Methylbenzene Cation Radical α-Fragmentation Selectivities Revealed in SET-Photoadditions of p-Xylene Derivatives to 1,4-Dicyanonaphthalene

Nicola d'Alessandro and Angelo Albini

Department of Organic Chemistry, University of Pavia, Pavia, Italy I-27100, and Institute of Organic Chemistry, University of Torino, Torino, Italy I-10125

Patrick S. Mariano*

Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742

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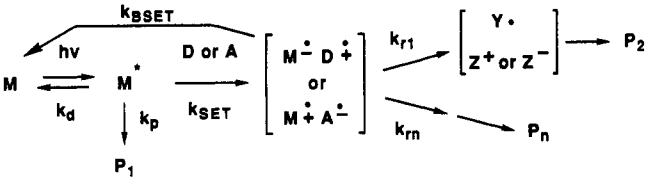
SET-promoted photoreactions of selected *p*-xylene derivatives, including *p*-xylene (**3a**), *p*-phenylenediacetic acid (**3b**), *p*-bis[(trimethylsilyl)methyl]benzene (**3c**), *p*-[(trimethylsilyl)methyl]toluene (**3d**), *p*-tolylacetic acid (**3e**), and *p*-[(trimethylsilyl)methyl]phenylacetic acid (**3f**), to 1,4-dicyanonaphthalene have been investigated. These processes lead to clean and selective formation of 1:1 adducts whose nature is controlled by α-heterolytic fragmentation reactions occurring at benzylic positions of arene cation radicals which serve as key reactive intermediates. The results indicate that the relative rates of cation radical fragmentations of the type ($[ArCH_2E]^{\bullet+}$ + B: → $ArCH_2^{\bullet}$ + BE) depend on the nature of the electrofugal group, E, in the following order: E = $SiMe_3$ > CO_2H > H. The experimental basis for these conclusions is discussed.

Introduction

Interest in photochemical processes promoted by single electron transfer (SET) in the excited-state manifold has continued to grow in recent years.[1] Results from studies probing both mechanistic and synthetic issues have combined with those focusing on factors governing SET rates and the detailed nature of ion radical intermediates to provide a fundamental understanding of SET-photochemical reactions. In their most simple form, sequences followed in SET-photochemical processes (Scheme I) involve (1) SET to or from an excited-state acceptor or donor (M*) from or to a ground-state donor (D) or acceptor (A), (2) secondary reactions of the ion radical intermediates leading to radical and/or charged intermediates, and (3) reactions of these intermediates leading to product P_2 formation. The quantum and chemical efficiencies of SET-photochemical processes following these sequences are dependent upon the rates of a number of competing pathways. For example, the quantum efficiency for SET-product (P_2) formation is governed by partitioning of M* to ion radical intermediates in a manner dependent on the intrinsic lifetime of the excited species ($1/(k_d + k_p)$), the concentration of A or D, and the rate constant k_{SET}. In addition, the competition between secondary reactions of the ion radical intermediates (k_{r_1} + ... k_{r_n}) and their return to ground-state reactants by back-electron transfer (k_{BSET}) influences efficiencies Finally, for high chemical yields and selectivities the ion radical intermediates in the SET-promoted photoreactions must be transformed cleanly (i.e., $k_{r_1} > k_{r_n}$) to neutral radical and/or charged precursors of P_2.

Both theory[2] and experiment[3] have provided important and useful information about the factors that govern rate

Scheme I



constants for SET in ground- and excited-state systems as well as in short-lived ion radical pairs.[4] Consequently, it is possible to evaluate how quantum efficiencies of SET-photochemical processes will vary with the redox potentials and energies of the donor–acceptor pairs (M* + D or M* + A) which govern k_{SET} and with the energies, multiplicities (singlet vs triplet), and nature (contact or solvent separated) of the ion radical pairs which control k_{BSET}. In contrast, less is known about the relative and absolute rates of ion radical reactions. Yet knowledge about the dynamics of these processes and how rates respond to alterations in electronics, structure, substituents, and media are key to predicting new, efficient, and selective SET-photochemistry.[5]

Ion radical intermediates, formed in the solution phase, can react by a number of interesting and predictable[6] pathways owing to their ionic and radical characters. Perhaps the most common of these reactions is α-heterolytic fragmentation, involving loss or transfer of an electrofugal group (E^+) from cation radicals resulting in generation of conjugated, neutral radicals (Scheme II). Amine or arene cation radical α-deprotonations,[7,8] desi-

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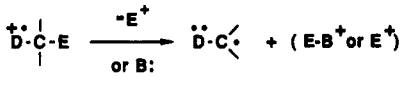
Scheme II

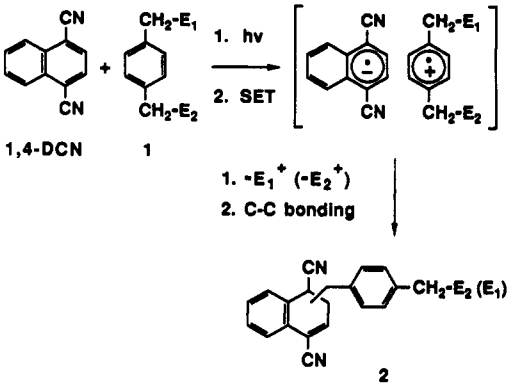


lylations,[9] decarboxylations,[10] and retro-Aldol-like cleavages[11] are among the most general fragmentation processes of this type.

