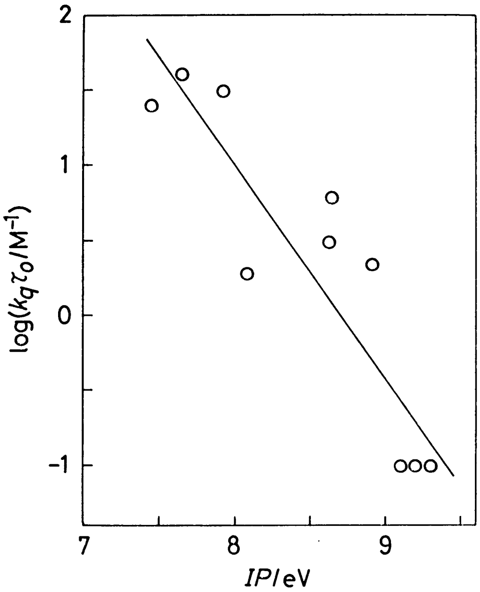
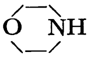
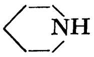


Fig. 1. Correlation of quenching constants of 1,2-diphenylcyclobutene fluorescence by amines with their ionization potentials.

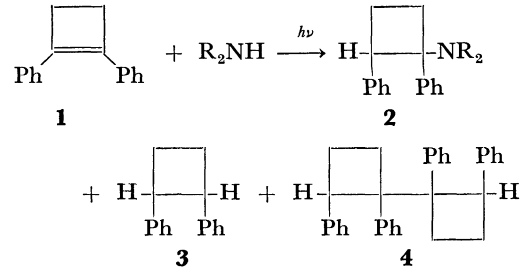
Table 1. Quenching of the fluorescence from 1,2-diphenylcyclobutene by amines in hexane[a)]

Amine	Ionization potential (eV)[b)]	$k_q\tau_0$ (M^{-1})
n-BuNH$_2$	9.20,[c)] 9.40[d)]	0.1
s-BuNH$_2$	9.20[c)]	0.1
t-BuNH$_2$	9.20[c)]	0.1
PhCH$_2$NH$_2$	9.10[e)]	0.1
	8.91[f)]	2.2
	8.64,[g)] 8.66[f,h)]	6.2
Et$_2$NH	8.63[g)]	3.1
Et$_3$N	8.08[i)]	1.9
Pr$_3$N	7.92[i)]	32
PhNHMe	7.65[j)]	41
PhNMe$_2$	7.45[j)]	26

a) Conducted under aerated conditions. b) Vertical ionization potentials obtained from photoelectron spectroscopy. c) H. Ogata, H. Onizuka, Y. Nihei, and H. Kamada, *Bull. Chem. Soc. Jpn.*, **46**, 3036 (1973), and Y. Nihei, private communication. d) S. Katsumata, T. Iwai, and K. Kimura, *ibid.*, **46**, 3391 (1973). e) T. P. Debies and J. W. Rabalais, *Inorg. Chem.*, **13**, 308 (1974). f) F. P. Colonna, G. Distefano, S. Pignataro, G. Pitacco, and E. Valentin, *J. Chem. Soc., Fraday Trans. 2*, **71**, 1572 (1975). g) K. Yoshikawa, M. Hashimoto, and I. Morishima, *J. Am. Chem. Soc.*, **96**, 288 (1974). h) D. H. Aue, H. M. Webb, and M. T. Bowers, *ibid.*, **97**, 4137 (1975). i) D. H. Aue, H. M. Webb, and M. T. Bowers, *ibid.*, **97**, 4136 (1975). j) J. P. Maier and D. W. Turner, *J. Chem. Soc., Faraday Trans. 2*, **69**, 521 (1973).

is reported to be shorter than 5 ns,[7)] the quenching rate constants (k_q) of the secondary and tertiary amines can be estimated to be 10^8—10^9 M^{-1} s^{-1}, close to the diffusion limit, whereas the primary amines interact less efficiently with the cyclobutene. Plots of logarithms of the $k_q\tau_0$ values against the ionization potentials of the amines give a linear relationship (Fig. 1). These results suggest that the singlet excited **1** interacts with the ground states of amines, possibly forming exciplex intermediates.[8)]

