

Photoadditions of Ethers, Thioethers, and Amines to 9,10-Dicyanoanthracene by Electron Transfer Pathways

Eietsu Hasegawa, Martha A. Brumfield, and Patrick S. Mariano*

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

Ung-Chan Yoon

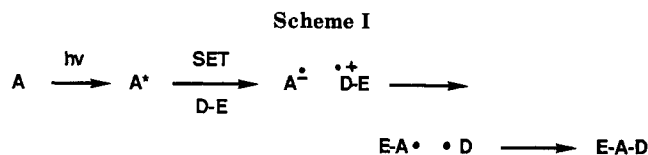
Department of Chemistry, Pusan National University, Pusan, Korea 607

Received July 15, 1988

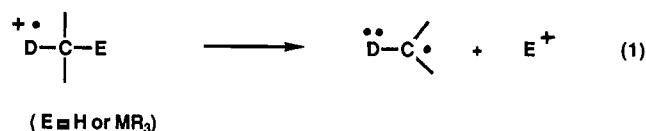
Studies were conducted to explore single electron transfer (SET) induced photoaddition reactions of 9,10-dicyanoanthracene (DCA) with a variety of n-electron donors including silicon-containing substrates (EtOCH₂TMS, EtSCH₂TMS, and Et₂NCH₂TMS). Photoadditions of EtOCH₂TMS and EtSCH₂TMS to DCA in MeCN occur in high yields to produce 10-substituted 9,10-dicyano-9,10-dihydroanthracenes in which the anthracenyl unit is bonded to the ether or thioether in place of the TMS substituent. The photoadducts undergo base-induced dehydrocyanation and oxidation to generate the respective 10-substituted 9-cyanoanthracenes and 10-substituted 10-cyano-9-anthrones. Photoaddition of Et₂NCH₂TMS to DCA in MeCN produces the corresponding dihydroanthracene adduct, which spontaneously dehydrocyanates under the reaction conditions to yield the corresponding 10-substituted 9-cyanoanthracene. This process is inefficient as compared to the O and S analogues; other products from this reaction include 9-cyano-10-aminoanthracene, 9-cyanoanthracene, and 9-cyano-10-methylanthracene. The latter product is shown to arise by secondary photoreaction of the Et₂NCH₂TMS-DCA anthracene adduct. Mechanisms for these photoadditions involving SET from the n donors to DCA⁸¹ followed by selective desilylation of the intermediate cation radicals and radical coupling are proposed. In contrast, photoadditions of Et₂O and THF occur in high yield while that of Et₂NMe to DCA is inefficient. These processes follow sequential electron-transfer-deprotonation pathways. Finally, the α-amino radical, Et₂NCH₂, an intermediate in the DCA + Et₂NCH₂TMS photoreaction, is trapped by added cyclohex-2-en-1-one and its 4,4-dimethyl analogue via routes involving conjugate radical addition. Adduct formation between these enones and Et₂NCH₂TMS represents a novel method for initiating radical addition processes by use of SET photosensitization.

Photochemical processes operating via single electron transfer (SET) mechanisms continue to receive active attention owing to their mechanistic interest¹ and unique synthetic potential.² Reaction pathways in these systems are promoted by thermodynamically and kinetically favorable³ SET occurring between ground and electronic excited states of acceptor-donor pairs. The sequence outlined in Scheme I typifies a photoelectron-transfer process in which ion radical intermediates are formed by SET from a donor to an excited acceptor. Product formation in SET reactions is often governed by secondary processes of the initially formed ion radicals as exemplified in Scheme I by transfer of an electrofugal group, E, between donor cation and acceptor anion radicals.

A vast majority of studies in this area have focused on processes in which the chemistry of cation radical intermediates plays a dominant role in controlling the nature of adducts generated.⁴⁻⁶ Perhaps the most common are reactions of cation radicals that involve proton and metal cation (–SiR₃⁺ or SnR₃⁺) transfer from sites adjacent to the charged radical center (eq 1). Examples of this are



found in photoadditions of heteroatom-centered, n-electron donors including amines,⁷ ethers, and alcohols⁸ as well as in reactions involving olefin⁹ and arene-derived¹⁰ cation radicals.



