

A Novel Type of Cyanomethylation Reaction of Diarylethenes with Acetonitrile Photosensitized by Benzophenone in the Presence of *tert*-Butylamine

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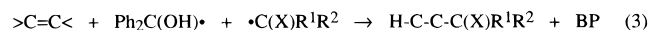
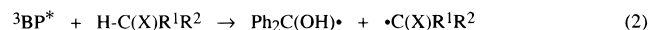
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It is well-known that benzophenone (BP) in the triplet state is potentially capable of abstracting a hydrogen atom from the H–C(X)R¹R² linkage of various reactants. Triplet-state BP (³BP*) can undergo the H-atom abstraction at reasonable rate constants for reactants possessing electron-donating groups, e.g., primary and secondary alcohols, aliphatic and aromatic amines, ethers, and hydrocarbons (X = OH, RO, NH₂, RNH, R₂N, alkyl, or aryl; R¹, R² = H, alkyl, and aryl).¹ The H-atom transfer from these reactants to ³BP* generates the free-radicals •C(X)R¹R², being thus applied to BP-photosensitized carbon–carbon bond formation by the addition of •C(X)R¹R² to olefins (eqs 1–3).² On the other hand, the



H-atom abstraction from H–C(X)R¹R² by ³BP* is very slow in the cases where X is an electron-withdrawing group, typically CN. In those cases, therefore, the BP-photosensitized addition of the H–C(X)R¹R² linkage to olefins does not occur at all or is very inefficient, if any. In this paper, we wish to report the BP-photosensitized cyanomethylation of 1,1-diarylethenes (**1**) with acetonitrile that can efficiently proceed only in the presence of *tert*-butylamine (Scheme 1).

Results and Discussion

Irradiation of an MeCN solution of **1a–f**, *tert*-butylamine (*t*-BuNH₂), and a diaryl ketone (Ar₂CO) gave the corresponding cyanomethylated products (**2a–f**) (Table 1). As a typical run, the BP-photosensitized reaction of 1,1-diphenylethene (**1a**) with MeCN occurred in the presence of *t*-BuNH₂ to give 4,4-diphenylbutanenitrile (**2a**) in 77% yield but did not occur at all in its absence (entries 1 and 3). The cyanomethylated products **2c–e** of the cyclic olefins were obtained as *cis/trans* mixtures. When *i*-PrNH₂, Et₂NH, or Et₃N was used in place of *t*-BuNH₂, the BP-photosensitized reaction of **1a** resulted

Scheme 1

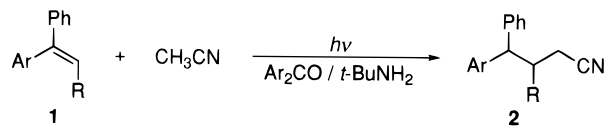


Table 1. The Cyanomethylations of Diarylethenes **1a–f** with MeCN by Ar₂CO-Photosensitization in the Presence of Amine^a

entry	substrate	Ar ₂ CO	amine	product	yield ^b (%)
1	1a	Ph ₂ CO	<i>t</i> -BuNH ₂	2a	77
2 ^c	1a	Ph ₂ CO	<i>t</i> -BuNH ₂	2a	70
3	1a	Ph ₂ CO	none ^d	2a	0
4 ^e	1a	Ph ₂ CO	<i>i</i> -PrNH ₂	2a	10
5 ^f	1a	Ph ₂ CO	Et ₂ NH	2a	2
6 ^g	1a	Ph ₂ CO	Et ₃ N	2a	0
7	1a	DCBP ^h	<i>t</i> -BuNH ₂	2a	78
8	1a	TFBP ⁱ	<i>t</i> -BuNH ₂	2a	80
9	1b	Ph ₂ CO	<i>t</i> -BuNH ₂	2b	40
10	1c	Ph ₂ CO	<i>t</i> -BuNH ₂	2c	71
11	1c	DCBP ^h	<i>t</i> -BuNH ₂	2c	90
12	1c	TFBP ⁱ	<i>t</i> -BuNH ₂	2c	56
13	1c	DMBP ^j	<i>t</i> -BuNH ₂	2c	34
14	1c	DBS ^k	<i>t</i> -BuNH ₂	2c	28
15	1c	ANAP ^l	<i>t</i> -BuNH ₂	2c	0
16	1d	Ph ₂ CO	<i>t</i> -BuNH ₂	2d	58
17	1e	Ph ₂ CO	<i>t</i> -BuNH ₂	2e	34
18	1f	Ph ₂ CO	<i>t</i> -BuNH ₂	2f	46 ^m
19	1f	DCBP ^h	<i>t</i> -BuNH ₂	2f	50 ^m