In only a few cases have the dynamics of these ion radical fragmentations been scrutinized. Understandably, greatest attention in this area has been given to radical cation α-deprotonation. This has resulted in knowledge about absolute rates[8a,12,13] and how they respond to base strength,[13] cation radical energies,[8a] and steric[7a] and electronic[14] effects. Recent investigations of α-trialkylsilyl-substituted cation radical desilylations promoted by nucleophilic attack on silicon have shown that these processes are fast[15,16] and, depending on silicon substituents, cation radical structures, and reaction media, they are competitive with or dominant over cation radical α-deprotonation and radical coupling.[9,14b,17]

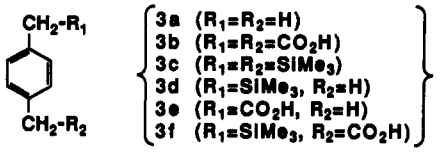
Recently, we initiated a program designed to gain detailed information about the relative and absolute[18] rates of a variety of cation radical α-heterolytic fragmentation reactions. A convenient method for evaluating relative rates of processes of this type is through analysis of product distributions from reactions in which competitive fragmentation pathways are available to cation radical intermediates. Processes used for this purpose must have bone fide SET-mechanisms and must lead to clean and efficient formation of products whose identities can be correlated with specific ion radical fragmentations. In this regard, a number of studies by Albini and his co-workers[19] have shown that methylarene and related electron donors undergo clean SET-promoted photoadditions to 1,4-dicyanonaphthalene (1,4-DCN). Methylarene cation radicals serve as intermediates in these reactions; their α-deprotonation is followed by radical pair coupling to produce dihydronaphthalene adducts (Scheme III). On the basis of the sound precedent found in this work, we have developed a potentially useful method for evaluating the relative rates of cation radical α-heterolytic fragmentation. This method employs photoadditions of unsymmetrically substituted *p*-xylene derivative **1** to 1,4-DCN and analysis of the dihydronaphthalene adducts **2** produced (Scheme III). Below, we describe the results of preliminary studies exploring this methodology and qualitatively evaluate the relative rates of arene cation radical α-deprotonation, α-desilylation, and α-decarboxylation.

Scheme III



Results

***p*-Xylene Derivatives.** The *p*-xylene derivatives employed in these photochemical studies include *p*-xylene (**3a**), *p*-phenylenediacetic acid (**3b**), *p*-bis[(trimethylsilyl)-methyl]benzene (**3c**), *p*-[(trimethylsilyl)methyl]toluene (**3d**), *p*-tolylacetic acid (**3e**), and *p*-[(trimethylsilyl)methyl]-phenylacetic acid (**3f**). The arenes **3c**[20] and **3d**[21] were



prepared by known procedures, and **3a**, **3b**, and **3e** are commercial materials. The silylphenylacetic acid derivative **3f** was synthesized by the sequence shown in Scheme IV and described fully in the Experimental Section.

Photoreactions of the *p*-xylenes **3a–f** and 1,4-DCN were conducted by irradiation of 1:1 MeCN–MeOH solutions in a preparative apparatus by using Pyrex-filtered light ($\lambda > 290$ nm). In each case an ca. 3–10 molar equiv excess of the *p*-xylene was used. In each case, the crude photolysate was subjected to ^{1}H NMR analysis to show that minor photoadducts were not present in >ca. 5%. Adduct yields obtained are based upon consumed 1,4-DCN and are for materials purified by silica gel chromatography.

In order to prepare and identify the adducts that could be generated in photoadditions of the unsymmetrically substituted *p*-xylene derivatives **3d–f** to 1,4-DCN, photoreactions with the symmetric H-, CO_2H-, and $SiMe_3$-

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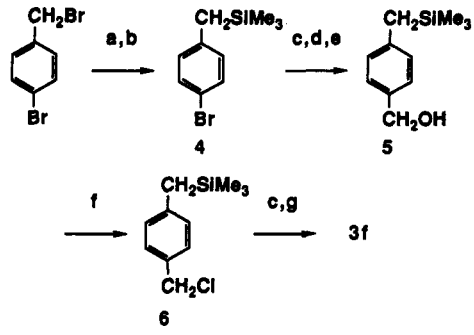
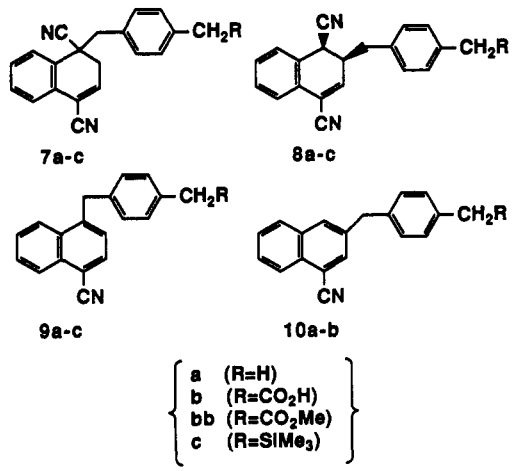
Scheme IV[a]



[a] Key: (a) Mg, Et_2O; (b) Me_3SiCl; (c) Mg, THF; (d) HCHO; (e) $NaBH_4$; (f) HCl (concd); (g) CO_2.

substituted analogs, **3a–c**, were first explored. Irradiation of a 1,4-DCN and *p*-xylene (**3a**) solution in MeOH–MeCN led to production of the dihydronaphthalene adducts **7a** and **8a** in respective yields of 75% and 12% along with the naphthalene derivative **9a** (3%). The structural and stereochemical assignments to these compounds were made by comparison of their spectroscopic properties to those of closely related materials prepared in earlier efforts.[19] The dihydronaphthalenes **7a** and **8a** were smoothly (ca. 90%) converted to the corresponding naphthalenes **9a** and **10a** by dehydrocyanation with 10% KOH–EtOH at reflux.



In a similar fashion irradiation of a solution of the diacetic acid derivative **3b** and 1,4-DCN led to clean formation of adducts. In this case, it was more convenient to isolate the acid products as their methyl ester derivatives, formed by treatment of the crude photolysates with HCl–MeOH. This gave the dihydronaphthalene esters **7bb** and **8bb** in 55% and 20% respective isolated yields. These esters upon hydrolysis with H_2SO_4 in aqueous THF furnished (73–83%) the corresponding acids **7b** and **8b** which in turn could be converted (74–86%) to the naphthalene acids **9b** and **10b** by dehydrocyanation (10% KOH–EtOH).