Acceptors of varying types have been employed in SET-initiated photoprocesses including compounds containing carbonyl, arene, olefin, and iminium cation groupings. Cyanoarenes have played a prominent role in this regard owing to their high excited-state reduction potentials, their participation in aromatic-substitution reactions, and in some cases their ability to act as electron-transfer photosensitizers. A key substance in this class has been 9,10-dicyanoanthracene (DCA), a long wavelength absorbing cyanoarene with a high excited-state reduction potential. Only a few examples exist in which

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(3) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

(4) (a) Davidson, R. S.; Steiner, P. R. *J. Chem. Soc., Perkin Trans. 2*, **1972**, 1357. (b) Kurauchi, Y.; Ohga, K.; Nobuhara, H.; Morita, S. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2711.

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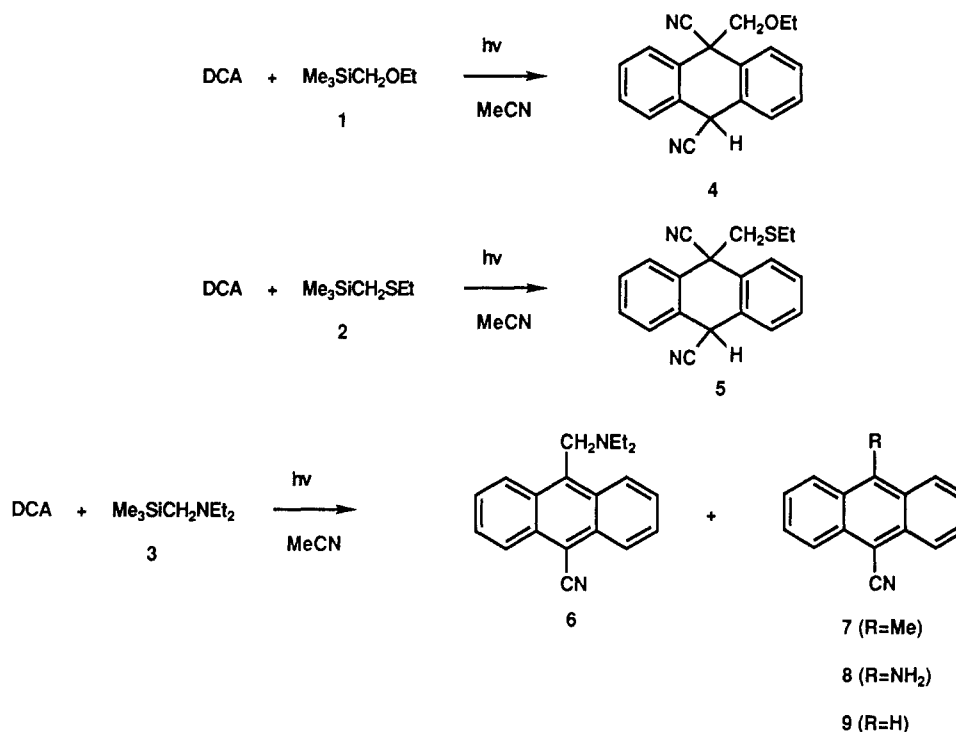
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Scheme II

Table I. Product Yields in Photoreaction of DCA with Amine and Ether n -Electron Donors

n -electron donor	products (yield, %) ^a
$\text{Me}_3\text{SiCH}_2\text{OEt}$ (1)	4 (89)
$\text{Me}_3\text{SiCH}_2\text{SEt}$ (2)	5 (90)
$\text{Me}_3\text{SiCH}_2\text{NEt}_2$ (3)	6 (19), 7 (5), 8 (29), 9 (3)
Et_2O	11 (93)
THF	12 (99)
MeNEt_2	6 (2), 7 (4), 8 (41), 9 (1)

^a Product yields are based upon recovered DCA.

adduct formation occurs upon irradiation of DCA in the presence of electron donors.¹¹

As a result of our interest in developing new photoelectron-transfer processes and in probing mechanistic aspects of these reactions, we have recently initiated a program to investigate the electron-transfer photochemistry of systems comprising α -silyl-substituted, n -electron donors and acceptors of the enone and cyanoarene class. In this report, we describe the results of our exploratory study of the electron-transfer photochemistry of DCA with a variety of n -electron donors. We have found that adduct formation between DCA and these donors is reasonably efficient and that DCA photosensitizes additions of α -silyl amines to α,β -unsaturated ketones.

Results

α -Silyl Ether and Amine Photoadditions to DCA.