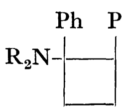
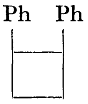
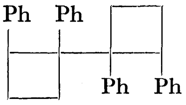
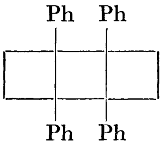
A solution of 1,2-diphenylcyclobutene (**1**, 0.01 M) in a mixture of diethylamine and hexane (1 : 4 by volume) was irradiated with light of longer wavelengths than 300 nm using a 500-W xenon lamp through a filter. The reaction mixture was separated by column chromatography on silica gel into three principal components in addition to the recovered starting material. The products isolated were *N,N*-diethyl-1,2-diphenylcyclobutanamine (**2a**), 1,2-diphenylcyclobutane (**3**), and 1,1′,2,2′-tetraphenylbicyclobutyl (**4**). These were identified mainly on the basis of their elemental analyses and spectral data. The NMR spectrum of the N-adduct, **2a**, of the amine and **1** displayed a six-proton triplet at δ 1.03 (J=7 Hz) and a four-proton quartet at δ 2.55 (J=7 Hz) attributable to the ethyl groups, and a one-proton multiplet at δ 3.7—4.2 attributable to the methine proton. Gas chromatographic analysis showed that **2a** consists of only one isomer. From the NMR spectrum the reduction product, **3**, was found to be a *ca.* 2 : 1 mixture of *cis*- and *trans*-diphenylcyclobutane. The reduction dimer, **4**, was a mixture of more than two isomers, the ratio and configuration of which have not been determined.



a : R=CH_3CH_2-
b : R_2=-$CH_2CH_2OCH_2CH_2$-

Similar irradiation of a solution of **1** (0.02 M) in a mixture of morpholine and hexane or benzene (1 : 4 by volume) afforded *N*-(1,2-diphenylcyclobutyl)morpholine (**2b**), **3**, and **4**. Small amounts of diphenylacetylene and 1,2,5,6-tetraphenyltricyclo[4.2.0.0^{2,5}]octane, the cleavage and dimerization products, respectively, were also obtained on irradiation in hexane.[7,9)] The adduct, **2b**, displayed two four-proton triplets (δ 2.37 and 3.59, J=4.5 Hz) attributable to the ethylene groups in the morpholine moiety in the NMR spectrum. The gas chromatographic analysis showed that **2b** also consists of one isomer. The addition products, **2a** and **2b**, as well as aforementioned 1,2-diphenyl-1-methoxycyclobutane and 1,2-diphenylcyclobutyl acetate exhibited a multiplet or a broad

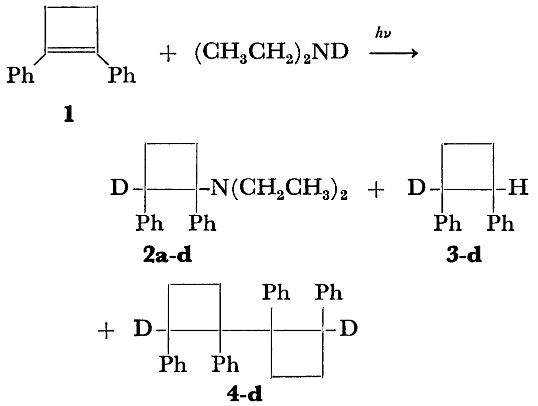
Table 2. Products from the irradiation of 1,2-diphenylcyclobutene and amines[a)]

Amine (R$_2$NH)	Et$_2$NH	Et$_2$ND	O NH (morpholine ring)	
Solvent	Hexane	Hexane	Benzene	Hexane
Product (%)[b)]				
	26	17[c)]	39	41
	25	12[d)]	trace	6
	17	5[e)]	40	8
PhC≡CPh				5
				6

a) In a mixture of an amine and a solvent (1 : 4 by volume). b) Yield based on the diphenylcyclobutene reacted. c) *N,N*-Diethyl-1,2-diphenylcyclobutanamine-2-*d*. d) 1,2-Diphenylcyclobutane-1-*d*. e) 1,1′,2,2′-Tetraphenylbicyclobutyl-2,2′-d_2.

triplet due to the methine proton at the same region (δ 3.7—4.2) as did *cis*-1,2-diphenylcyclobutane, while *trans*-1,2-diphenylcyclobutane displayed a multiplet at a somewhat higher field (δ 3.2—3.6).[6,10] Taking into account the small effect of the β-substituents on the chemical shift of a methine proton,[11] **2a** and **2b** can be safely assigned to *cis*-configuration. The results are summarized in Table 2. Although the UV spectra of the amines extend to longer wavelengths than 300 nm, their absorbances are very small in this region, more than 99.9% of the incident light being absorbed by **1**.