^a Irradiation of an acetonitrile solution (60 mL) of **1a–f** (2 mmol), Ar₂CO (0.5–1 mmol), and amine (30 mmol) for 12–24 h. ^b Isolated yield based on **1** used. ^c In the presence of H₂O. ^d In the absence of amine. ^{e–g} The adducts **3a**, **3b**, and **3c** were obtained in 42, 36, and 60% yields, respectively. ^h 4,4'-Dichlorobenzophenone. ⁱ 4-(Trifluoromethyl)benzophenone. ^j 4,4'-Dimethylbenzophenone. ^k Dibenzosuberone. ^l 2-Acetonaphthone. ^m At 80% conversion.

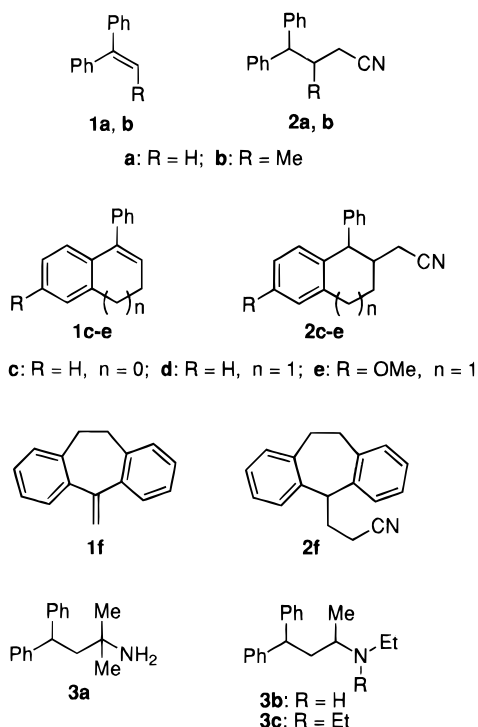
in no or very inefficient cyanomethylation but the dominant adduct formation of **1a** with the amines (entries 4–6). Among Ar₂CO investigated, 4,4'-dichlorobenzophenone (DCBP) and 4-(trifluoromethyl)benzophenone (TFBP) were found to be as effective as BP, while the cyanomethylation of **1c** was less efficient with 4,4'-dimethylbenzophenone (DMBP), dibenzosuberone (DBS), and 2-acetonaphthone (ANAP) (entries 7, 8, and 11–15). In all the photoreactions, the diaryl ketones were consumed by the reduction to form the diarylmethanols and/or pinacols. In entry 1, for instance, 84% BP was consumed along with the formation of benzpinacol in 65% yield based on the BP used, whereas the reduction of DCBP and TFBP to the diarylmethanols occurred in 66 and 70% yields, respectively (entries 7 and 8).