Solutions of DCA (saturated, ca. 0.4 mM) in MeCN and the α -silyl ether 1,¹² thioether 2,¹³ and amine 3 (see Experimental Section) (ca. 16.6 mM) were irradiated with flint glass filtered light ($\lambda > 290$ nm) for the time periods

Table II. Chemical Shifts for H-9 in the ¹H NMR Spectra of 9,10-Dihydroanthracene Adducts Arising from Photoaddition of DCA to Ether Donors

adducts	H-9 chemical shifts ^a (relative intensity)
4	5.26 (52), 5.37 (48)
5	5.26 (54), 5.46 (46)
11	5.27 (38), 5.51 (62)
12	5.29 (40), 5.51 (60)

^a In parts per million relative to Me_4Si for both stereoisomers.

given in the Experimental Section. Chromatographic separation of the crude photolysates provided the adducts shown in Scheme II in yields given in Table I. The dihydroanthracene adducts 4 and 5 arising in high yields from photoreactions of DCA with the respective silyl ethers 1 and 2 were produced as ca. 1:1 mixtures of stereoisomers. Characteristic resonances in the ¹H NMR spectra of these substances associated with protons at C-9 were used to determine isomer ratios (Table II). These resonances along with those corresponding to the arene-ring and side-chain protons provided preliminary evidence for these structural assignments. More definitive structural information has come from chemical transformations of these substances (see below).

Unlike the case of ethers 1 and 2, photoreaction of DCA with the silyl amine 3 leads to formation of a variety of products including the anthracene adduct 6, methylcyanoanthracene 7, aminocyananthracene 8, and 9-cyanoanthracene (9). Interestingly, the dicyanodihydroanthracene 10, which presumably serves as the precursor of 6, cannot be detected in the crude photolysate. Characteristic spectroscopic data for 6 were used in assigning its structure. The cyanoanthracenes 8¹⁴ and 7¹⁵ are known substances.

The origin of 10-methyl-9-cyanoanthracene (7) in the photolysate arising from reaction of DCA with silyl amine

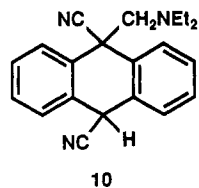
(11) (a) Brown-Wensley, K. A.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1978**, *100*, 4162. (b) Ichinose, N.; Mizuno, K.; Hiromoto, A.; Otsugi, Y. *Tetrahedron Lett.* **1986**, *27*, 5619. (c) Reference 9b.

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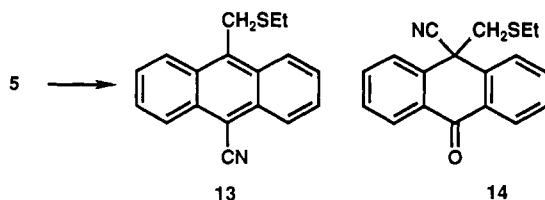
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3 is interesting. We have shown that this substance is a secondary photoproduct of the adduct 6. Accordingly, irradiation of MeCN solutions of 6 in the presence or absence of added 3 leads to production of the methylcyanoanthracene 7. The efficiency for conversion of 6 to 7 is enhanced ca. 3-fold when the amine 3 is present at a concentration of 2.6×10^{-2} M.

Photoadditions of Non-Silicon-Containing Ethers and Amines to DCA. Photoreactions of DCA with diethyl ether, THF, and *N*-methyl-*N,N*-diethylamine were conducted under conditions (MeCN, $\lambda > 290$ nm) similar to those utilized in reactions of the silicon analogues. Chromatographic separations of the photolysates arising from reactions of Et₂O and THF led to isolation in high yields of the dihydroanthracene adducts 11 and 12 as ca. 1:1 mixtures of C-9 epimers (Scheme III, Tables I and II).¹⁶ In addition, irradiation of DCA (MeCN, $\lambda > 290$ nm) in the presence of *N*-methyl-*N,N*-diethylamine leads to production of the same products (6-9) as are formed from reaction of silyl amine 3 with DCA (Table I). Major differences exist, however, in these processes. Specifically, the relative yields of the adduct 6 (19% vs 2%), aminocyananthracene 8 (29% vs 41%), and 9-cyanoanthracene 9 (3% vs 1%) differ significantly depending upon whether silyl amine 3 or methyl-diethylamine serves as the addend.

