Photocatalyzed Multiple Additions of Amines to α,β-Unsaturated Esters and Nitriles[1]

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Photoelectron-transfer-catalyzed intermolecular carbon–carbon bond formation of primary, secondary, and tertiary amines with α,β-unsaturated esters and nitriles using photosensitizers such as anthraquinone, acridone, and dicyanoanthracene has been investigated. The addition of α-aminoalkyl radicals, generated via photoelectron-transfer processes, to olefinic substrates and the subsequent 1,5-hydrogen abstraction reactions of the amine–olefin adduct radicals lead to a number of interesting multiple-olefin-added products. The adducts of the primary and secondary amines with α,β-unsaturated esters undergo further cyclizations to give spiro and cyclic lactams, respectively.

Introduction

The generation and subsequent reactions of α-aminoalkyl radicals have been topics of extensive studies in recent years.[3–11] Such radicals can be utilized for the construction of carbon–carbon bonds adjacent to nitrogen, which is of significant importance in alkaloid chemistry.[12–14] There have been numerous studies on the mechanistic and synthetic aspects of additions of amines to alkenes, initiated by the direct excitation of the alkenes.[3,4] More recently, the intra- and intermolecular carbon–carbon bond forming reactions of α-aminoalkyl radicals, generated via photosensitized electron-transfer reactions of α-silylamines, using sensitizers such as dicyanoanthracene (DCA) and dicyanonaphthalene (DCN), have been investigated.[3,7,14] Following the formation of the alkylamino radical cation in the initial electron transfer process, the loss of the α-silyl group facilitates the generation of α-aminoalkyl radicals in good yields.

Although there are several reports on the mechanistic aspects of α-aminoalkyl radical generation from amines, using a variety of sensitizer systems such as ketones, flavins, porphyrins, and semiconductors,[10,11] there have been only a few attempts to utilize these processes for carbon–carbon bond forming reactions. Electron-transfer reactions between excited state ketones and ground-state amines have been extensively studied.[10,11,15–19] Picosecond laser flash photolysis studies have shown that the mechanism of electron transfer in acetonitrile solutions involves the formation of a triplet exciplex which changes to a contact ion-pair. The contact ion-pair decays via intramolecular proton transfer within the picosecond time domain. The intramolecular proton transfer is facilitated by the strongly basic nature of the ketyl radical anion[3,20] and the acidic nature of the alkylamine radical cation.[21] Thus, even with α-silylamine–enone systems, direct excitation of enones in aprotic solvents leads to the deprotonated α-aminoalkyl radical in preference to the desilylated aminoalkyl radical.[3]

Here we report on our studies on the photosensitized generation and subsequent intermolecular carbon–carbon bond forming reactions of α-aminoalkyl radicals from underivatized amines using anthraquinone and acridone as sensitizers and have compared these to the reactions sensitized by DCA. The addition of primary, secondary, and tertiary amines to a few α,β-unsaturated esters and nitriles has been investigated. Both anthraquinone and acridone will generate ketyl radicals, following the initial electron-transfer process, and based on the above discussions, would be expected to generate α-aminoalkyl radicals from underivatized amines more efficiently than DCA.

Results

Photosensitized Addition Reactions of Triethylamine (2) with Methyl Methacrylate (5) and Acrylonitrile (18). The photosensitized addition of triethylamine (2) to methyl methacrylate (5) was effected by

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Scheme 1

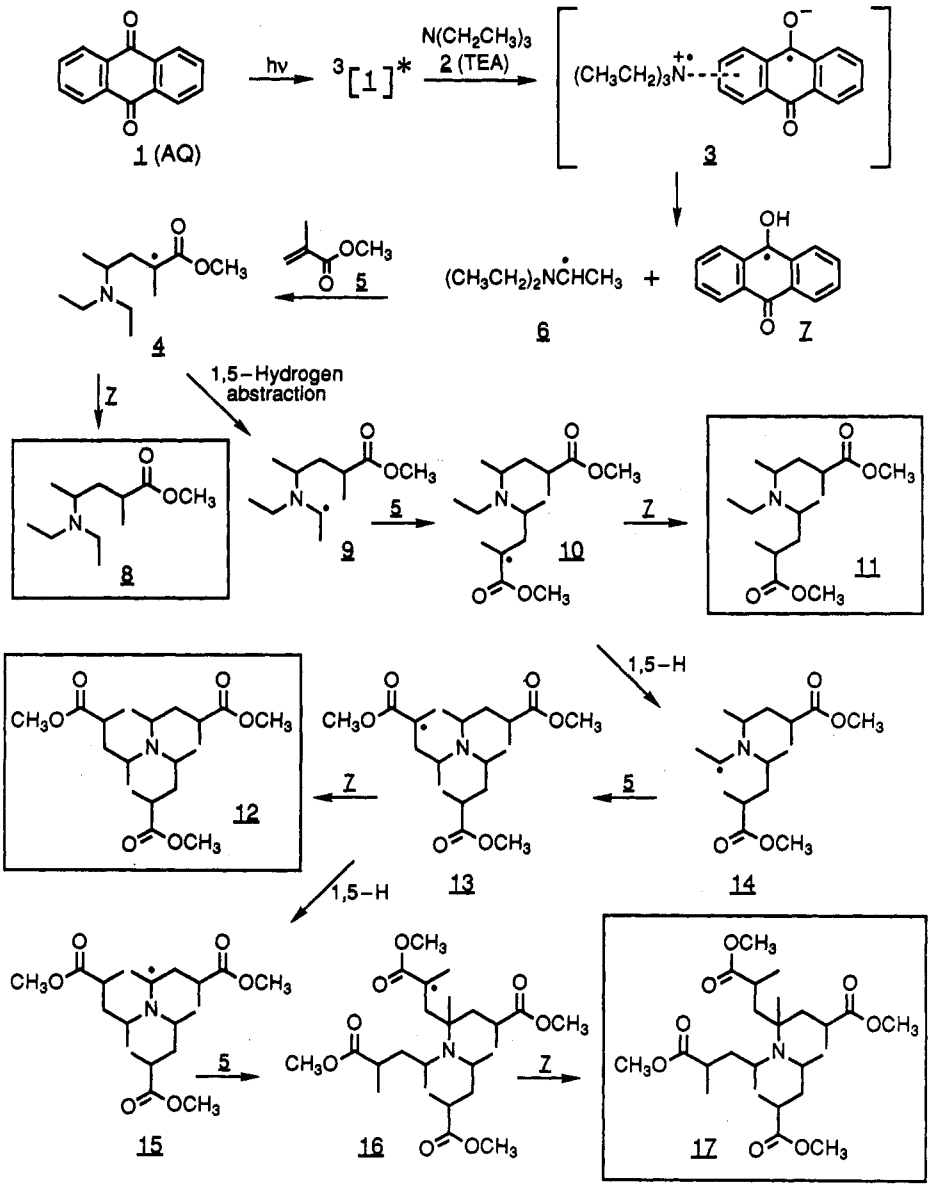


Table 1. Photosensitized Addition of Triethylamine (2) to Methyl Methacrylate (5) in Acetonitrile (350 mL) at 290 K[a]