Although various 1,1-diarylethenes (**1a–f**) were successfully cyanomethylated upon photosensitization by BP, all attempts for the photocyanomethylation of stilbene, styrene, several derivatives of them, and various cycloalkenes under similar conditions were unsuccessful. Presumably, the 1,1-diarylethene structure appears to be a requisite for the photosensitized alkylation with MeCN. However, it can be easily expected that the BP photosensitization in the presence of *t*-BuNH₂ may be generally applicable to the alkylations of 1,1-diarylethenes with H–C(X)R¹R². This expectation was demonstrated by the BP-photosensitized alkylation of **1a** using propionitrile (X = CN, R¹ = H, R² = Me), dichloromethane (X = R¹ = Cl, R² = H), chloroform (X = R¹ = R² = Cl), and acetone (X = MeCO, R¹ = R² = H) (Scheme 2). The corresponding alkylation products (**4a–d**) were formed

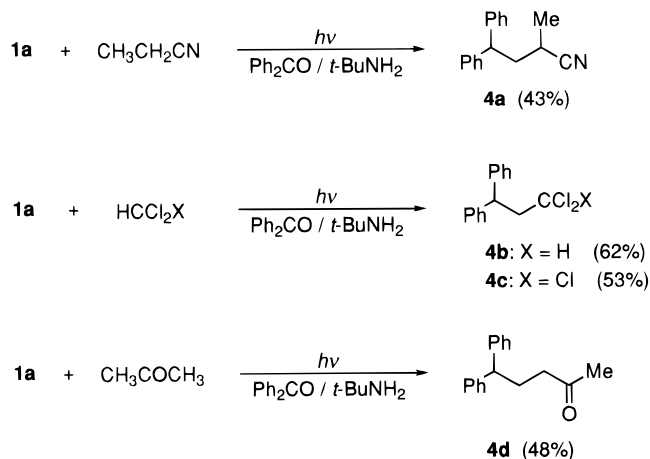
(1) Turro, N. J. *Modern Molecular Photochemistry*; The Benjamin/Cummings Publishing Co., Inc: California, 1978; p 362.

(2) (a) Schenck, G. O.; Steinmetz, R. *Naturwissenschaften* **1960**, *22*, 514. (b) Elad, D. *Fortschr. Chem. Forsch.* **1967**, *7*, 428. (c) *The Chemistry of the Ether Linkage*, Patai, S., Ed.; J. Wiley: New York, 1967; p 353.

Chart 1



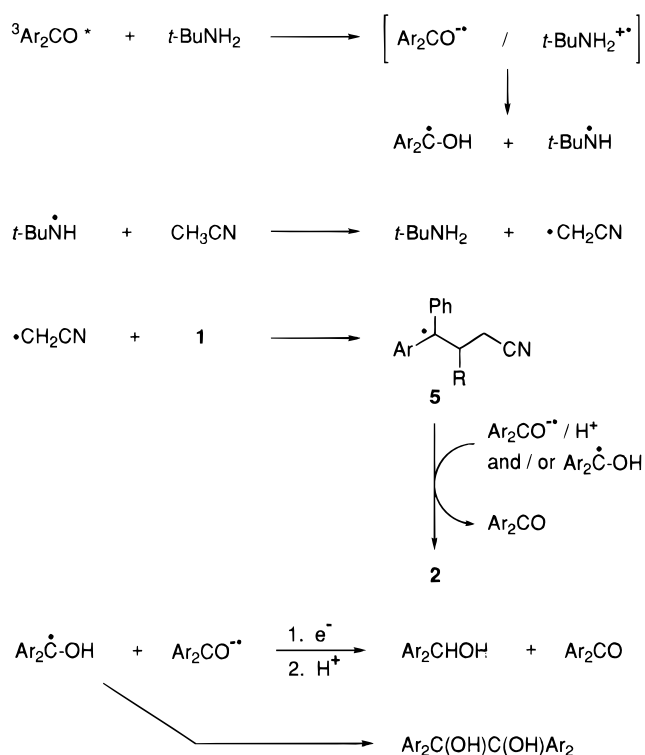
Scheme 2



in moderate yields only in the presence of *t*-BuNH₂ but were not formed at all in its absence.