Chemistry of the 9,10-Dihydroanthracene Adducts. In order to simplify characterization of the adducts arising from photoaddition of the ethers and thioethers to DCA (products are mixtures of stereoisomers) and to determine why addition of amine 3 results in production of anthracene rather than dihydroanthracene products, we briefly explored base-induced reactions of 4, 5, 11, and 12. Initially, we anticipated that these substances would undergo dehydrocyanation to generate the corresponding 10-cyanoanthracenes under basic conditions. Surprisingly, treatment of the adduct 5 with triethylamine in nitrogen-prepurged solutions of MeCN at 20 °C led not only to formation of anthracene 13 but also to the anthrone 14 in a ratio of 1.5:1. Also, only the anthrone 14 was produced when this same process was performed on air-saturated MeCN solutions. Similarly, the anthracene 13 and trace quantities of anthrone 14 were obtained by treatment of 5 with K₂CO₃ in 15% aqueous MeCN at 20 °C under a nitrogen atmosphere. An additional curiosity is seen when dehydrocyanation of 5 is conducted at elevated temperature (75 °C) with morpholine in MeCN. In this case, the anthrone 14 was formed as a minor product (21%) along with DCA (60%). Analogous results were obtained from studies of dehydrocyanation reactions of the other dihydroanthracenes, 4, 11, and 12 (Table III).



Scheme III

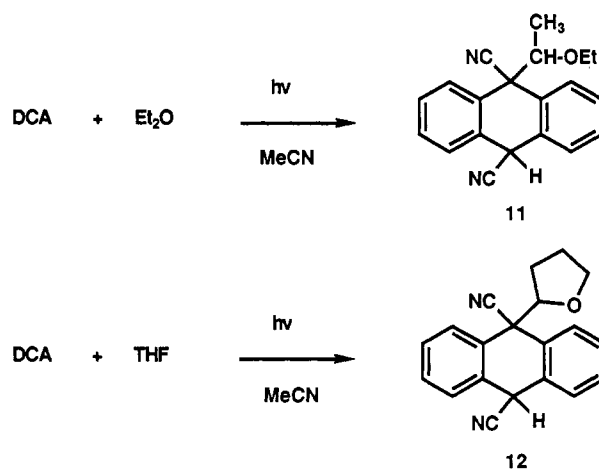
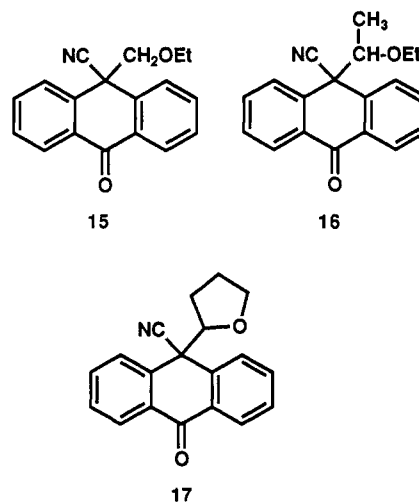


Table III. Base-Induced Reactions of Dihydroanthracenes 4, 9, 11, and 12

dihydroanthracene	base	solvent	condtns	products (yields, %)
5	Et ₃ N	MeCN	air satd, 20 °C	14 (ca. 100)
5	Et ₃ N	MeCN	N ₂ , 20 °C	13 (39), 14 (61)
5	K ₂ CO ₃	aq MeCN	N ₂ , 20 °C	13 (87), 14 (5)
5	morpholine	C ₆ H ₆	N ₂ , 75 °C	1j (21), DCA (60)
4	morpholine	C ₆ H ₆	N ₂ , 75 °C	15 (61), DCA (22)
11	Et ₃ N	MeCN	N ₂ , 20 °C	16 (66)
12	Et ₃ N	MeCN	N ₂ , 70 °C	17 (80)

It appears that subtle changes in the reaction conditions have a pronounced effect upon the nature of products arising from base treatment of the dihydroanthracenes. Strictly anaerobic conditions (even more than nitrogen prepurging affords) and low temperatures are required to insure that simple dehydrocyanation occurs to produce anthracene products. The presence of even trace quantities of oxygen is apparently sufficient to cause diversion of the reaction pathway toward anthrone formation. Finally, generation of DCA appears to be favorable at high temperatures.



The mechanism for anthrone formation is most probably similar to that followed in related oxidations of benzylic nitriles.¹⁸

(16) In the case of adducts 11 and 12, four diastereomers are possible. ¹H NMR analysis indicated the presence of two sets of isomers of undefined stereochemistry in the ratios shown in Table II.