sensitizer (30–40 μM)	2 (mmol)	5 (mmol)	time of irradiation (h)	% conversion of 5	product distribution (%)[b] 8	11	12	17
anthraquinone	15	15	1	20	10	20	28	12
anthraquinone	15	15	2	26	10	18	28	16
anthraquinone	15	15	3	30	10	15	25	18
anthraquinone	15	15	4	40	10	14	24	22
anthraquinone	15	2	1	42	8	18	26	8
anthraquinone	15	45	1	17	10	14	24	15
anthraquinone	1000	15	1	20	20	25	30	10
acridone	15	15	1	28	10	20	32	18
acridone	15	15	4	38	10	18	30	20
dicyanoanthracene	15	15	4	8	35	22	18	5
dicyanoanthracene	15	15	8	12	30	24	20	8

[a] Irradiation by Pyrex-filtered light of a 450-W medium pressure Hanovia Lamp. [b] Yield based on conversion of 5.

irradiating argon-saturated acetonitrile solutions of triethylamine and methyl methacrylate containing catalytic amounts of anthraquinone (1), under Pyrex-filtered light ($\lambda > 290$ nm). Four products were isolated from the reaction mixture (8, 11, 12, 17, Scheme 1) and they were characterized on the basis of spectral information. The yields and percentage conversion and distribution of products under a variety of irradiation conditions are shown in Table 1. Change of irradiation time as well as substrate concentration brought about only minor changes in the product distribution. On use of large excess of triethylamine (0.15–1 mol) there was some increase in the yield of 8 at the expense of 17. On using acridone as sensitizer, instead of anthraquinone, the percentage conversion and product yields were comparable (Table 1). Dicyanoanthracene however was observed to be much less efficient as sensitizer when compared to anthraquinone and acridone (Table 1). Also, the percentage distribution

Scheme 2

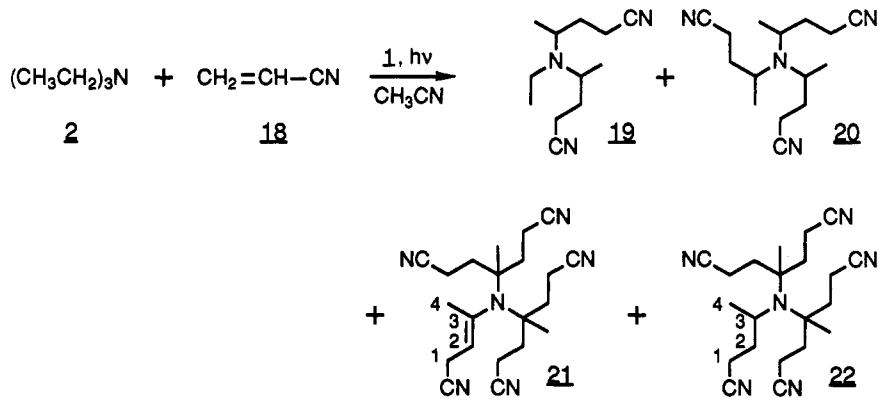


Table 2. Photosensitized Addition of Triethylamine (2) to Acrylonitrile (18) in Acetonitrile (350 mL) at 290 K[a]

sensitizer (10^{-4} M)	2 (mmol)	18 (mmol)	time of irradiation (h)	% conversion of 18	product distribution (%)[b] 19	20	21 + 22
anthraquinone	15	15	1	17	8	10	60
anthraquinone	15	45	1	11	8	12	50
anthraquinone	150	15	1	21	10	15	40
acridone	15	15	1	30	18	42	28
dicyanoanthracene	15	15	1	<2%	–	–	–

[a] Irradiation by Pyrex-filtered light of a 450-W medium pressure Hanovia Lamp. [b] Yield based on conversion of 18.

of products indicated that more of the lower molecular weight product, 8 was formed at the expense of the higher molecular weight products 12 and 17 as compared to the anthraquinone- and acridone-sensitized reactions.

The photoreaction of 2 with acrylonitrile (18) in the presence of catalytic amounts of 1 gave a mixture of four products, 19–22 (Scheme 2). The products 19 and 20 were separated and identified on the basis of their spectral data (see Experimental Section). The ^1H and ^{13}C NMR spectra of 19 and 20 indicate the presence of isomeric mixtures in these compounds. Products 21 and 22 had nearly identical physical properties and could not be separated using chromatographic techniques including HPLC. Evidence for two components in the product mixture was obtained by the presence of two distinct spots on silver nitrate doped silica gel TLC plates. The high resolution NMR spectrum (500 MHz) clearly showed that two compounds were present in the purified mixture, in roughly equal concentrations. The ^1H NMR spectrum of this mixture showed a doublet at δ 3.1 (2 H, J = 7 Hz) which has been assigned to the methylene protons at the C_1 position and the triplet at δ 5.3 (1 H, J = 7 Hz) has been assigned to the olefinic proton at the C_2 position of 21. The methine proton at the C_3 position of 22 appears as a broad multiplet centered at δ 3.25. The methine protons of similar products 19 and 20 appeared in the same region. Three methyl protons of 22 and two methyl protons of 21 appeared as a bunch (singlets and doublets) centered at δ 1.2 (15 H, 5 CH_3). The C_4 methyl protons adjacent to the olefinic carbon appeared as a singlet centered at δ 1.85 (3 H, 1 CH_3). The methylene protons of 21 and 22 also appeared together around the same position (see Experimental Section). The ^{13}C NMR spectrum of the mixture showed two peaks at δ 117.36 and 142.16, characteristic of the olefinic carbons of 21.