In order to clarify the origin of hydrogen atoms incorporated in the products, labeling experiments were undertaken using diethylamine-*N-d* as the additive. A solution of 1,2-diphenylcyclobutene (**1**) in a mixture of diethylamine-*N-d* and hexane (1 : 4 by volume) was irradiated similarly and the products were isolated in a way similar to that described above (Table 2). The NMR spectra of the products showed that a deuterium atom is incorporated in each cyclobutane ring of the product; 1,2-diphenylcyclobutane (**3-d**) undergoes deuteration at C-1, 1,1′,2,2′-tetraphenylbicyclobutyl (**4-d**) at C-2 and C-2′, and *N*,*N*-diethyl-1,2-diphenylcyclobutanamine (**2a-d**) at C-2. From these results it might be concluded that the photoreaction proceeds through an initial amino hydrogen transfer with the formation of diphenylcyclobutyl radicals (**7**), which in turn undergo four competing reactions: a) hydrogen atom abstraction from the solvent to afford **3**, b) dimerization affording **4**, c) recombination with the concurrently generated aminyl radicals to afford **2**, and d) disproportionation with the aminyl radicals which regenerates starting materials. The fact that only *cis*-isomer of **2** was produced supports the view that **2** arises from the combination of the diphenylcyclobutyl radical and the aminyl radical within the solvent cage in contrast to the out-of-cage formation of **3** and **4**.



The quantum yields of the reactions of **1** were measured in hexane under aerated conditions in the presence of various amounts of the amines by monitoring the decrease of the starting olefin on irradiation with 330±7-nm light. Although a linear relationship is found between the reciprocal of the quantum yield (Φ) for the decrease of the olefin and the reciprocal of the concentration of the amine, the intercept is not unity but 6.2 and 11 for diethylamine and morpholine, respectively. Since only bimolecular process need be considered upon extraporation to infinitely concentrated amine solution, these results indicate that there should be a bimolecular energy wastage step in the reaction. The following simplest mechanistic scheme accounts for all the above results.

$$\mathbf{1} + h\nu \longrightarrow \mathbf{1}^*$$

$$\mathbf{1}^* \xrightarrow{k_f} \mathbf{1} + h\nu'$$

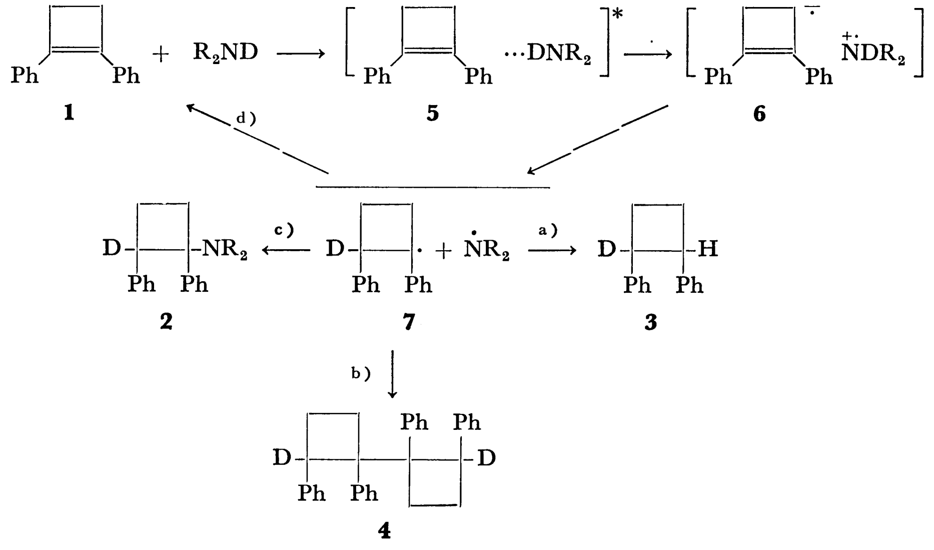
$$\mathbf{1}^* + O_2 \xrightarrow{k_o} \mathbf{1} + O_2$$