(17) (a) Ware, W. R.; Holms, J. D.; Arnold, D. R. *J. Am. Chem. Soc.* 1974, 96, 7861. (b) The oxidation potentials of these silyl ethers and amines is not known. However, the effects of R₃Si substitution on donor oxidation potentials have been measured (ref 24).

Table IV. DCA Fluorescence Quenching by n-Electron Donors

n-electron donors	Stern-Volmer slopes ($k_q\tau$)	k_q , $M^{-1} s^{-1}$ (20 °C, MeCN)
EtOCH ₂ TMS (1)	7.5	4.9×10^8
EtSCH ₂ TMS (2)	196	1.3×10^{10}
Et ₂ NCH ₂ TMS (3)	243	1.6×10^{10}
Et ₂ NCH ₃	242	1.6×10^{10}
Et ₃ N	271	1.8×10^{10}

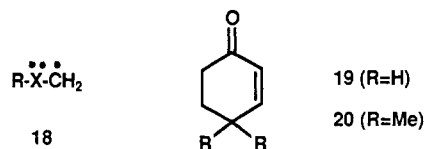
On the basis of these results, it is clear that dihydroanthracene adducts produced in the photolysates (oxygen free) from reaction of DCA with the tertiary amine substrates would undergo rapid and efficient dehydrocyanation. This explains why dihydroanthracene adducts are not detected in these cases. Finally, the anthracenes and anthrones generated in the chemical processes described above were useful in assigning structures since in most (not all) of these cases problems with diastereomeric mixtures were absent.

Fluorescence Quenching. In order to gather evidence to support assignment of the singlet excited state of DCA as the reactive intermediate in the above processes and of mechanistic pathways involving electron transfer, we investigated DCA fluorescence quenching by the n-electron donors. Fluorescence measurements were made in MeCN at 20 °C, and quenching rate constants (k_q) were determined by use of Stern-Volmer techniques (giving $k_q\tau$) and on the basis of the known singlet lifetime ($\tau = 15.2$ ns)^{17a} of DCA. The data, summarized in Table IV, indicate that the ethers, thioethers, and amines serve as efficient quenchers of the DCA singlet excited state and that k_q values parallel the expected oxidation potentials of the donors.^{17b}

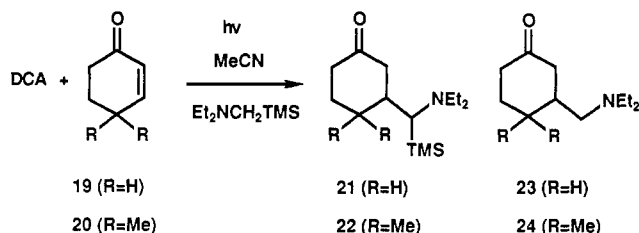
Additional Mechanistic Studies. As indicated above, photoadducts arising from reaction of DCA with the silyl ether 1 and thioether 2 are 9,10-dihydroanthracenes (4 and 5, respectively). Since the origin of the proton at C-9 in these adducts has a mechanistic consequence, experiments were performed to gain information about this question. Deuterium labeling techniques were used in this case. Solutions of DCA and thioether 2 (6.2×10^{-2} M) in MeCN (6 mL) containing either H₂O (0.2 mL) or D₂O (0.2 mL) were independently irradiated for 10 h. To the respective photolysates were added 0.2 mL of D₂O (for the H₂O-MeCN reaction) and 0.2 mL of H₂O (for the D₂O-MeCN reaction). The resulting solutions were stirred at 20 °C for 10 h and concentrated in vacuo, giving photolysates, which were analyzed by ¹H NMR to determine the protio/deuterio content at C-9. The results show that deuterium incorporation at this position occurred to the extent of 13% in the process involving irradiation in a H₂O-MeCN solution followed by addition of D₂O and to the extent of 46% in the reaction where D₂O was present during irradiation. Clearly, a mechanism for adduct formation involving transfer of a proton from H₂O or other acids to C-10 of the anthracene skeleton must be an important contributor. The lower than 100% *d* incorporation could be due to silylated MeCN serving as an alternative proton source (see below).