As in the case of methyl methacrylate addition, the product distribution was fairly independent of the substrate concentration. Acridone was found to sensitize the reaction much more efficiently; however there was some increase in the percentage yield of 20 at the expense of 21 + 22, as compared to the anthraquinone-sensitized reaction. Under identical conditions, DCA was found to be highly inefficient as sensitizer. These results are summarized in Table 2.

Photosensitized Addition of Secondary and Primary Amines to Olefinic Substrates. Two products 24 and 25 (Scheme 3) were isolated from the reaction of diisopropylamine with acrylonitrile catalyzed by small amounts of anthraquinone or acridone. Acridone was slightly more efficient as sensitizer, whereas DCA did not sensitize the reaction to any extent.

Two products 26 and 28 (Scheme 3) were isolated from the photoreaction of diisopropylamine with methyl methacrylate in the presence of catalytic amounts of anthraquinone or acridone. Acridone was marginally more efficient in terms of conversion of the olefinic substrate. In the anthraquinone-sensitized reaction, 26 was formed in higher yields as compared to that for the acridone-sensitized reactions. DCA did not sensitize these reactions.

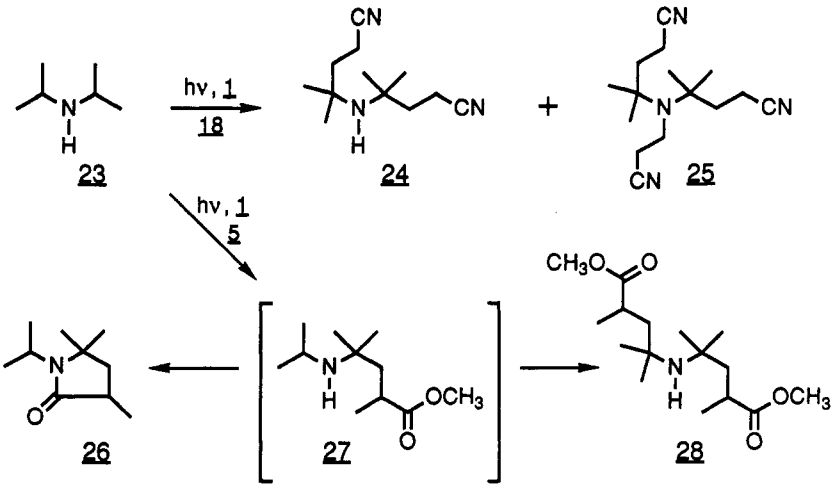
A major product 30 was isolated from the anthraquinone-photosensitized reactions of pyrrolidine with methyl methacrylate, whereas the reaction of piperidine, under similar conditions gave 32 as the major product (Scheme 4).

The photosensitized addition of cyclohexylamine to methyl acrylate, methyl methacrylate, and methyl crotonate gave the spirolactams 34, 35, and 36, respectively (Scheme 5). Only anthraquinone was found to sensitize these reactions. The yields and percentage conversion were observed to be much better on using benzene instead of acetonitrile as the solvent.

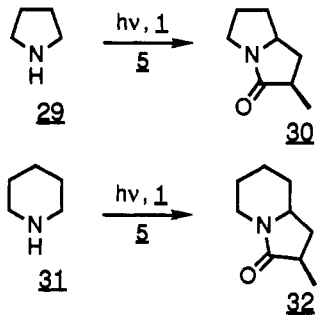
Discussion

Photosensitized Addition Reactions of Triethylamine to Methyl Methacrylate and Acrylonitrile. Excitation of the reaction mixtures with Pyrex-filtered light would lead to the selective excitation of the sensitizers since triethylamine as well as the α,β-unsaturated substrates, methyl methacrylate and acrylonitrile, do not have

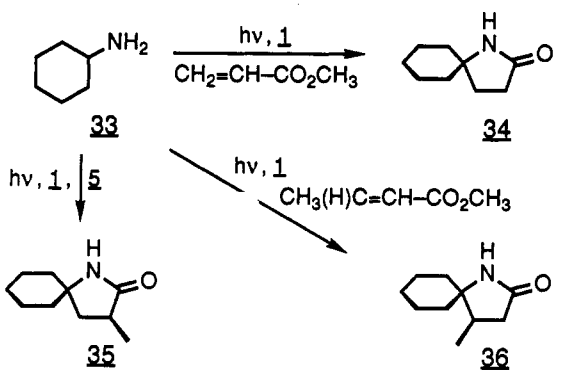
Scheme 3



Scheme 4



Scheme 5



significant absorbance above 290 nm. Excitation of anthraquinone (1) would lead to the formation of anthraquinone triplets ($\phi_T \sim 0.93$).[23] Quenching of anthraquinone triplets by triethylamine (2) would result in the contact ion pair (CIP) (3), involving the amine radical cation and the anthraquinone radical anion. As discussed earlier, the basic nature of the anthraquinone ketyl radical anion can facilitate abstraction of a proton from the relatively acidic alkylamine radical cation to yield α-aminoalkyl radials. The thermal reactions of the α-aminoalkyl radical, as depicted in Scheme 1, is proposed as the mechanism for the formation of products, 8, 11, 12, and 17. Addition of the aminoalkyl radical 6 to methyl methacrylate would give rise to the adduct radical 4, which can be quenched by the ketyl radical 7 to yield 8 and anthraquinone, or undergo 1,5-hydrogen abstraction to bring about a translocation of the radical center to give 9. Intramolecular 1,5-hydrogen atom abstractions are well-documented in free radical chemistry.[24-27] Radical adducts of α-aminoalkyl radicals are also known to undergo 1,5-hydrogen atom abstraction reactions.[28] A sequence of addition reactions of the adduct radical to the olefinic ester and subsequent quenching by anthraquinone ketyl radicals as 1,5-hydrogen atom abstraction reactions as shown in Scheme 1 could subsequently lead to the rest of the observed products, 11, 12, and 17. The formation of these products may be attributed to the inefficiency of the anthraquinone ketyl radical to terminate the initially formed 1:1 adduct radical. The ketyl radical anion of anthraquinone is known to be relatively stable in argon-purged solutions and is only quenched very slowly by electron acceptors.[29]