$$\mathbf{1}^* + HNR_2 \xrightarrow{k_q} [\mathbf{1}\cdots HNR_2]^*$$

$$[\mathbf{1}\cdots HNR_2]^* \xrightarrow{k_d} \mathbf{1} + HNR_2$$

$$[\mathbf{1}\cdots HNR_2]^* \xrightarrow{k_r} \mathbf{7} + \cdot NR_2 \longrightarrow \text{products},$$

where **1*** denotes the excited singlet state of **1**, and $[\mathbf{1}\cdots HNR_2]^*$ the exciplex between **1** and the amine. At infinite dilution under degassed conditions the quantum yield for the fluorescence of **1** is unity[7] and therefore intersystem crossing to the triplet state can be neglected. Furthermore, the unimolecular reactions, ring fission giving diphenylacetylene and ethylene, and dimerization, are minor perturbations under the conditions



employed, and can be neglected. Thus, by adopting the usual steady-state assumption, the quantum yield for the decrease of **1** is written as follows:

$$1/\Phi = (1+k_d/k_r)(1+1/k_q\tau_0[\mathrm{HNR_2}]).$$

The k_d/k_r values, *i.e.*, the ratio of rates for the decay process and the amino hydrogen transfer in the charge-transfer complex, can be estimated to be 5.2 for diethylamine and 10 for morpholine, and the $k_q\tau_0$ values, the quenching constants, are evaluated to be 3.0 $\mathrm{M^{-1}}$ for diethylamine and 2.2 $\mathrm{M^{-1}}$ for morpholine. These values are in good agreement with those obtained in the fluorescence quenching experiments: 3.1 $\mathrm{M^{-1}}$ for diethylamine and 2.2 $\mathrm{M^{-1}}$ for morpholine (Table 1). These results substantiate the above mechanism.

The present results together with those reported previously[6,10] show that 1,2-diphenylcyclobutene (**1**) reacts, in its excited singlet state, not only with alcohols and acetic acid by ionic process but with secondary amines by radical process through the charge-transfer complex, to give the addition products, respectively.

Experimental

The IR and UV spectra were recorded on a Hitachi EPI-G3 grating infrared spectrophotometer and a Hitachi EPS-3 recording spectrophotometer, respectively. The NMR spectra were recorded on a JEOL C-60HL NMR spectrometer. GLPC analysis was performed on a Hitachi 163 gas chromatograph equipped with a flame ionization detector. Fluorescence intensities were determined with a Hitachi MPF-2A fluorescence spectrophotometer.

Materials. 1,2-Diphenylcyclobutene was prepared according to the method of Dodson and Zielske.[12] Amines were purified by distillation or recrystallization. Special grade hexane and benzene were distilled prior to use.

Photoreaction of 1,2-Diphenylcyclobutene with Diethylamine. A solution of 1,2-diphenylcyclobutene (400 mg) in a mixture of diethylamine (35 ml) and hexane (140 ml) was irradiated for 50 h using a 500-W xenon lamp through a Corning 0—54 filter. This procedure was repeated five times. The reaction mixtures were combined, concentrated, and subjected to chromatography on silica gel affording four components. The first white solid (trace amounts) was found to be the starting diphenylcyclobutene by GLPC analysis. The second white crystalline solid (500 mg) was deduced to be 1,2-diphenylcyclobutane by comparing its NMR spectrum with that of an authentic specimen of *cis*-1,2-diphenylcyclobutane, prepared by catalytic reduction of 1,2-diphenylcyclobutene,[12] and the reported NMR data of *cis*- and *trans*-1,2-diphenylcyclobutane.[12] The diphenylcyclobutane obtained was found to be a *ca.* 2 : 1 mixture of *cis*- and *trans*-isomers from the NMR and GLPC data. Found: C, 92.28; H, 7.55%. Calcd for $\mathrm{C_{16}H_{16}}$: C, 92.26; H, 7.74%.

The third white crystalline solid (340 mg) was 1,1′,2,2′-tetraphenylbicyclobutyl, the structure of which was established by the spectral data and elemental analysis. The NMR spectrum of the solid showed that it consists of more than two isomers. Recrystallization from ethanol gave a single isomer; mp 143—144 °C. NMR($\mathrm{CDCl_3}$) δ 1.7—3.0 (m, 8H, $\mathrm{CH_2CH_2}$), 4.54 (t, 2H, methine H), 6.0—7.2 (m, 20H, aromatic H). Mass spectrum (*m/e*) 414 ($\mathrm{M^+}$). Found: C, 92.62; H, 7.37%. Calcd for $\mathrm{C_{32}H_{30}}$: C, 92.71; H, 7.29%.