The nature of the products formed in these photoinduced addition reactions is suggestive of a mechanistic route involving the intermediacy of heteroatom stabilized carbon radicals 18 (RX = RO, RS, or R₂N). In order to gain information about the intermediacy of radicals of this

type in the DCA photoadditions, we performed trapping experiments. We anticipated that radicals of type 18 would be "nucleophilic" (i.e., high SOMO energy) and, therefore, that trapping by electrophilic olefins (e.g., α,β -unsaturated ketones) would be likely. Our preliminary studies employed trapping of intermediates in the DCA-silyl amine 3 photoreaction by cyclohex-2-en-1-one (19) and its 4,4-dimethyl derivative 20.



Irradiation of DCA solutions (MeCN) containing either enone 19 or 20 and silyl amine 3 ($2-3 \times 10^{-2}$ M) was conducted by utilizing uranium glass filtered light ($\lambda > 310$ nm). Two types of amine-enone adducts (21 and 22, and 23 and 24) were detected in the crude photolysates by GLC methods. The adducts were shown to be identical in all respects with substances we had already observed¹⁹ as products formed by direct irradiation ($\lambda > 320$ nm) of the enones 19 and 20 in the presence of 3. Because of this and since competitive light absorption by the enones and DCA occurs under the irradiation conditions used, enone-amine adduct ratios were determined as a function of enone concentration.^{20,22} Extrapolation of the data to zero enone concentration provides adduct ratios that are reflective of the processes that are sensitized by DCA. The data, presented elsewhere,²¹ show that the non-silicon-containing adducts 23 and 24 are formed predominantly in the DCA electron transfer sensitized additions of 3 to 19 and 20.



Discussion

The observations presented above clearly show that the cyanoarene DCA participates in photoaddition reactions with a variety of α -silyl and non-silicon-containing ether, thioether, and amine substrates. Reactions of DCA with the α -silyl n-electron donors are highly chemoselective, leading to adducts 26 (Scheme IV) in which the dihydrodicyanoanthracenyl unit is bonded to the α -carbon in place of the trimethylsilyl group. In the case of substrates lacking silicon substitution, such as Et₂O, THF, and Et₂NMe, photoadditions lead to substitution of the anthracenyl moiety for a hydrogen at carbon sites adjacent to the heteroatoms. Importantly, in the reactions of DCA with α -silyl donors, silicon-containing adducts (27) are not generated by formal C-H substitution pathways. Finally, in most cases (except for amines), the photoaddition reactions occur in moderate to high yields.

(19) Yoon, U. C.; Kim, J. U.; Hasegawa, E.; Mariano, P. S. *J. Am. Chem. Soc.* 1987, 109, 4421.

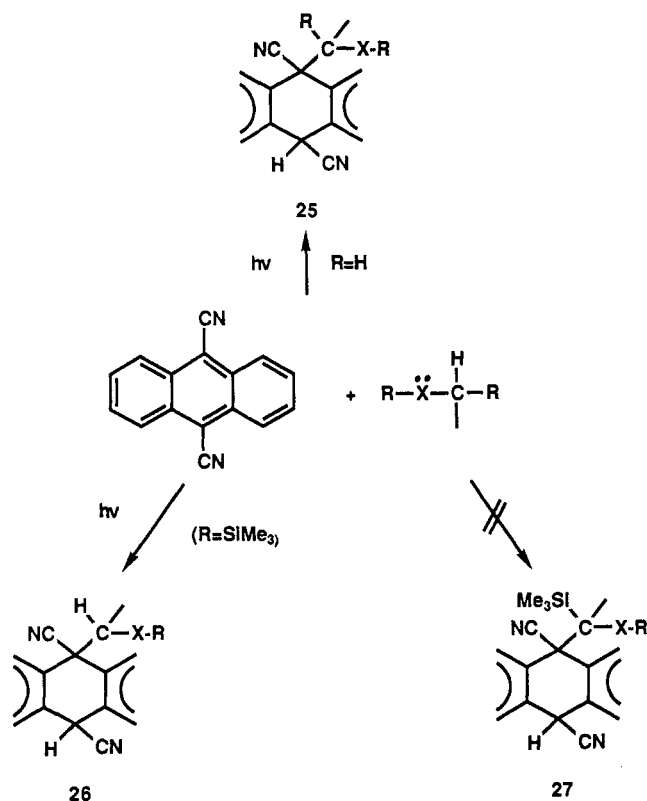
(20) The ratios of silicon-containing and non-silicon-containing adducts in the DCA-sensitized reactions vary with amine 3 concentration (ref 21). This phenomenon appears to be related to an amine base effect on the relative rates of deprotonation versus desilylation of the intermediate cation radical.