The present Ar₂CO-photosensitized alkylation reactions of 1,1-diarylethenes cannot be interpreted in terms of eqs 1–3, since no alkylation of the olefins with the reactants (H–C(X)R¹R²) occurred at all in the absence of *t*-BuNH₂. Direct H-atom abstraction from H–C(X)R¹R² by ³BP* should be negligible or minor. Therefore, a primary interaction between *t*-BuNH₂ and ³BP* should be taken into consideration to explain the essential role of *t*-BuNH₂, though this amine has no C–H linkage susceptible to H-atom abstraction by ³BP* like the other ineffective amines (*i*-PrNH₂, Et₂NH, and Et₃N). With regard to the essential role of *t*-BuNH₂, it is of mechanistic importance to note the work by Cohen and his co-workers³ that the hydrogen-atom transfer from the amino group of *t*-BuNH₂ to ³BP* occurs *via* charge-transfer interactions to generate *t*-BuN(H)• and Ph₂C(OH)•. It is

Scheme 3



therefore reasonable to assume that *t*-BuN(H)• is responsible for H-atom abstraction from H–C(X)R¹R² to generate •C(X)R¹R². The photosensitized alkylation might thus proceed through the addition of •C(X)R¹R² to the double bond of diarylethenes followed by the reduction of the adduct radicals with Ar₂CO^{•-} and/or Ar₂C(OH)•, as shown in Scheme 3 for the photosensitized cyanomethylation of the diarylethenes. It was reported that the cyanomethyl radical (•CH₂CN) undergoes the free-radical addition to norbornene.^{4,5} The adduct radicals 5 formed by the addition of •CH₂CN to 1a–f should be reduced not by H-atom abstraction from MeCN or any other hydrogen-atom donors but by Ar₂CO^{•-} and/or Ar₂C(OH)•, since the DCBP-photosensitized cyanomethylation of 1f in the presence of D₂O resulted in 84% deuterium incorporation at the 5 position of 2f. Moreover, it is very unlikely that the adducts 2 would be formed by the addition of the cyanomethylidene anion (–CH₂CN) to the olefins following proton abstraction from MeCN by Ar₂CO^{•-} and/or *t*-BuNH₂, since the presence of water exerted no effects on the photosensitized cyanomethylation at all. This mechanism can also explain the reduction of Ar₂CO to (Ar₂COH)₂ and/or Ar₂CHOH that occurred concomitantly with the photosensitized alkylation.

The “alkylation reactants” (MeCN, EtCN, CH₂Cl₂, CHCl₃, and acetone) used in the present investigation have been regarded as “inert” solvents in a variety of aromatic ketone-photosensitized reactions as well as in many other photoreactions. Only a few examples have been reported on photoaddition of “inert” acetonitrile used as solvent, i.e., the addition of photogenerated radical cations to the CN bond of MeCN⁶ and the photomethy-

(3) (a) Inbar, S.; Linschitz, H.; Cohen, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 1048. (b) Cohen, S. G.; Parola, A.; Parsons, G. H., Jr. *Chem. Rev.* **1973**, *73*, 141.

(4) Bruno, J. W.; Marks, T. J.; Lewis, F. D. *J. Am. Chem. Soc.* **1982**, *104*, 5580.

(5) (a) Schroeter, S. H. *Liebigs Ann. Chem.* **1974**, 1890. (b) Weng, H.; Roth, H. D. *J. Org. Chem.* **1995**, *60*, 4136.

(6) (a) Evans, T. R.; Wake, R. W.; Jaenicke, O. *The Exciplex*; Gordon, M.; Ware, W. R. Ed.; Academic Press: New York, 1975; p 345. (b) Mattes, S.; Farid, S. *J. Chem. Soc., Chem. Commun.* **1980**, 126.

lation of 1,2,4,5-tetracyanobenzene with MeCN.⁷ However, these examples are "unexpected" side reactions accompanied by relevant major photoreactions. The present photoinduced alkylation reactions provide a new synthetic route using a combination of Ar₂CO and *t*-BuNH₂ for the effective generation of [•]C(X)R¹R² from the corresponding solvents.