An alternative reaction mechanism would involve the formation of the 1:1 amine adduct 8 and its subsequent secondary electron transfer reactions with the excited state of anthraquinone. This can, however, be ruled out since the product distribution is fairly independent of the reaction conditions. For irradiation periods of 1, 2, 3, and 4 h where the conversion of methyl methacrylate varies from 20 to 40% (Table 1), the product distribution remains unchanged within experimental error, indicating that secondary photoprocesses are not important. Under these conditions substantial amounts of unreacted amine would exist, preventing secondary photoreactions. Even on using larger excess of triethylamine, wherein the excited state of anthraquinone would be preferentially quenched by the parent amine, rather than any of the initially formed photoproducts, 12 is formed in substantial amounts (30%). Under these conditions there is some enhancement in the percentage yields of the lower molecular weight products and this may be attributed to the quenching of the adduct radicals by the parent amine by donating hydrogen atoms, thus inhibiting the 1,5-hydrogen abstraction process.

Acridone-sensitized reactions of triethylamine and methyl methacrylate were comparable (Table 1). Dicy-

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anoanthracene, however was found to be highly inefficient in sensitizing these reactions. This clearly supports the role of the anion radical base strength in bringing about the deprotonation of the alkylamine radical cation. Unlike the ketyl radical anion, the DCA radical anion is more acidic.[3] Also, the product distribution for the DCA-sensitized reactions clearly indicates the ability of the DCA radical anion to quench the amine–alkene adducts more efficiently than ketyl radicals. Thus the lower molecular weight products are formed in better yields than the higher molecular weight products unlike in the anthraquinone- and acridone-sensitized reactions.

Triethylamine possesses six abstractable methylene hydrogen atoms, and six olefinic moieties can, in principle, add to the amine moiety. However, the formation of the five and six addition products is probably inhibited by steric factors, due to the bulkiness of methyl methacrylate.

Photosensitized addition reactions of a less bulkier substrate, acrylonitrile, with triethylamine indicate that the amine can add up to five molecules, to give highly branched functional amines. The products **19–22** can be formed by pathways similar to those of the reaction of methyl methacrylate with triethylamine, shown in Scheme 1. The formation of **21** in this reaction may be through a hydrogen atom abstraction of its precursor or through a disproportionation reaction, leading to nearly equal amounts of both **21** and **22**, as observed experimentally.

Acridone-sensitized reactions were slightly more efficient with regard to the percentage conversion of acrylonitrile. The product distribution, however indicated that the lower molecular weight products were formed in preference to the higher molecular weight products. DCA was found to be least efficient in sensitizing these reactions.

Photosensitized Addition of Primary and Secondary Amines to Olefinic Substrates. Single electron transfer, followed by deprotonation or hydrogen atom abstraction from primary and secondary amines can lead to either aminyl or α-aminoalkyl radicals.[30] Since α-aminoalkyl radicals are known to be thermodynamically more stable and since aminyl radicals can readily convert to α-aminoalkyl radicals via hydrogen abstractions from the parent amines,[31] these processes lead predominantly to the α-aminoalkyl radicals. In the present study the photosensitized reactions of primary and secondary amines led specifically to products from reactions of α-aminoalkyl radicals.

Since primary and secondary amines are known to undergo Michael type addition reactions with electron-deficient alkenes, only those systems were chosen wherein the thermal Michael-type of additions were insignificant, as evidenced from blank runs.

Anthraquinone-sensitized reactions of diisopropylamine with acrylonitrile led to two major products **24** and **25**. Anthraquinone sensitization would generate the α-aminoalkyl radical of diisopropylamine, which could add to acrylonitrile to yield the adduct radical. Radical translocation by 1,5-hydrogen abstraction, addition of the subsequent radical to acrylonitrile, and quenching of the adduct radical by ketyl radicals, a mechanism which is analogous to the one shown in Scheme 1, would account for the formation of **24**. The product **25** could arise through a thermal Michael-type addition reaction of **24** with acrylonitrile.

The anthraquinone-photosensitized reaction of diisopropylamine with methyl methacrylate leads to a 1:2-addition product **28**. However, the major fraction of the product mixture consisted of **26**, which could arise through the cyclization of the monoadduct **27**, as shown in Scheme 3. The adduct **27** was not isolated from the reaction mixture. However, there are several reports in support of such intramolecular cyclization reactions.[32,33]

The above-mentioned anthraquinone-sensitized reactions offer a convenient route to the synthesis of heterocyclic ring systems. Acridone was also found to sensitize this reaction, although the percentage distribution of **26** in the reaction mixture was very low, compared to the anthraquinone-sensitized reaction. DCA did not sensitize the photoaddition reaction of diisopropylamine to either acrylonitrile or methyl methacrylate.

The anthraquinone-photosensitized reaction of pyrrolidine with methyl methacrylate gave **30** as the major product, whereas piperidine gave **32**, under analogous conditions (Scheme 4). Both these products can arise from the thermal intramolecular cyclization of the amine olefin-adduct. There are several natural products which contain pyrrolizidine and indolizidine ring systems. Our studies indicate that anthraquinone-sensitized generation of pyrrolizidine and indolizidine ring systems could offer a convenient route to the synthesis of such compounds.

Interestingly both acridone and DCA do not sensitize these reactions. These results suggest that the photosensitized generation of aminoalkyl radicals from secondary amines such as pyrrolidine and piperidine may by proceeding predominantly via a hydrogen abstraction process, rather than via photoelectron transfer.

The anthraquinone-photosensitized addition of a primary amine to olefinic substrates was also investigated. It was observed that cyclohexylamine did not undergo thermal Michael-type addition reactions with methyl acrylate, methyl methacrylate, and methyl crotonate under the conditions of our experiments. Anthraquinone-sensitized photoreactions of cyclohexylamine with these olefinic substrates gave rise to the spirolactams **34**, **35**, and **36**, respectively. Acridone and DCA were unable to sensitize these reactions, indicating that anthraquinone sensitization occurs via a hydrogen abstraction process. This was further confirmed by studying these photoreactions in benzene. The higher efficiency of cyclic spirolactams formed in a nonpolar solvent such as benzene, than in a polar solvent such as acetonitrile again supports that these reactions occur predominantly via a hydrogen abstraction process than photoinduced electron transfer.