(21) Hasegawa, E.; Mariano, P. S.; Yoon, U. C.; Kim, J. U. *J. Am. Chem. Soc.*, in press.

(22) The low solubility of DCA in MeCN prevents the conduct of alternative experiments in which [DCA] is increased.

(18) (a) Donetti, A.; Boniardi, O.; Ezhaya, A. *Synthesis* 1980, 1009. (b) Freerksan, R. W.; Selikson, S. J.; Wroble, R. R.; Kyler, K. S.; Watt, D. S. *J. Org. Chem.* 1983, 48, 4097.

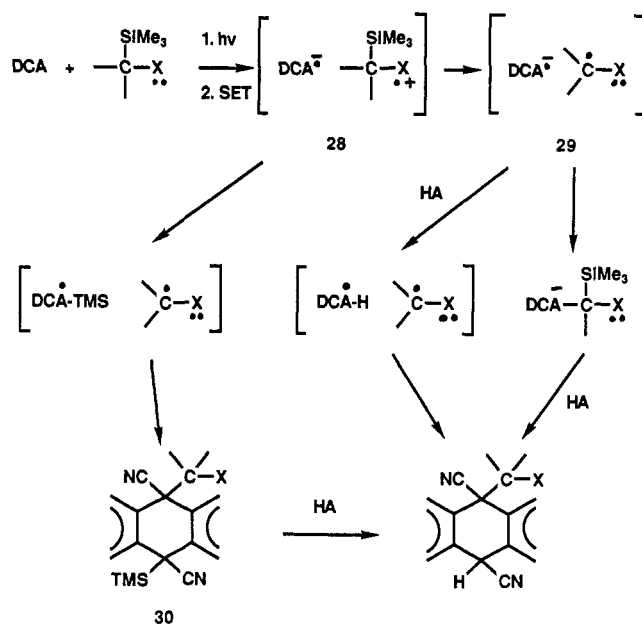
Scheme IV



The nature of the photoadducts along with an analysis of excited- and ground-state electrochemical potentials suggests that these reactions follow electron-transfer mechanisms. Fluorescence-quenching data for the silyl substrates are consistent with this view and implicate the DCA singlet as the reactive excited state. For example, on the basis of donor oxidation potentials, the free energy for SET to DCA^{S1} should become less negative in the series R₃N > RSR > ROR.^{3,23} The observed fluorescence-quenching rate constants bear an inverse relationship to this trend as is expected for moderately exergonic, outer-sphere SET pathways for DCA^{S1} deactivation.³ Furthermore, quenching rate constants are large for the silyl donors, approaching the diffusion-controlled limit (ca. 2 × 10¹⁰ M⁻¹ s⁻¹ in MeCN). It is important to note in this regard that neither Et₂O nor THF serves as an efficient quencher for DCA fluorescence. The lower rates for these substrates as compared to those of the silicon-containing analogues is probably reflective of silicon-substituent effects on lowering donor oxidation potentials.²⁴

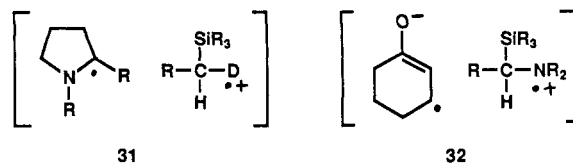
Electron donation in α-silyl donor-DCA^{S1} pairs results in initial formation of ion radical pairs 28 (Scheme V). Unlike the case of benzophenone-tertiary amine photoinduced SET, studied in detail by Peters^{25a,b} and Mataga,^{25c} information is not available on the nature (contact

Scheme V



or solvent-separated ion pair) of the initially formed or reacting charged radical pairs. Independent of this and on the basis of the high yields for product formation, we can conclude that the cation radicals generated from silyl ether and silyl thioether donors undergo efficient desilylation to produce neutral radicals 29. Acetonitrile most probably serves as the nucleophile in the desilylation process. Coupling of the donor-derived radical with DCA anion radical followed by protonation of the formed anion (from trace water or the CH₃CNTMS cation) then would generate the stereoisomeric mixture of adducts. Other variations exist for the final steps of this process. For example, protonation of the DCA anion radical would occur prior to radical coupling. Alternatively, silyl transfer to the DCA anion radical rather than acetonitrile is possible, generating after coupling a silyl adduct 30, which would be expected to undergo rapid hydrolysis of the labile Si-C bond by unavoidable or added water present in the photolysate. Importantly, all of these mechanistic pathways are consistent with results described above.