Experimental Section

General. Melting points were measured using open capillary tubes and are uncorrected. Only noteworthy IR absorptions are listed. ¹H and ¹³C NMR spectra were recorded in CDCl₃ at 250 MHz and 75 MHz, respectively. Chemical shifts are reported in ppm relative to TMS (0 ppm, ¹H) or CDCl₃ (77.0 ppm, ¹³C) as internal standards. Mass spectra were operated at an ionization voltage of 70 eV. GLC analysis was performed using a 25 m fused-silica capillary column.

MeCN, EtCN, CH₂Cl₂, and CHCl₃ were distilled from CaH₂. The amines and ketones were used as received. Commercially available **1a** was distilled from sodium under reduced pressure before use, and **1b** was prepared according to literature method.⁸ The other diarylethenes (**1c–f**) were prepared by reactions of the corresponding ketones with PhMgBr or MeMgBr followed by the dehydration of the diarylcarbinols using Ac₂O.⁹

Photoreactions. A solution of **1a–f** (2 mmol), a diaryl ketone (0.5–1 mmol), and *t*-BuNH₂ (30 mmol) in MeCN, EtCN, CH₂Cl₂, CHCl₃, or acetone (60 mL) was poured into a Pyrex glass tube, purged with argon gas, sealed with a rubber septum, and irradiated with a high-pressure mercury lamp at the ambient temperature. After the irradiation, the products were isolated by removal of the solvent from the photolysates followed by chromatography on silica gel (BW-300, Wako Chemicals). The structure determination of the products was performed on the basis of their spectroscopic and physical properties and, in the case of **2a**, **2b**, and **3a**, by comparisons of the data with those published in literature.¹⁰ It was confirmed that similar results can be obtained by the irradiation at 366 nm using an aqueous filter solution of BiCl₃ (>350 nm), though a longer period of irradiation time was required.

2-(Cyanomethyl)-1-phenylindan (2c). The ratio of the trans to cis isomer was 34:66. IR (CHCl₃) 2240 (CN) cm⁻¹. Trans isomer; ¹H NMR δ 2.45 (d, 1H, *J* = 7.3 Hz), 2.49 (d, 1H, *J* = 4.6 Hz), 2.55–2.67 (m, 1H), 2.88 (dd, 1H, *J* = 15.1, 8.1 Hz), 3.24 (dd, 1H, *J* = 15.5, 7.4 Hz), 4.03 (d, 1H, *J* = 9.0 Hz), 6.84–7.36 (m, 9H); ¹³C NMR δ 20.37, 37.06, 46.70, 56.59, 118.28, 124.34, 124.86, 126.89, 127.18, 128.39, 128.77, 128.89, 141.52, 141.94, 145.07; exact mass calcd for C₁₇H₁₅N 233.1206, found 233.1212. Cis isomer; ¹H NMR δ 1.93 (d, 1H, *J* = 6.7 Hz), 1.93 (d, 1H, *J* = 8.3 Hz), 2.88 (dd, 1H, *J* = 15.1, 8.1 Hz), 2.94–3.09 (m, 1H), 3.18 (dd, 1H, *J* = 14.9, 7.2 Hz), 4.50 (d, 1H, *J* = 7.6 Hz), 6.84–7.36 (m, 9H); ¹³C NMR δ 19.37, 37.06, 41.48, 53.68, 119.15, 124.70, 125.37, 127.18, 127.18, 127.36, 128.64, 128.89, 139.25, 141.79, 144.48.