The bis-silyl xylene derivative **3c** also undergoes photoaddition to 1,4-DCN to generate the silyldihydronaphthalenes **7c** (65%) and **8c** (<10%, impure). Finally, **7c** can be converted to naphthalene **9c** by treatment with 10% KOH–EtOH at reflux.

With the adducts expected from photoadditions of the unsymmetrically substituted *p*-xylenes **3d–f** to 1,4-DCN fully characterized, it was then possible to probe these processes in order to determine the nature and distributions of products and, thus, to evaluate how the electrofugal groups and reaction conditions influence the relative rates of cation radical α-heterolytic fragmentations. As the results described below show, photoadditions of *p*-xylenes **3d–f** to 1,4-DCN are clean processes leading to selective and high-yielding production of adducts. For example, irradiation of 1:1 MeOH–MeCN solutions of 1,4-DCN and the monosilylxylene **3d** (α-condition) followed by chromatography gives the dihydronaphthalenes **7a** and **8a** in 42% and 38% respective yields, along with the naphthalene derivative **9a** (20%). With the intent of determining the effect of base on this reaction, irradiation was carried out on a 1,4-DCN and **3d** solution in 1:1 MeOH–MeCN containing 0.1 M nBu_4NOH (β-condition). This led to production of the naphthalenes **9a** (50%) and **10** (25%). To confirm that base has no effect on the nature of this photoreaction, the photolysate obtained from irradiation of a 1:1 MeOH–MeCN solution of 1,4-DCN and **3d** was treated with nBu_4NOH (0.1 M final concentration) and stirred for 2 h prior to workup (γ-condition) and chromatographic separation. Under these conditions, **9a** and **10a** were again produced in 55% and 22% yields, respectively.

Likewise, photoadditions of 1,4-DCN and the tolylacetic acid **3e** proceed with high chemical selectivities both in the presence and absence of base. Accordingly, irradiation of a 1:1 MeOH–MeCN solution of these substances (α-condition) leads to the adducts **7a**, **8a**, and **9a** in respective purified yields of 40%, 15%, and 5%. When 0.1 M nBu_4NOH (β-condition) is present in the solution irradiated, **9a** and **10a** are obtained in respective 45% and 28% yields, which are nearly identical (42% and 20%) to those for the γ-condition (see above).

Unlike the reactions above, those occurring between 1,4-DCN and the silyl acid **3f**, while being highly selective, are dependent of the photoreaction conditions used. For example, irradiation of a 1:1 MeOH–MeCN solution of these substances (α-condition) gives the dihydronaphthalene acids **7b** and **8b** (55% and 25%, respectively) exclusively. Careful analysis failed to reveal the presence of silicon-containing adducts **7c** or **8c**, in the photolysate formed under these conditions. In contrast, the silylnaphthalene derivative **9c** (41%) is generated along with only a trace quantity (5%) of the acid analogs **9b** and **10b** when irradiation of the 1,4-DCN and **3f** mixture is carried out on 1:1 MeOH–MeCN solutions containing 0.1 M nBu_4NOH (β-condition). Finally, employment of the γ-condition to conduct this reaction provides the naphthalene acids **9b** and **10b** in 45% and 15% yields, respectively. The results of these photoreactions are accumulated in Table I.

Discussion

The results presented above show that SET-promoted photoadditions of the xylene derivative **3a–f** to 1,4-DCN are efficient and highly selective processes resulting in the formation of 1- and 2-substituted (arylmethyl)-dihydronaphthalene adducts. On the basis of the sound precedent established in earlier investigations of toluene and related arene photoadditions to 1,4-DCN[19] it is certain that the mechanistic pathways followed in these process, as depicted in Scheme III, involve (1) SET from the arene to the singlet excited state of 1,4-DCN, (2) transfer of the electrofugal group of the arene cation radical to solvent

Table I. Results from Photoreactions of 1,4-DCN with the p-Xylene Derivatives 3a–f

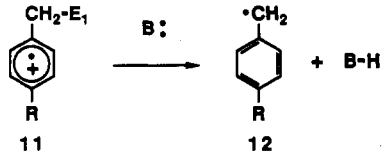
p-xylene deriv	reactn condns	products (% yields)[a]
3a	α[b]	7a (75), 8a (12), 9a (3)
3b	α	7b (55), 8b (25)
3c	α	7c (65), 8c (10)
3d	α	7a (42), 8a (38), 9a (20)
3d	β[c]	9a (50), 10a (25)
3d	γ[d]	9a (55), 10a (22)
3e	α	7a (40), 8a (15), 9a (5)
3e	β	9a (45), 10a (28)
3e	γ	9a (42), 10a (20)
3f	α	7b (55), 8b (25)
3f	β	9c (41), 9b + 10b (5%)
3f	γ	9b (45), 10b (15)

[a] Yields are for isolated, pure materials and are based upon reacted 1,4-DCN. [b] α-Condition involves irradiation in 1:1 MeOH–MeCN. [c] β-Condition involves irradiation in 0.1 M nBu_4NOH in 1:1 MeOH–MeCN solution. [d] γ-Condition involves irradiation in 1:1 MeOH–MeCN solution followed by treatment of the photolysate with 0.1 M nBu_4NOH.

or the 1,4-DCN anion radical, and (3) radical pair or radical–radical anion coupling. Consequently, the products obtained from reactions of the unsymmetrically substituted xylene derivatives **3d–f** reflect the preferences for α-heterolytic fragmentations in the cation radical intermediates. Moreover, the selective formation of adducts in photoreactions of **3d–f** demonstrates that large rate differences exist for electrofugal group loss from the benzylic centers of arylmethyl cation radicals in the order $-SiMe_3^+ > -(CO_2 + H^+) > -H^+$. The observation that <5% of products results from the competitive fragmentation mode in each case suggests that the rates differ between members of this series by >10.