Experimental Section

General Procedures. ^{1}H and ^{13}C NMR spectra were recorded on JEOL EX 90, Brüker WH 270, or Varian VXR 500S NMR spectrometers. Unless otherwise stated, 90-MHz ^{1}H NMR spectra are reported. ^{13}C NMR (22.5 MHz) resonances were assigned using QUART and DEPT programs to determine the number of hydrogen attachments. Mass spectra were recorded on a Finnigan MAT Model 8430 or JEOL JMS AX 505HA mass spectrometer. Preparative photochemical reactions were carried out under irradiation from a 450-W medium pressure mercury vapor lamp in Pyrex-jacketed, water-cooled immersion wells. Anthraquinone was purified by vacuum sublimation and dicyanoanthracene was purified either by column chromatography

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or by recrystallization from benzene. Acridone (99%) from Aldrich was used as obtained. All other reagents and solvents were purified by distillation before use.

The photolysis mixture, typically consisting of the amine (15–150 mmol) and olefinic substrate (2–45 mmol) in acetonitrile (350 mL) containing sensitizer (30–40 μM), was purged with argon or nitrogen before irradiation (1–8 h). The solvent and unchanged reactants were removed under reduced pressure, and the product mixture was chromatographed (flash column) on silica gel (230–400 mesh) or using a Harrison Chromatotron. All the photoproducts were finally purified using a semipreparative HPLC (ODS-semipreparative column 20 mm i.d. × 25 cm long, methanol eluent). The yields reported are based on the olefinic substrate consumed, which was estimated by HPLC before removal of the solvent from the irradiation mixture. The sensitizers were recovered quantitatively (>90%) under all the irradiation conditions that we have studied.

All new compounds were characterized on the basis of their spectral and high-resolution molecular mass data.

Photosensitized Addition of Triethylamine to Methyl Methacrylate. Irradiation of an argon-degassed solution of **2** (1.5 g, 15 mmol) and **5** (1.5 g, 15 mmol) in acetonitrile (350 mL), containing anthraquinone (30–40 μM) for 1 h and separation of the photoproducts by column chromatography using a mixture (1:9) of ethyl acetate and petroleum ether gave 40 mg (10%) of **8**, 80 mg (20%) of **11**, 150 mg (28%) of **12**, and 48 mg (12%) of **17**. These yields are based on **5** that reacted (22%), as estimated by HPLC.

The reactions were repeated under a variety of conditions and also using acridone and dicyanoanthracene as sensitizers instead of anthraquinone. The percentage conversion and product yields of these reactions are given in Table 1.

8: IR ν_{max} (neat), 2975, 2870 (CH), 1736 (C=O) cm^{-1}; UV λ_{max} (CH_3CN) 205 nm (ϵ 2500), 254 (408, sh); ^{1}H NMR ($CDCl_3$) δ 0.8–1.3 (12 H, m, 4 CH_3), 1.5-1.8 (2 H, m, CH_2), 1.8–2.9 (6 H, m, 2 CH_2, 2 CH), 3.5–3.8 (3 H, s, OCH_3); ^{13}C NMR (22.5 MHz) ($CDCl_3$) δ 13.50, 14.25, 17.50 (CH_3), 37.10 (CH), 38.20, 42.60 (CH_2), 51.15 (OCH_3), 52.5 (CH), 174.0 (C=O, ester); mass spectrum *m/e* (rel inten) 201 (M^+, 4) 186 (11), 170 (7), 154 (4), 143 (6), 126 (8), 100 (100), 83 (10), 72 (7); mol wt calcd for $C_{11}H_{23}NO_2$ 201.1728, found (high-resolution mass spectrometry) 201.1714.

11: IR ν_{max} (neat), 2972, 2875 (CH), 1738 (C=O) cm^{-1}; UV λ_{max} (CH_3CN) 205 nm (ϵ 2550), 254 (418 sh); ^{1}H NMR ($CDCl_3$) δ 0.8–1.2 (15 H, m, 5 CH_3), 1.7-2.1 (4 H, m, 2 CH_2), 2.2–2.9 (6 H, m, CH_2, 4 CH), 3.5–3.7 (6 H, s, 2 OCH_3); ^{13}C NMR ($CDCl_3$) δ 15.35, 15.58, 17.05, 17.55, 17.80 (CH_3), 36.20, 36.80 (CH), 38.00, 39.50, 40.2 (CH_2), 49.50, 50.20 (CH), 51.20 (OCH_3) 177.54 (C=O, ester); mass spectrum *m/e* (rel inten) 301 (M^+, 6), 286 (12), 270 (4), 200 (100), 170 (30), 142 (28), 129 (40), 97 (32), 83 (15), 69 (16); exact mol wt calcd for $C_{16}H_{31}O_4N$ 301.22531, found (high-resolution mass spectrometry) 301.2245.

12: IR ν_{max} (neat), 2975, 2875 (CH), 1730 (C=O) cm^{-1}; UV λ_{max} (CH_3CN) 205 nm (ϵ 3400), 254 (460, sh); ^{1} H NMR ($CDCl_3$) δ 0.93–1.1 (9 H, m, 3 CH_3), 1.1-1.26 (9 H, m, 3 CH_3), 1.26–1.5 (6 H, m, 3 CH_2), 2.3–2.56 (3 H, m, CH), 2.66–2.93 (3 H, m, 3 CH), 3.5–3.67 (9 H, m, 3 OCH_3); ^{13}C NMR ($CDCl_3$) δ 17.7, 20.7 (CH_3) 36.8 (CH), 41.2 (CH_2), 47.1 (CH), 51.4 (OCH_3), 177.4 (C=O); mass spectrum *m/e* (rel inten) 401 (M^+, 6), 386 (12), 370 (8), 300 (100), 271 (20), 243 (34), 211 (20), 183 (54), 151 (30), 129 (54), 123 (36) and other peaks; mol wt calcd for $C_{21}H_{39}O_6$ 401.2777, found (high-resolution mass spectrometry) 401.2773.