2-(Cyanomethyl)-1-phenyl-1,2,3,4-tetrahydronaphthalene (2d). The ratio of the trans to cis isomer was 33:67. IR (CHCl₃) 2190 (CN) cm⁻¹. Trans isomer; ¹H NMR δ 1.76–1.85 (m, 1H), 2.18–2.26 (m, 2H), 2.21 (dd, 1H, *J* = 19.4, 7.2 Hz), 2.37 (dd, 1H, *J* = 19.4, 7.5 Hz), 2.90–3.10 (m, 2H), 3.85 (d, 1H, *J* = 8.7 Hz), 6.70 (d, 1H, *J* = 7.7 Hz), 6.93 (d, 1H, *J* = 7.5 Hz), 7.01–7.34 (m, 7H); ¹³C NMR δ 22.37, 27.36, 28.61, 39.54, 51.02, 118.49, 126.09, 126.26, 127.01, 128.67, 128.87, 129.19, 130.27, 135.86, 138.15, 144.02; exact mass calcd for C₁₈H₁₇N 247.1362, found 247.1338. Cis isomer; ¹H NMR δ 1.76–1.85 (m, 2H), 1.98 (dd, 1H, *J* = 16.7, 7.8 Hz), 2.12 (dd, 1H, *J* = 16.7, 7.8 Hz), 2.39–2.54 (m, 1H), 2.90–3.10 (m, 2H), 4.30 (d, 1H, *J* = 5.2 Hz), 6.70 (d, 1H, *J* = 7.7 Hz), 6.93 (d, 1H, *J* = 7.5 Hz), 7.01–7.34 (m, 7H); ¹³C NMR δ 21.98, 23.35, 28.48, 36.19, 47.81, 119.15, 126.18,

126.56, 126.90, 128.22, 128.80, 130.18, 130.68, 135.63, 137.92, 141.17; exact mass calcd for C₁₈H₁₇N 247.1362, found 247.1353.

2-(Cyanomethyl)-6-methoxy-1-phenyl-1,2,3,4-tetrahydronaphthalene (2e). The ratio of the trans to cis isomer was 32:68. Trans isomer; mp 110.0–110.5 °C (from hexane/benzene); IR (CHCl₃) 2240 (CN) cm⁻¹; ¹H NMR δ 1.75–1.91 (m, 1H), 2.14–2.26 (m, 3H), 2.37 (dd, 1H, *J* = 19.0, 6.8 Hz), 2.87–3.11 (m, 2H), 3.74 (s, 3H), 3.79 (d, 1H, *J* = 10.6 Hz), 6.60–6.66 (m, 3H), 7.10–7.36 (m, 5H); ¹³C NMR δ 22.14, 27.19, 28.74, 39.56, 50.31, 55.06, 112.42, 112.87, 118.43, 126.84, 128.65, 128.98, 130.27, 131.19, 136.98, 144.17, 157.77; exact mass calcd for C₁₉H₁₉NO 277.1468, found 277.1474. Anal. Calcd for C₁₉H₁₉NO: C, 82.28; H, 6.90; N, 5.05. Found: C, 82.01; H, 7.12; N, 4.83. Cis isomer; IR (CHCl₃) 2240 (CN) cm⁻¹; ¹H NMR δ 1.73–1.86 (m, 2H), 1.95 (dd, 1H, *J* = 16.7, 7.8 Hz), 2.10 (dd, 1H, *J* = 16.8, 7.8 Hz), 2.39–2.50 (m, 1H), 2.84–3.09 (m, 2H), 3.76 (s, 3H), 4.23 (d, 1H, *J* = 5.2 Hz), 6.61–6.85 (m, 3H), 7.00–7.31 (m, 5H); ¹³C NMR δ 21.84, 23.18, 28.68, 36.28, 47.03, 55.05, 112.81, 112.81, 119.04, 126.72, 128.07, 129.98, 130.11, 131.48, 136.70, 141.35, 157.99; exact mass calcd for C₁₉H₁₉NO 277.1468, found 277.1477.