These results both confirm and extend earlier observations made in studies of arylmethane and arylmethylsilane photoaddition and photocyclization reactions with iminium salt acceptors.[9b-d] Importantly, we are now able to conclude that decarboxylation ($-CO_2 - H^+$) of cation radicals derived from arylacetic acids is slower than loss of a trimethylsilyl group but faster than deprotonation of analogous positively charged radical intermediates. Furthermore, as observed earlier desilylation involving transfer of a trimethylsilyl group to solvent (MeOH)[9,16,17] is faster than benzylic deprotonation. In MeOH–MeCN, the proton is likewise transferred to MeOH.[22] Indeed, the nearly invariant 1- to 2-naphthalene product distributions observed suggest that the C–C bond-forming step in each of these reactions is the same (i.e., radical–radical anion coupling). In contrast, the 1- to 2-naphthalene product ratio is much smaller for photoadditions occurring in pure MeCN where the benzylic proton of the arene cation radical is transferred to the 1,4-DCN anion radical and product formation is by neutral radical-pair coupling.

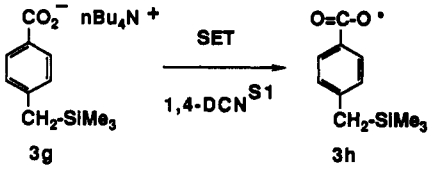
It is important to note that the three α-heterolytic fragmentation reactions open to the cation radicals **11** derived from **3d–f** result in generation of nearly isoenergetic benzylic radicals **12**. Thus, the differences in the rates of these reactions must be governed by the nature of the cation fragment lost (i.e., C–E bond energies) and the bond being formed to the migrating electrofugal groups (i.e., E–B bond energies) and not those of the resulting carbon-centered radicals. In the absence of added base, both the decarboxylation and deprotonation processes



11 12

involve transfer of a proton to MeOH. However, in the former case CO_2 is formed most probably in concert with this proton transfer. This difference could account for a greater thermodynamic driving force and, thus, kinetic preference for decarboxylation over direct deprotonation involving cleavage of a benzylic C–H bond. Desilylation of the arylmethylsilane cation radical differs from the above fragmentations since when the TMS group is transferred to methanol a strong Si–O bond is formed, contributing to the larger driving force of this process.

The opposite chemoselectivities observed for the photoadditions of the silylphenylacetic acid **3f** to 1,4-DCN run under neutral and basic conditions are intriguing. Specifically, the exclusive formation of non-TMS adducts **7b** and **8b** or **9b** and **10b** from reactions promoted by irradiation of neutral MeOH–MeCN solutions is nearly completely reversed when 0.1 M nBu_4NOH is present in the photoreaction medium. The source of his difference could be due to an electrofugal group loss ranking of $-CO_2 > -SiMe_3^+ > -(CO_2 + H^+)$. However, a more reasonable explanation of these differences surfaces when consideration is given to the nature of the SET-donor under basic conditions. Accordingly, in 0.1 M base, **3f** exists exclusively as the carboxylate salt **3g**. Electron transfer from **3g** to the 1,4-DCN singlet likely occurs from the carboxylate rather than the arene center owing to the large differences which exist between the oxidation potentials of carboxylic acid anions (ca. +1.0 V) and arenes (ca. 1.8–2.0 V).[6] This gives the carboxy radical **3h**, a species which is known[23] to have an exceptionally short lifetime owing to its rapid expulsion of CO_2.



3g 3h

The results presented above further demonstrate the utility of product distribution studies as a method for qualitatively assesing the relative rates of cation radical reactions. Studies combining this technique with direct absolute rate measurements are continuing with the aim of developing a general understanding of the dynamics of cation radical α-heterolytic fragmentation reactions.

Experimental Section

General. ^1H and ^{13}C NMR spectra were recorded on $CDCl_3$ solutions, and chemical shifts are reported in ppm relative to Me_4Si. Column chromatographic separations employed Merck-EM type 60 (230–400 mesh) silica gel and preparative TLC was performed on Merck-EM type 60 GF-254 silica gel coated plates. All reactions were performed under N_2. Drying of all organic layers in workup of reaction mixtures was by use of $MgSO_4$. nBu_4NOH (1.0 M MeOH solution), *p*-xylene (**3a**), *p*-phenylenediacetic acid (**3b**), and *p*-tolylacetic acid (**3e**) are commercial materials (Aldrich), and *p*-bis[(trimethylsilyl)methyl]benzene (**3c**)[20] and *p*-[(trimethylsilyl)methyl]toluene (**3d**)[21] were prepared according

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to the published procedures. The purities of all substances prepared in this study were judged to be >95% by ^1H and ^{13}C NMR analysis.

All photochemical reactions were performed by using N_2-purged MeCN–MeOH solutions (100 mL) of 1,4-dicyanonaphthalene (1,4-DCN) (180 mg, 1 mmol) containing the arene substrate in an immersion well apparatus with a 450-W medium-pressure lamp and Pyrex glass filter. Workup of the photolysates involved concentration in vacuo and chromatographic separation. The yields recorded for the photoreactions are based on consumed 1,4-DCN.

Preparation of *p*-[(Trimethylsilyl)methyl]phenylacetic Acid (3f). *p*-[(Trimethylsilyl)methyl]bromobenzene (4). To a suspension of 3.0 g (0.12 g-at) of Mg-turnings in 100 mL of Et_2O was added a solution of 30 g (0.12 mol) of *p*-bromobenzyl bromide (Aldrich) in 200 mL of Et_2O. To the resulting Grignard reagent was added 26 g (31 mL, 0.24 mol) of chlorotrimethylsilane (Aldrich), and the resulting mixture was stirred at 25 °C for 12 h. Addition of ice–water followed by separation, drying, and concentration of the mixture gave an oil which was subjected to molecular distillation (0.05 mm, 40 °C) to yield 19.8 g (68%) of the silylbromoarene 4 as an oil: ^1H NMR 0.04 (s, 9 H, $SiMe_3$), 2.06 (s, 2 H, CH_2), 6.90 and 7.35 (ABq, J = 7.5 Hz, 4 H, aromatic); ^{13}C NMR –2.0 ($SiMe_3$), 26.6 (CH_2), 117.4, 139.5 (quart arom), 129.6, 131.1 (CH arom); HRMS m/z 242.0126 ($C_{10}H_{15}BrSi$ requires 242.0086).