17: IR ν_{max} (neat) 2975, 2872 (CH), 1741 (C=O) cm^{-1}; UV λ_{max} (CH_3CN) 203 nm (ϵ 2600), 254 (415, sh); ^{1}H NMR (300 MHz) ($CDCl_3$)[29] δ 0.8–1.25 (21 H, m, 7 CH_3) 1.25–1.8 (8 H, m, 4 CH_2), 2.35–2.75 (4 H, m, 4 CH), 2.75–3.00 (2 H, m, 2 CH), 3.55–3.75 (12 H, m, 4 OCH_3); ^{13}C NMR ($CDCl_3$)[34] δ 16.95–18.4, 19.25-20.85 (CH_3), 35.45–37.57, 39.99–41.2, 44.32–44.46, 45.60–46.18, 47.55–47.90, 48.3, 51.33–51.63 (OCH_3), 176.80–177.48 (C=O, ester); mass spectrum (FAB) *m/e* (rel inten) 502 (MH^+, 65) 486 (16), 400 (70), 300 (100), 229.2 (30), 169.2 (48), 154 (30) and other peaks; mol wt calcd for $C_{26}H_{47}NO_8$ 501.33017, found (high-resolution mass spectrometry) 501.3290.

Photosensitized Addition of Triethylamine to Acrylonitrile. Irradiation of an argon-degassed solution of **2** (1.5 g, 15 mmol), **18** (2.4 g, 45 mmol) in acetonitrile (350 mL) containing 30–40 μM of **1** for 1 h, and separation by column chromatography using a solvent mixture of (4:1) petroleum ether (bp 60–80 °C) and ethyl acetate gave 40 mg (8%) of **19**, 60 mg (12%) of **20**, and 250 mg (~50%) of **21** and **22** (unseparated mixture). The reactions were repeated under a variety of conditions and also using acridone and DCA as sensitizers instead of anthraquinone. The percentage conversion and product distribution are tabulated in Table 2.

19: IR ν_{max} (neat) 2972, 2897 (CH), 2248 (C≡N) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.9–1.2 (9 H, m, 3 CH_3), 1.3–1.9 (4 H, m, 2 CH_2), 2.2–2.6 (6 H, m, 3 CH_2), 2.8–3.2 (1 H, m, CH); ^{13}C NMR ($CDCl_3$)[34] δ 14.67, 14.85 (CH_2), 15.36, 16.30, 17.06, 17.89 (CH_3), 30.93, 31.38, 36.93, 38.30 (CH_2), 50.85, 53.28 (CH), 119.96 (C≡N), 120.10; mass spectrum *m/e* (rel inten) 208 (MH^+, 4), 171 (30), 143 (92), 127 (8), 115 (16), 111 (58), 102 (72), 83 (100) and other peaks; mol wt calcd for $C_{12}H_{21}N_3$ 207.1813, found (high-resolution mass spectrometry) 207.1815.

20: IR ν_{max} (neat) 2969, 2886 (CH), 2248 (C≡N) cm^{-1}; ^{1}H NMR ($CDCl_3$)[34] δ 0.9–1.2 (9 H, dd, 3 CH_3), 1.4–1.9 (6 H, m, 3 CH_2), 2.2–2.6 (6 H, m, 3 CH_2), 2.8–3.2 (1 H, m, CH); ^{13}C NMR ($CDCl_3$) δ 15.06, 15.27, 16.14, 19.98, 20.19, 24.22, 31.26, 48.41, 48.65, 120.10, 120.54, 120.61; mass spectrum *m/e* (rel inten) 260 (M^+, 7), 245 (12), 206 (100), 164 (9), 125 (32), 82 (12), 68 (18) and other peaks; mol wt calcd for $C_{15}H_{24}N_4$ 260.2001, found (high-resolution mass spectrometry) 260.2004.

21 + 22:[35] IR ν_{max} (neat) 2977, 2880 (CH), 2248 (C≡N) cm^{-1}; UV λ_{max} (CH_3CN) 213 nm (ϵ 1400), 254 (1300); ^{1}H NMR (500 MHz) ($CDCl_3$) δ 1.0–1.36 (15 H, m, 5 CH_3), 1.7–2.0 (18 H, m, 9 CH_2 and 3 H, s, CH_3), 2.25–2.50 (18 H, m, 9 CH_2), 3.05–3.15 (2 H, d, CH_2), 3.2–3.3 (1 H, m, CH), 5.25–5.35 (1 H, t, CH); ^{13}C NMR (22.5 MHz) ($CDCl_3$) δ 12.16, 12.25, 14.67, 15.83 (CH_2), 33.08, 33.44 (CH_2), 20.22, 21.53, 21.98 (CH_3), 33.08, 33.49 (CH_2), 49.34 (CH), 59.33 (C), 117.36 (C, olefinic), 119.24, 119.57 (C≡N), 142.16 (C, olefinic); mass spectrum *m/e* (rel inten) 366 (M^+, 2), 351 (9), 312 (60), 257 (50), 231 (8), 206 (40), 176 (58), 137 (100), 123 (56), 108 (16) and other peaks; mol wt calcd for $C_{21}H_{29}N_6$ (MH^+, **21**) 365.2454, found 365.2439 (FAB, high-resolution mass spectrometry); mol wt calcd for $C_{21}H_{31}N_6$ (MH^+, **22**) 367.2610, found 367.2598 (FAB, high-resolution mass spectrometry).

Photosensitized Addition of Diisopropylamine (23) to Acrylonitrile (18). Irradiation of an argon-degassed solution of **23** (1.5 g, 15 mmol) and **18** (0.8 g, 15 mmol) in acetonitrile (350 mL) containing (30–40 μM) of **1** for 1 h and separation by column chromatography using a mixture (20:1) of petroleum ether–ethyl acetate yielded 100 mg (50%) of **24** and 40 mg (20%) of **25**. The yields are based on **18** reacted (12%). On using acridone as sensitizer instead of anthraquinone, the percentage conversion of **18** after 1 h of irradiation was higher (20%), while the product distribution was the same. DCA-sensitized reactions did not indicate measurable conversion of **18** even after 8 h of irradiation.