2-(2-Cyanoethyl)dibenzo[*a,d*]cycloheptane (2f): mp 107.5–108.0 °C (from hexane); IR (CHCl₃) 2240 (CN) cm⁻¹; ¹H NMR (at 40 °C) δ 2.10 (t, 2H, *J* = 9.1 Hz), 2.37 (q, 2H, *J* = 8.3 Hz), 2.89–3.02 (m, 2H), 3.20–3.33 (m, 2H), 4.06 (t, 1H, *J* = 8.0 Hz), 6.99–7.32 (m, 10H); ¹³C NMR (at 40 °C) δ 16.04, 33.35, 33.35, 52.42, 119.25, 126.41, 127.18, 130.01, 130.67, 139.55, 139.55; exact mass calcd for C₁₈H₁₇N 247.1362, found 247.1378. Anal. Calcd for C₁₈H₁₇N: C, 87.41; H, 6.93; N, 5.66. Found: C, 87.28; H, 6.96; N, 5.49.

3-(Ethylamino)-1,1-diphenylbutane (3b). **3b** was acetylated with Ac₂O. The acetamide was obtained as a mixture of two isomer. IR (CHCl₃) 1610 (C=O) cm⁻¹; ¹H NMR δ 1.04 (t, 3H, *J* = 7.1 Hz), 1.15–1.22 (m, 9H), 1.52 (s, 3H), 1.94 (s, 3H), 2.09–2.34 (m, 3H), 2.45 (dt, 1H, *J* = 14.2, 8.1 Hz), 2.85 (dq, 1H, *J* = 15.9, 7.4 Hz), 3.05 (dq, 1H, *J* = 14.7, 7.3 Hz), 3.17 (dq, 1H, *J* = 13.7, 6.8 Hz), 3.42 (dq, 1H, *J* = 13.8, 6.9 Hz), 3.57–3.71 (m, 1H), 3.85 (t, 1H, *J* = 8.1 Hz), 3.88 (t, 1H, *J* = 7.3 Hz), 4.26–4.41 (m, 1H), 7.11–7.35 (m, 20H); ¹³C NMR δ 14.81, 15.09, 19.09, 19.97, 21.53, 22.15, 35.53, 39.89, 40.33, 40.81, 48.03, 48.66, 49.64, 51.61, 126.14, 126.14, 126.47, 126.70, 127.37, 127.71, 127.77, 127.82, 128.41, 128.44, 128.67, 128.84, 143.18, 144.23, 144.43, 145.07, 170.34, 170.45; exact mass calcd for C₂₀H₂₅NO 295.1938, found 295.1941.

3-(Diethylamino)-1,1-diphenylbutane (3c): ¹H NMR δ 1.04 (d, 3H, *J* = 7.0 Hz), 1.05 (t, 6H, *J* = 6.8 Hz), 2.09 (ddd, 1H, *J* = 14.4, 8.4, 6.0 Hz), 2.31 (ddd, 1H, *J* = 14.1, 7.0, 7.0 Hz), 2.42 (dq, 2H, *J* = 13.3, 6.9 Hz), 2.64 (dq, 2H, *J* = 13.0, 7.3 Hz), 2.73–2.81 (m, 1H), 4.35 (dd, 1H, *J* = 8.7, 6.8 Hz), 7.16–7.64 (m, 10H); ¹³C NMR δ 13.68, 14.10, 14.10, 40.25, 43.05, 43.05, 47.72, 51.51, 125.80, 125.83, 127.73, 128.04, 128.17, 128.25, 144.97, 145.53; exact mass calcd for C₂₀H₂₇N 281.2145, found 281.2116. Anal. Calcd for C₂₀H₂₇N: C, 85.35; H, 9.67; N, 4.98. Found: C, 85.35; H, 9.79; N, 4.80.