***p*-[(Trimethylsilyl)methyl]benzyl Alcohol (5).** To a suspension of 2 g (0.08 g-at) of Mg-turnings in 50 mL of THF was added solution of 19.8 g (0.08 mol) of bromide 4 in 100 mL of THF. To the formed Grignard reagent was added formaldehyde (gas, generated from heating paraformaldehyde at 180–200 °C under an N_2 stream). The resulting mixture was stirred at 25 °C for 8 h and diluted with a mixture of ether and ice–water. The organic layer was separated, dried, and concentrated giving an oil from which excess formaldehyde was removed by treatment with $NaBH_4$. The resulting mixture was dissolved in ether, washed with an aqueous HCl, dried, and concentrated giving benzyl alcohol 5 (10.2 g, 65%) as an oil and judged to be sufficiently pure (>95%) to be used in the next process: ^1H NMR 0.02 (s, 9 H, $SiMe_3$), 2.12 (s, 2 H, CH_2), 4.6 (s, 2 H, CH_2), 7.00, 7.22 (ABq, J = 8.0 Hz, 4 H, arom).

***p*-[(Trimethylsilyl)methyl]benzyl Chloride (6).** A solution of the benzyl alcohol 5 (13 g, 0.07 mol) in 100 mL of concd HCl was stirred at 0 °C for 3 h. Extraction of the mixture with ether, separation, drying, and concentration of the ether layer gave an oil which was subjected to column chromatography (cyclohexane) giving an oil which was then subjected to molecular distillation (0.2 mm, 75 °C) to give the benzyl chloride 6 (7.4 g, 66%) as an oil: ^1H NMR 0.05 (s, 9 H, $SiMe_3$), 2.15 (s, 2 H, CH_2), 4.61 (s, 2 H, CH_2), 7.02, 7.27 (ABq, J = 8.0 Hz, 4 H, arom); ^{13}C NMR –2.0 ($SiMe_3$), 26.9 (CH_2Si), 46.5 (CH_2Cl), 128.2, 128.5 (arom CH), 132.9, 141.0 (arom quart); HRMS m/z 212.0791 ($C_{11}H_{17}ClSi$ requires 212.0788).

***p*-[(Trimethylsilyl)methyl]phenylacetic Acid (3f).** To the Grignard reagent prepared from 1.0 g (41 mg-at) of Mg and benzyl chloride 6 (7.4 g, 35 mmol) in 150 mL of THF was bubbled CO_2 for 12 h. The mixture was diluted with an ice–2 N HCl solution and extracted with ether. The ethereal extracts were dried and concentrated to give a residue which was subjected to column chromatography on silica gel (1:1 cyclohexane–iPrOH) to give 2.4 g (31%) of the phenylacetic acid 3f as an oil: ^1H NMR –0.05 (s, 9 H, $SiCH_3$), 2.05 (s, 2 H, CH_2Si), 3.60 (s, 2 H, CH_2), 6.9 and 7.1 (ABq, J = 8.0 Hz, 4 H, arom); ^{13}C NMR –1.9 ($SiCH_3$), 26.7 (CH_2Si), 40.6 (CH_2), 128.2 and 129.1 (arom CH), 128.6 and 139.6 (arom quart), 178.0 (CO_2H); HRMS m/z 222.1067 ($C_{12}H_{18}O_2Si$ requires 222.1076).

Photoaddition of *p*-Xylene (3a) to 1,4-DCN. Irradiation of a solution of 1,4-DCN (180 mg, 1.0 mmol) and *p*-xylene (3a) (1.30 g, 12.2 mmol) in 100 mL of 1:1 MeOH–MeCN followed by workup and silica gel column chromatography (hexane–EtOAc) under the general conditions described above gave 144 mg (75%) (mp 73–76 °C, MeOH) of 1-[(4-methylphenyl)methyl]-1,2-dihydronaphthalene-1,4-dicarbonitrile (7a), 23 mg (12%) (mp 147–148 °C, MeOH) of 2-[(4-methylphenyl)methyl]-1,2-dihydronaphthalene-1,4-dicarbonitrile (8a), and 5 mg (3%) (mp 88–89 °C, cyclohexane) of 4-[(methylphenyl)methyl]naphthalene-1-carbonitrile (9a), all as crystalline substances.

7a: ^1H NMR 2.32 (s, 3 H, CH_3), 2.89 (dd, J = 18.0 and 4.0 Hz, 1 H, ABX-CH_2), 2.96 (dd, J = 18.0 and 6.0 Hz, 1 H, ABX CH_2), 2.87 and 2.99 (ABq, J = 14.0 Hz, 2 H, Ar-CH_2), 6.76 (dd, J = 4.0 and 6.0 Hz, 1 H, C=CH), 6.91–7.08 (ABq, J = 8.0 Hz, 4 H, C_6H_4), 7.35 and 7.43 (m, 3 H, arom), 7.58 (d, J = 7.0 Hz, 1 H, arom-H_5); ^{13}C NMR 21.1 (CH_3), 32.4 (CH_2), 41.9 (C-1), 43.4 (Ph CH_2), 114.9 and 115.8 (CN), 121.5, 125.9, 126.4, 127.3, 129.2, 129.3, 130.3, 130.7, 132.1, 127.6, 127.9 (arom and vinyl). Anal. Calcd for $C_{20}H_{16}N_2$: C, 84.48; H, 5.67; N, 9.85. Found: C, 84.28; H, 5.34; N, 10.09.