24: IR ν_{max} (neat) 3400 (broad, NH) 2975, 2912 (CH), 2248 (C≡N) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.9–1.1 (12 H, s, 4 CH_3), 1.35–1.65 (4 H, t, 2 CH_2), 2.15–2.35 (4 H, t, 2 CH_2); ^{13}C NMR ($CDCl_3$) 12.07 (CH_2), 29.51 (CH_3), 40.48 (CH_2), 53.07 (C), 120.61 (C≡N); mass spectrum *m/e* (rel inten) 208 (MH^+, 32), 192 (35), 153 (100), 113 (65), 97 (25) and other peaks: mol wt calcd for $C_{12}H_{22}N_3$ (MH^+) 208.1814, found (high-resolution mass spectrometry, FAB) 208.1813.

25: IR ν_{max} (neat) 2970, 2905 (CH), 2248 (C≡N) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.1–1.3 (12 H, s, 4 CH_3), 1.6–2.1 (6 H, m, 3 CH_2), 2.4–2.7 (6 H, m, 3 CH_2); ^{13}C NMR ($CDCl_3$) δ 10.80, 13.50, 25.38 (CH_2), 28.51, 29.10, 29.25, 29.50, 29.60, 39.50, 46.80 (CH_2), 52.50, 52.68 (C), 120.50, 120.61 (C≡N); mass spectrum *m/e* (rel inten) 261 (MH^+, 40) 245 (55), 206 (82), 166 (60), 153 (100), 113 (68), 97 (30) and other peaks; mol wt calcd for $C_{15}H_{25}N_4$ (MH^+) 261.2079, found 261.2079 (FAB, high-resolution mass spectrometry).

Photosensitized Addition of Diisopropylamine (23) to Methyl Methacrylate (5). Argon-degassed solution of **23** (1.5 g, 15 mmol) and **5** (4.5 g, 45 mmol) in acetonitrile (350 mL) containing 30–40 μM of **1** was irradiated for 2 h and separation

(34) The poor resolution of the peaks may be attributed to the possibility of mixtures, arising due to the presence of several chiral centers in the molecule.

(35) Our attempts to separate this mixture were unsuccessful. Based on the spectral data, it is inferred that this is a mixture of **21** and **22**, in nearly equal amounts.

of the photoproducts by column chromatography using a mixture (20:1) of petroleum ether and ethyl acetate gave 150 mg (30%) of **28** and 300 mg (50%) of **26**. These yields are based on percentage conversion of **5** (18%). Under the same conditions of irradiation, acridone-sensitized photoreactions yielded 90 mg (30%) of **28** and 15 mg (5%) of **26**. DCA does not sensitize these addition reactions.

28: IR ν_{max} (neat) 3400 (broad, NH), 2977 (CH), 1740 (C=O) cm^{-1}; UV λ_{max} (CH_3CN) 203 nm (ϵ 2500), 254 (500, sh); ^1H NMR ($CDCl_3$) δ 0.9–1.2 (18 H, m, 6 CH_3), 1.8–2.2 (4 H, m, 2 CH_2), 2.4–2.8 (2 H, m, 2 CH), 3.5–3.7 (6 H, s, 2 OCH_3); ^{13}C NMR ($CDCl_3$) δ 19.85, 29.52, 29.85, 30.85, 30.95 (CH_3), 35.85 (CH), 49.55, 49.95 (C), 51.50 (CH_2), 53.85 (OCH_3), 179.60 (C=O, ester); mass spectrum *m/e* (rel inten) 302 (MH^+, 55), 286 (18), 200 (100), 143 (100), 111 (30) and other peaks; mol wt calcd for $C_{16}H_{31}NO_4$ 301.2253, found (high-resolution mass spectrometry) 301.2249.

26: IR ν_{max} (neat) 2980, 2868 (CH), 1658 (C=O) cm^{-1}; UV λ_{max} (CH_3CN) 203 nm (ϵ 2500), 254 (460 sh); ^1H NMR ($CDCl_3$) δ 1.1–1.6 (15 H, m, 5 CH_3), 2.0-2.3 (3 H, m, CH_2, CH), 3.2–3.6 (1 H, m, CH); ^{13}C NMR ($CDCl_3$) δ 15.94, 19.61, 20.66, 25.04, 28.18 (CH_3), 35.01 (CH), 43.33 (CH_2), 44.05 (CH), 58.62 (C), 176.87 (C=O, lactam); mass spectrum (rel inten) 169 (M^+, 30), 154 (100), 112 (72), 84 (13), 69 (13) and other peaks; mol wt calcd for $C_{10}H_{19}NO$ 169.1466, found (high-resolution mass spectrometry) 169.1495.

Photosensitized Addition of Pyrrolidine (29) to Methyl Methacrylate (5). Irradiation of an argon-degassed solution of **29** (1.1 g, 15 mmol), **5** (0.2 g, 2 mmol), and 1 (30–40 μM) in acetonitrile and separation by column chromatography gave **30** (90 mg, 68%). The yield was based on **5** that reacted (45% conversion). Acridone and DCA did not sensitize these addition reactions.

30: IR ν_{max} (neat), 2970, 2880 (CH), 1684 (C=O) cm^{-1}; UV λ_{max} (CH_3CN) 205 nm (ϵ 3080), 254 (540 sh); ^1H NMR ($CDCl_3$) δ 1.0–1.4 (3 H, dd, CH_3), 1.8–2.2 (4 H, m, 2 CH_2), 2.3–3.2 (4 H, m, 2 CH_2), 3.3–4.0 (2 H, m, 2 CH); ^{13}C NMR ($CDCl_3$) δ 15.29, 16.93 (CH_3), 26.24, 26.30, 31.49 (CH_2), 31.84, 33.81 (CH), 37.24, 40.50, 40.62 (CH_2), 40.79, 41.15, 58.81, 59.62 (CH), 175.89 (C=O, lactam); mass spectrum *m/e* (rel inten) 139 (M^+, 83), 124 (15), 111 (100), 96 (15), 83 (28), and other peaks; mol wt calcd for $C_8H_{13}NO$ 139.0997, found 139.0990 (high-resolution mass spectrometry).