3-Cyano-1,1-diphenylbutane (4a): mp 73.0–73.5 °C (from hexane/benzene); IR (CHCl₃) 2240 (CN) cm⁻¹; ¹H NMR δ 1.27 (d, 3H, *J* = 6.6 Hz), 2.15–2.42 (m, 3H), 4.15–4.21 (m, 1H), 7.13–7.33 (m, 10H); ¹³C NMR δ 18.10, 23.93, 39.89, 48.77, 122.58, 126.62, 126.87, 127.46, 127.82, 128.64, 128.85, 142.55, 143.40; exact mass calcd for C₁₇H₁₇N 235.1362, found 235.1359. Anal. Calcd for C₁₇H₁₇N: C, 86.77; H, 7.28; N, 5.95. Found: C, 86.91; H, 7.33; N, 5.90.

1,1-Dichloro-3,3-diphenylpropane (4b): mp 61.5–62.5 °C (from hexane); ¹H NMR δ 2.88 (t, 2H, *J* = 7.3 Hz), 4.25 (t, 1H, *J* = 7.8 Hz), 5.35 (t, 1H, *J* = 6.7 Hz), 7.12–7.34 (m, 10H); ¹³C NMR δ 48.05, 49.05, 71.99, 126.80, 127.64, 128.74, 142.14; exact mass calcd for C₁₅H₁₄Cl₂ 264.0474, found 264.0422. Anal. Calcd for C₁₅H₁₄Cl₂: C, 67.94; H, 5.32; Cl, 26.74. Found: C, 67.72; H, 5.17; Cl, 27.11.

1,1,1-Trichloro-3,3-diphenylpropane (4c). The photoreaction of **1a** with CHCl₃ gave **4c** in 53% yield, accompanying the formation of 1,1-dichloro-2,2-diphenylcyclopropane (9%, mp 111.5–112.0 °C, lit.¹¹ mp 113–114 °C). Mp 33.5–34.0 °C (from hexane); ¹H NMR δ 3.55 (d, 2H, *J* = 5.9 Hz), 4.51 (t, 1H, *J* = 5.9 Hz), 7.10–7.29 (m, 10H); ¹³C NMR δ 49.45, 59.95, 99.04, 126.62, 127.85, 128.68, 143.41; exact mass calcd for C₁₅H₁₃Cl₃ 298.0085,

(7) Tsujimoto, K.; Abe, K.; Ohashi, M. *J. Chem. Soc., Chem. Commun.* **1983**, 984.

(8) Nakabayashi, K.; Kojima, J.; Tanabe, K.; Yasuda, M.; Shima, K. *Bull. Chem. Soc. Jpn.* **1989**, 62, 96.

(9) Weiss, R. *Organic Syntheses*; Wiley: New York, 1959; Coll. Vol. III, p 729.

(10) Yamashita, T.; Shiomori, K.; Yasuda, M.; Shima, K. *Bull. Chem. Soc. Jpn.* **1991**, 64, 366.

(11) Hoeg, D. F.; Lusk, D. I.; Crumbliss, A. L. *J. Am. Chem. Soc.* **1965**, 87, 4147.

found 298.0064. Anal. Calcd for $C_{15}H_{13}Cl_3$: C, 60.13; H, 4.37; Cl, 35.50. Found: C, 60.21; H, 4.35; Cl, 35.74.

5,5-Diphenyl-2-pentanone (4d): mp 87.0–88.0 °C (from hexane/benzene); IR ($CHCl_3$) 1705 (C=O) cm^{-1} ; 1H NMR δ 2.01 (s, 3H), 2.25–2.38 (m, 4H), 3.87 (t, 1H, $J = 7.3$ Hz), 7.11–7.32 (m, 10H); ^{13}C NMR δ 29.19, 29.95, 41.92, 50.33, 126.29, 127.80, 128.50, 144.31, 208.31; exact mass calcd for $C_{17}H_{18}O$ 238.1358, found 238.1382. Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.57; H, 7.51.

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Supporting Information Available: The 1H NMR spectra of new compounds (**2c–e** and **3b**) lacking combustion data (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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