8a: ^1H NMR 2.35 (s, 3 H, CH_3), 2.83 and 3.12 (m, 2 H, $ArCH_2$), 3.08 (m, 1 H, CH), 3.95 (d, J = 8.5 Hz, 1 H, NCCH), 6.63 (d, J = 4.0 Hz, 1 H, C=CH), 7.08 and 7.15 (ABq, J = 8.0 Hz, 4 H, C_6H_4), 7.3–7.6 (m, 4 H, arom); ^{13}C NMR 21.0 (CH_3), 34.2 (CH), 36.1 (CH_2), 39.0 (CH), 114.8 and 115.7 (CN), 117.2, 125.9, 127.4, 128.0, 128.8, 129.6, 130.4, 133.5, 137.0, 143.8 (arom and vinyl). Anal. Calcd for $C_{20}H_{16}N_2$: C, 84.48; H, 5.67; N, 9.85. Found: C, 84.00; H, 5.20; N, 9.85.

9a: ^1H NMR 2.30 (s, 3 H, CH_3), 4.55 (s, 2 H, $ArCH_2$), 7.06 and 7.12 (ABq, J = 8.0 Hz, 4 H, C_6H_4), 7.32 (d, J = 7.5 Hz, 1 H, H-3), 7.50–7.70 (m, 2 H, arom), 7.85 (d, J = 7.5 Hz, 1 H, H-2), 8.13 (d, J = 8.5 Hz, 1 H, H-8), 8.27 (d, J = 8.5 Hz, 1 H, H-5); ^{13}C NMR 21.0 (CH_3), 38.8 (Ar CH_2), 109.0 (C-1), 118.1 (CN), 124.9, 125.9, 126.2, 127.6, 128.2, 128.6, 129.4, 131.8, 132.4, 132.7, 136.0, 136.2, 143.5 (arm); HRMS m/z 257.1198 ($C_{19}H_{15}N$ requires 257.1204).

Dehydrocyanations of Adducts 7a and 8a. The photoadducts 7a and 8a from 1,4-DCN and *p*-xylene (20 mg, 0.07 mmol) were independently reacted in 10% KOH in ethanol (20 mL) solutions at reflux for 2 h. Each mixture was diluted with saturated aqueous NH_4Cl and extracted with CH_2Cl_2. Concentrations of the CH_2Cl_2 layers after drying gave the xylylnaphthalenes **10a** (from 8a, 16 mg, 90%, mp 107–108 °C, methanol) and **9a** (from 7a, 16 mg, 90%).

10a: ^1H NMR 2.30 (s, 3 H, CH_3), 4.12 (s, 2 H, $ArCH_2$), 7.10 and 7.15 (ABq, J = 8.0 Hz, 4 H, C_6H_4), 7.55–7.90 (m, 5 H, arom), 8.18 (d, J = 8.0 Hz, 1 H, H-5); ^{13}C NMR 21.0 (CH_3), 41.0 ($ArCH_2$), 110.3 (C-1), 117.8 (CN), 124.9, 127.6, 127.9, 128.3, 128.8, 129.5, 131.0, 132.3, 133.1, 134.1, 136.3, 136.4, 138.5 (arom). Anal. Calcd for $C_{19}H_{15}N$: C, 88.68; H, 5.88; N, 5.44. Found: C, 88.55; H, 5.63; N, 5.55.

Photoaddition of 1,4-Phenylenediacetic Acid (3b) to 1,4-DCN. Irradiation of a 1:1 MeOH–MeCN solution of 1,4-DCN and the diacetic acid derivative **3b** (1.0 g, 5.0 mmol) for 1.5 h followed by workup by using the general condition described above gave a residue which was dissolved in an HCl–MeOH solution which was then stirred at reflux for 2 h and concentrated. The residue upon silica gel chromtography (hexane–EtOAc) provided the photoadduct methyl ester derivatives **7bb** (122 mg, 55%, oil) and **8bb** (44 mg, 20%, oil).

Acid hydrolysis of the esters **7bb** and **8bb** (20 mg, 0.06 mmol, H_2SO_4 in aqueous THF, reflux, 3 h) gave the respective carboxylic acids **7b** (12 mg, 78%, mp 147–148 °C, methanol) and **8b** (15 mg, 83%, mp 136–137 °C, methanol).

Dehydrocyanation reactions of the acids **7b** and **8b** (20 mg, 0.06 mmol, 10% KOH–EtOH, reflux 2 h, workup with saturated aqueous NH_4Cl) gave the respective naphthalene carboxylic acids **9b** (15 mg, 86%, mp 157–160 °C, methanol) and **10b** (13 mg, 74%, mp 150–155 °C, methanol).

7bb: ^1H NMR 2.82 (dd, J = 18.0, 3.0 Hz, 1 H, H-2), 2.96 (dd, J = 18.0, 6.5 Hz, 1 H, H-2), 2.90 and 3.03 (ABq, J = 13.0 Hz, 2 H, $ArCH_2$), 3.63 (s, 2 H, CH_2CO_2), 3.71 (s, 3 H, OCH_3), 6.79 (dd, J = 3.0, 6.5 Hz, 1 H, H-3), 7.01 and 7.22 (ABq, J = 8.0 Hz, 4 H, C_6H_4), 7.38 (d, J = 4.0 Hz, 1 H, H-8), 7.4–7.5 (m, 2 H, arom), 7.60 (d, J = 7.5 Hz, 1 H, H-5). Anal. Calcd for $C_{22}H_{18}N_2O_2$: C, 77.17; H, 5.30; N, 8.18. Found: C, 77.01; H, 5.15; N, 8.20.