Photosensitized Addition of Piperidine (31) to Methyl Methacrylate (5). Irradiation of an argon-degassed solution of **33** (1.5 g, 15 mmol) and **5** (0.20 g, 2 mmol) in acetonitrile (350 mL), containing 30–40 μM 1 for 2 h gave 110 mg (78%) of **32**. The yield of **32** was based on the amount of **5** that reacted (40% conversion). This reaction was not sensitized by either acridone or DCA.

32: IR ν_{max} (neat), 2937, 2862 (CH), 1692 (C=O) cm^{-1}; UV λ_{max} (CH_3CN) 205 nm (ϵ 3020), 254 (580 sh); ^1H NMR ($CDCl_3$) δ 1.1–1.4 (3 H, dd, CH_3), 1.5–2.2 (6 H, m, 3 CH_2), 2.3–2.9 (4 H, m, 2 CH_2), 3.1–3.6 (1 H, m, CH), 3.9–4.2 (1 H, m, CH); ^{13}C NMR ($CDCl_3$) δ 16.03, 16.60 (CH_3), 22.22, 23.40, 23.94, 24.09, 32.59, 33.07, 33.40, 35.01 (CH_2), 35.39, 35.90 (CH), 39.75, 39.96 (CH_2), 55.06, 55.67 (CH), 175.68 (C=O, lactam); mass spectrum *m/e* (rel inten) 153 (M^+, 72), 152 (100), 138 (29), 124 (20), 112 (12), 97 (12), 83 (32) and other peaks; mol wt calcd for $C_9H_{15}NO$ 153.1153, found 153.1153 (high-resolution mass spectrometry).

Photosensitized Addition of Cyclohexylamine (33) to Methyl Acrylate. Irradiation of an argon-degassed solution of **33** (1.45 g, 15 mmol), methyl acrylate (1.3 g, 15 mmol), and 30–40 μM 1 in acetonitrile (350 mL) for 4 h and separation of the irradiation mixture by column chromatography gave 500 mg of **34** (80%). The percentage yield is based on the amount of methyl acrylate that reacted (40% conversion). Acridone and DCA do not sensitize this reaction.

34: mp 106–108 °C; IR ν_{max} (neat) 3361 (NH), 2934, 2860 (CH), 1698 (C=O) cm^{-1}; UV λ_{max} (CH_3CN) 205 nm (ϵ 2530), 254 (520, sh); ^1H NMR ($CDCl_3$) δ 1.2–1.7 (10 H, m, cyclohexyl), 1.8–2.0 (2 H, t, CH_2), 2.2–2.5 (2 H, t, CH_2), 7.4–7.7 (1 H, broad, D_2O-exchangable, NH); ^{13}C NMR ($CDCl_3$) δ 22.70, 24.9, 29.86, 32.42, 38.09 (CH_2), 59.24 (C), 177.36 (C=O, lactam); mass spectrum *m/e* (rel inten) 153 (M^+, 32), 110 (100), 97 (22), 78 (62) and other peaks; mol wt calcd for $C_9H_{15}NO$ 153.1154, found 153.1154 (high-resolution mass spectrometry).

Photosensitized Addition of Cyclohexylamine (33) to Methyl Methacrylate (5). Irradiation of an argon-degassed solution of **33** (1.48 g, 15 mmol), **5** (1.5 g, 15 mmol), and 1 (30–40 μM) in acetonitrile (350 mL) for 4 h and separation by column chromatography using a mixture (3:1) of petroleum ether and ethyl acetate gave 350 mg (70%) of **35**. The yield is based on **5** that reacted (32% conversion).

35: mp 95–97 °C; IR ν_{max} (neat) 3220 (broad, NH), 2987, 2836 (CH), 1698 (C=O) cm^{-1}; UV λ_{max} (CH_3CN) 205 nm (ϵ 2890), 254 nm (520, sh); ^1H NMR ($CDCl_3$) δ 1.0–1.1 (3 H, d, CH_3), 1.2–1.6 (10 H, m, cyclohexyl), 1.9–2.6 (3 H, m, CH, CH_2) 7.5–7.8 (1 H, broad, D_2O-exchangable, NH); ^{13}C NMR ($CDCl_3$) δ 16.40 (CH_3), 22.76, 22.64, 24.87 (CH_2), 35.26 (CH), 39.40, 37.49, 41.28 (CH_2), 56.83 (C), 179.33 (C=O, lactam); mass spectrum *m/e* (rel inten) 167 (M^+, 27), 138 (8), 124 (100), 111 (23) and other peaks; mol wt calcd for $C_{10}H_{17}NO$ 167.1310, found 167.1301 (high-resolution mass spectrometry).

Photosensitized Addition of Cyclohexylamine (33) to Methyl Crotonate. Irradiation of an argon-degassed solution of **33** (1.48 g, 15 mmol), methyl crotonate (1.5 g, 15 mmol), and 1 (30–40 μM) in acetonitrile (350 mL) for 4 h and separation of the reaction mixture by column chromatography using a mixture (3:1) of petroleum ether and ethyl acetate gave **36** (250 mg, 50%). The yield is based on the methyl crotonate reacted (15%).

36: mp 92–94 °C; IR ν_{max} (neat) 3220 (broad, NH), 2987, 2836 (CH), 1698 (C=O) cm^{-1}; UV λ_{max} (CH_3CN) 205 nm (ϵ 2680), 254 (510, sh); ^1H NMR ($CDCl_3$) δ 0.9–1.1 (3 H, d, CH_3), 1.1–1.7 (10 H, m, cyclohexyl), 1.8–2.6 (3 H, m, CH, CH_2), 6.3–6.7 (1 H, broad, D_2O-exchangable, NH); ^{13}C NMR ($CDCl_3$) δ 14.37 (CH_3), 22.22, 23.32, 25.41, 31.77 (CH_2), 36.96 (CH), 38.12, 39.70 (CH_2), 60.97 (C), 178.93 (C=O, lactam); mass spectrum *m/e* (rel inten) 167 (M^+, 32), 124 (100), 111 (20), 96 (8) and other peaks; mol wt calcd for $C_{10}H_{17}NO$ 167.1310, found 167.1315 (high-resolution mass spectrometry).

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Supplementary Material Available: Copies of ^1H NMR spectra of compounds **8, 11, 12, 17, 19, 20, 21 + 22, 24, 25–26, 28, 30, 32,** and **34–36** (21 pages). This material is contained in libraries in 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.