The fourth colorless liquid (700 mg) was *N*,*N*-diethyl-1,2-diphenylcyclobutanamine, the structure of which was established by the spectral data and elemental analysis. The GLPC analysis showed that it consists of one isomer. NMR($\mathrm{CDCl_3}$) δ 1.03 (t, J=7 Hz, 6H, $\mathrm{CH_3}$), 1.7—2.5 (m, 4H, $\mathrm{CH_2CH_2}$), 2.55 (q, J=7 Hz, 4H, $\mathrm{CH_2}$), 3.7—4.2 (m, 1H, methine H), 6.6—7.3 (m, 10H, aromatic H). Mass spectrum (*m/e*) 279 ($\mathrm{M^+}$). Found: C, 85.97; H, 9.24; N, 5.02%. Calcd for $\mathrm{C_{20}H_{25}N}$: C, 85.97; H, 9.02; N, 5.01%.

Photoreaction of 1,2-Diphenylcyclobutene with Morpholine. A solution of 1,2-diphenylcyclobutene (1 g) in a mixture of morpholine (40 ml) and benzene (160 ml) was irradiated similarly for 110 h. The reaction mixture was separated similarly, affording the starting olefin (290 mg), 1,2-diphenylcyclobutane (trace amounts), 1,1′,2,2′-tetraphenylbicyclobutyl (280 mg), and *N*-(1,2-diphenylcyclobutyl)morpholine (395 mg). The structure of the last product was established by the spectral data and elemental analysis. The GLPC analysis showed that the adduct consists of one isomer. NMR($\mathrm{CDCl_3}$) δ 1.7—2.7 (m, 4H, $\mathrm{CH_2CH_2}$ of cyclobutane), 2.37 (t, J=4.5 Hz, 4H, $\mathrm{NCH_2}$), 3.59 (t, J=4.5 Hz, 4H, $\mathrm{OCH_2}$), 3.90 (t, J=7.5 Hz, 1H, methine H), 6.5—7.1 (m, 10H, aromatic H). Found: C, 82.01; H, 7.85; N, 4.74%. Calcd for $\mathrm{C_{20}H_{23}NO}$: C, 81.87; H, 7.90; N, 4.77%.

A solution of 1,2-diphenylcyclobutene (450 mg) in a mixture of morpholine (40 ml) and hexane (160 ml) was irradiated similarly for 110 h. The products separated similarly on silica gel were *N*-(1,2-diphenylcyclobutyl)morpholine (260 mg), diphenylacetylene (20 mg), 1,2-diphenylcyclobutane (25 mg), 1,1′,2,2′-tetraphenylbicyclobutyl (35 mg), and 1,2,5,6-tetraphenyltricyclo[4.2.0.$0^{2,5}$]octane (25 mg).[7,9]

*Photoreaction of 1,2-Diphenylcyclobutene with Diethylamine-*N*-d.* A solution of 1,2-diphenylcyclobutene (1.5 g) in a mixture of diethylamine-*N-d* (40 ml) and hexane (160 ml) was irradiated similarly for 150 h. The chromatographic separation of the reaction mixture gave the starting olefin (190 mg), 1,2-diphenylcyclobutane-1-*d* (160 mg), 1,1′,2,2′-tetraphenylbicyclobutyl-2,2′-d_2 (70 mg), 1,2,5,6-tetraphenyltricyclo[4.2.0.$0^{2,5}$]octane (160 mg), and *N*,*N*-diethyl-1,2-diphenylcyclobutanamine-2-*d* (300 mg). The position of deuteration in each product was determined by comparing its NMR spectrum with that for the corresponding non-deuterated product.

Quantum-Yield Measurements. The exciting light for the quantum-yield measurement was furnished by a JASCO CRM-FA spectroirradiator equipped with a 2-kW xenon lamp as the light source and a grating monochromator. The light intensity was measured by potassium ferrioxalate actinometry. Hexane solutions of 1,2-diphenylcyclobutene (10^{-3} M) and amine (0—1 M) were irradiated with 330±7-nm light for 3 min. The reaction mixture was diluted 20 times with the same solvent and its UV spectrum was measured.

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