8bb: ^1H NMR 2.85–3.18 (m, 2 H), 3.05–3.18 (m, 1 H, H-2), 3.64 (s, 2 H, CH_2CO_2), 3.72 (s, 3 H, OCH_3), 3.98 (d, J = 8.5 Hz, 1 H, H-1), 6.69 (d, J = 4.0 Hz, 1 H, H-3), 7.13 and 7.29 (ABq, J = 8.0 Hz, 4 H, C_6H_4), 7.3–7.6 (m, 4 H, arom). Anal. Calcd for $C_{22}H_{18}N_2O_2$: C, 77.17, H, 5.30; N, 8.18. Found: C, 77.12; H, 5.22; N, 8.35.

7b: ^1H NMR 2.82 (dd, J = 18.0, 3.0 Hz, 1 H, H-2), 2.96 (dd, J = 18.0, 6.5 Hz, 1 H, H-2), 2.90 and 3.03 (ABq, J = 13.0 Hz, 2 H, $ArCH_2$), 3.65 (s, 2 H, CH_2CO_2), 6.79 (dd, J = 3.0, 6.5 Hz, 1 H,

H-3), 7.01 and 7.22 (ABq, J = 8.0 Hz, 4 H, C_6H_4), 7.38 (m, 1 H, H-8), 7.4–7.5 (m, 2 H, H-6, H-7), 7.6 (D, J = 7.5 Hz, 1 H, H-5); ^{13}C NMR 32.4 (C-2), 40.5 (CH_2CO_2), 41.7 (C-1), 43.3 ($ArCH_2$), 114.9 (CN), 115.8 (CN), 121.4, 126.0, 126.3, 127.3, 129.5, 130.4, 131.8, 132.9, 133.0, 137.8 (arom and vinyl), 176.8 (CO_2H). Anal. Calcd for $C_{21}H_{16}N_2O_2$: C, 76.81; H, 4.91; N, 8.53. Found: C, 76.56; H, 4.75; N, 8.65.

8b: ^{1}H NMR 2.86 and 3.18 (m, 2 H, CH_2), 3.03–3.18 (m, 1 H, H-2), 3.67 (s, 2 H, CH_2CO_2), 3.98 (d, J = 8.5 Hz, 1 H, H-1), 6.68 (d, J = 4.0 Hz, 1 H, H-3), 7.18 and 7.27 (ABq, J = 8.0 Hz, 4 H, C_6H_4), 7.3–7.6 (m, 4 H, arom); ^{13}C NMR 34.0 (C-2), 36.0 ($ArCH_2$), 38.6 (C-1), 40.4 (CH_2CO_3) 114.8 (CN), 115.6 (CN), 117.1, 125.7, 127.0, 127.8, 127.9, 129.1, 129.7, 129.9, 130.4, 132.3, 135.6, 143.4 (arom and vinyl), 176.8 (CO_2H). Anal. Calcd for $C_{21}H_{16}N_2O_2$: C, 76.81; H, 4.91; N, 8.53. Found: C, 76.85; H. 4.83; N, 8.35.

9b: ^{1}H NMR 3.62 (s, 2 H, CH_2CO_2), 4.48 (s, 2 H, $ArCH_2$), 7.13 and 7.22 (ABq, J = 8.0 Hz, 4 H, C_6H_4), 7.31 (D, J = 7.5 Hz, 1 H, H-3), 7.55–7.70 (m, 2 H, H-6, H-7), 7.86 (d, J = 7.5 Hz, 1 H, H-2), 8.09 (d, J = 8.5 Hz, 1 H, H-8), 8.29 (d, J = 8.5 Hz, 1 H, H-5); ^{13}C NMR 38.8 ($ArCH_2$), 40.5 (CH), 40.5 (CH_2CO_2H), 109.1 (C-1), 118.0 (CN), 124.9, 125.9, 126.4, 127.7, 128.2, 129.0, 129.7, 131.7, 132.4, 132.6, 138.3 (arom), 177.4 (CO_2H); HRMS m/z 301.1107 ($C_{20}H_{15}NO_2$ requires 301.1103).

10b: ^{1}H NMR 3.65 (s, 2 H, CH_2CO_2H), 4.13 (s, 2 H, $ArCH_2$), 7.15 and 7.28 (ABq, J = 8.0 Hz, 4 H, C_6H_4), 7.55–7.90 (m, 5 H), 8.20 (d, J = 8.0 Hz, 1 H, H-5); ^{13}C NMR 38.8 ($ArCH_2$), 40.5 (CH_2CO_2H), 110.7 (C-1), 117.8 (CN), 125.0, 127.7, 128.0, 128.2, 129.2, 129.7, 131.0, 132.4, 132.4, 133.1, 134.1, 138.1, 138.4 (arom), 172.0 (CO_2H); HRMS m/z 301.1068 ($C_{20}H_{15}NO_2$ requires 301.1103).

Photoaddition of *p*-[(Trimethylsilyl)methyl]benzyltrimethylsilane (3c) to 1,4-DCN. Irradiation of 1:1 MeOH–MeCN solution of 1,4-DCN and the bis-silyl xylene **3c** (1.0 g, 2.8 mmol) for 1.5 h followed by workup by using the general conditions gave after silica gel chromatography (hexanes–EtOAc) 120 mg (65%) of the adduct **7c** as an oil and a fraction containing the adduct **8c** (ca. 10%) contaminated with an inseparable, unidentified impurity. Adduct **7c** was subjected to dehydrocyanation (KOH, EtOH, reflux, 2 h) giving the naphthalene derivative **9c** (86%) as an oil.

7c: ^{1}H NMR 0.02 (s, 9 H, TMS), 2.83 (dd, J = 18.0, 3.0 Hz, 1 H, H-1), 2.95 (dd, J = 18.0, 6.5 Hz, 1 H, H-1), 2.88 and 3.01 (ABq, J = 14.0 Hz, 2 H, $ArCH_2$), 6.78 (dd, J = 3.0, 6.5 Hz, 1 H, H-3), 6.82 and 6.89 (ABq, J = 8.0 Hz, 4 H, C_6H_4), 7.25–7.48 (m, 3 H), 7.58 (d, J = 7.5 Hz, 1 H, H-5); ^{13}C NMR –2.0 ($SiCH_3$), 26.6 (CH_2Si), 32.5 (C-2), 41.8 (C-1), 43.1 ($ArCH_2$), 114.6 (CN), 115.8 (CN), 121.6, 125.7, 126.2, 127.4, 127.9, 129.1, 129.2, 129.7, 130.0, 131.9, 138.0 and 140.2 (arom and vinyl); HRMS m/z 356.1705 ($C_{23}H_{24}NSi$ requires 356.1709).

8c: ^{1}H NMR –0.01 (s, 9 H, $SiCH_3$), 2.05 (s, 2 H, CH_2Si), 2.85 and 3.06 (m, 2 H, $ArCH_2$), 3.00–3.15 (m, 1 H, H-2), 3.95 (d, J = 8.5 Hz, 1 H, H-1), 6.64 (d, J = 4.0 Hz, 1 H, H-3), 7.00 (ABq, J = 8.0 Hz, 4 H, C_6H_4), 7.3–7.6 (m, 4 H).

9c: ^{1}H NMR 0.02 (s, 9 H, $SiCH_3$), 2.07 (s, 2 H, CH_2Si), 4.45 (s, 2 H, $ArCH_2$), 6.96 and 7.05 (ABq, J = 8.0 Hz, 4 H, C_6H_4), 7.32 (d, J = 7.5 Hz, 1 H, H-3), 7.5–7.7 (m, 2 H), 7.86 (d, J = 7.5 Hz, 1 H, H-2), 8.15 (d, J = 8.5 Hz, 1 H, H-8), 8.28 (d, J = 8.5 Hz, 1 H, H-5); ^{13}C NMR –2.0 ($SiCH_3$), 28.5 (CH_2Si), 38.7 ($ArCH_2$), 108.8 (C-1), 118.1 (CN), 124.9, 125.8, 126.1, 127.4, 128.1, 128.3, 128.6, 131.7, 132.3, 132.5, 134.3, 138.7, 143.7 (arom); HRMS m/z 329.1583 ($C_{22}H_{23}NSi$ requires 329.1600).

Photoaddition of (*p*-Methylbenzyl)trimethylsilane (3d) to 1,4-DCN. Irradiation of a 1:1 MeOH–MeCN solution of 1,4-DCN and the (*p*-methylbenzyl)silane **3d** (1.80 g, 10.0 mmol) for 1.5 h followed by the general workup procedure and silica gel chromatography (hexanes–EtOAc) gave adducts **7a** (115 mg, 42%), **8a** (104 mg, 38%), and **9a** (50 mg, 20%). When irradiation was conducted on a 1:1 MeOH–MeCN solution of 1,4-DCN and **3d** containing 0.1 M nBu_4NOH for 1.5 h followed by workup and silica gel column chromatography, the naphthalene derivatives **9a** and **10a** were obtained in 50% and 25% respective yields. Finally, irradiation of a 1,4-DCN and **3d** solution in 1:1 MeOH–MeCN for 1.5 h followed by addition of nBu_4NOH to a concentration of 0.1 M and stirring at 25 °C for 2 h gave after workup **9a** and **10a** in respective yields of 55% and 22%.

Photoaddition of *p*-Methylphenylacetic Acid (3e) to 1,4-DCN. Irradiation of a 1:1 MeOH–MeCN solution of 1,4-DCN and the *p*-tolylacetic acid **3e** (1.50 g, 10.0 mmol) for 1.5 h followed by the general workup procedure and silica gel chromatography (hexanes–EtOAc) gave the adducts **7a** (85 mg, 40%), **8a** (32 mg, 15%), and **9a** (8 mg, 5%). When a solution of 1,4-DCN and **3e** in 1:1 MeOH–MeCN containing 0.1 M nBu_4NOH was irradiated for 1 h followed by acidification (NH_4Cl), workup and silica gel chromatography (hexanes–EtOAc), the naphthalene derivatives **9a** and **10a** were obtained in 45% and 28% respective yields. Finally, when the photolysate obtained by irradiation of 1,4-DCN and **3e** in 1:1 MeOH–MeCN was brought to 0.1 M in nBu_4NOH, stirred for 2 h at 25 °C, and subjected to workup, the naphthalene derivatives **9a** and **10a** were obtained in respective 42% and 20% yields.

Photoaddition of *p*-[(Trimethylsilyl)methyl]phenylacetic Acid (3f) to 1,4-DCN. Irradiation of a 1:1 MeOH–MeCN solution of 1,4-DCN and the silylphenylacetic acid **3f** (1.0 g 4.5 mmol) for 1.5 h followed by concentration gave a residue which was dissolved in HCl–MeOH and stirred at 25 °C for 1.5 h. Concentration of this mixture gave a residue which was chromatographed on silica gel (hexanes–EtOAc) to give the ester derivatives **7bb** (135 mg, 55%) and **8bb** (50 mg, 20%). A 1:1 MeCN solution of 1,4-DCN and **3f** containing 0.1 M nBu_4NOH was irradiated for 45 min, acidified (NH_4Cl), and concentrated to give a residue which was dissolved in HCl–MeOH and stirred at 25 °C for 2 h. Concentration followed by silica gel chromatography and hydrolysis of the individual substances with H_2SO_4 in aqueous THF gave the naphthalene derivative **9c** (26 mg, 41%) and a trace quantity of both **9b** and **10b** (5%). Finally, irradiation of a 1:1 MeOH–MeCN solution of 1,4-DCN and **3f** followed by addition of nBu_4NOH to a concentration of 0.1 M, stirring for 2 h, and workup, followed by esterification and chromatography and hydrolysis as above, gave the naphthalene derivatives **9b** (76 mg, 45%) and **10b** (25 mg, 15%).

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Supplementary Material Available: ^{1}H NMR spectra of **3f**, **4–6**, **7a,c**, and **9a,c** (8 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.