Proton transfer from amine,^{10b,c} alkylbenzene,^{10a} and ether²⁶ cation radicals to arene carbonitrile anion radicals are common in SET photochemistry. Indeed, the additions of Et₂O, THF, and Et₂NMe to DCA reported above serve to exemplify reactions in which these processes play a key role. Thus, the absence of silicon-containing products in reactions of DCA with the silyl donors suggests that proton transfer in the radical ion pair 28 (Scheme V) is slow compared to desilylation or silyl transfer. This is expected on the basis of previous observations made in studies of allylsilane,^{9a} α-silyl ether,^{8b} and benzylsilane²⁷ SET-induced additions to iminium salts. In these cases, cation radical pairs 31 undergo exclusive desilylation to provide non-silicon-containing adducts. However, ion radicals 32 de-



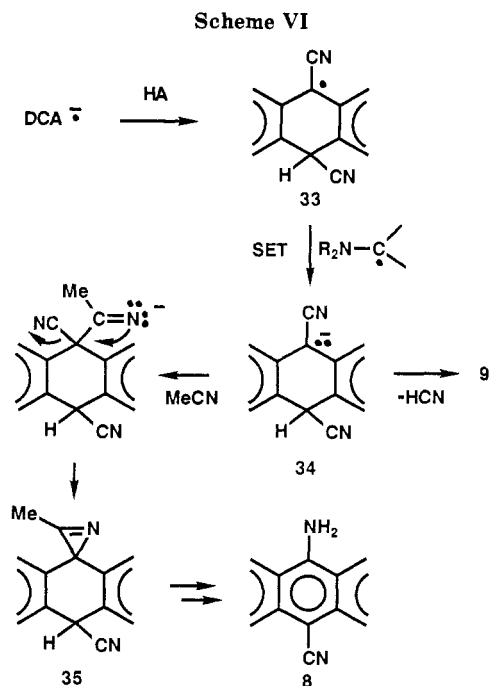
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rived from SET in α -silyl amine–enone systems partition between proton-transfer and desilylation pathways depending on the nature (contact or solvent-separated) of the ion pair.¹⁹ Proton transfer in **32** occurs only at the contact ion pair stage. It appears then that deprotonation of α -silyl radical cations which also possess α -C–H bonds is not an efficient process as compared to desilylation unless it is intimately paired with a strongly basic anion radical²⁸ or in a strongly basic medium.²⁰ Obviously, in reactions of Et_2O , THF, and Et_2NCH_3 with DCA, deprotonation of intermediate cation radicals occurs since no alternative pathway exists. Finally, the combined observations suggest that SET–deprotonation or –desilylation sequences can serve as the basis for DCA-photosensitized routes for α -alkoxy or α -amino radical generation, processes that might find synthetic utility in radical addition and cyclization chemistry (see below).²⁹

The photochemistry of the DCA in the presence of silyl amine **3** differs dramatically from that observed with the analogous ether **1** and thioether **2**. In the former process, a variety of products are produced. Adducts (**6** and **7**) arising by the sequence outlined in Scheme VII are only minor constituents of the product mixture, and only in this case are the aminoanthracene **8** (the major product) and monocycanoanthracene **9** formed. Similar trends are noted in products from reaction of DCA with the non-silyl-containing *n*-electron donors. In the case of Et_2NCH_3 photoaddition, the adduct **6** is a minor component of the

product mixture and the aminoanthracene **8** dominates.

These observations gain further significance when compared with those made by Ohashi and his co-workers¹⁴ in their study of the DCA– Et_3N photoreaction in acetonitrile. These workers report that aminoanthracene **8** is the exclusive product, formed in high yield by a pathway involving the intermediacy of anion **34** (Scheme VI), derived by protonation of the DCA anion radical followed by electron transfer. ¹⁵N-labeling studies were used to support the proposal that addition of anion **34** to acetonitrile serves to generate **8** via the spiro azirine **35**. Formation of aminoanthracene **8** in reactions of DCA with Et_2NMe or silyl amine **3** could involve similar mechanistic routes. The monocycanoanthracene **9** observed in our studies might also come from anion **34** by protonation and dehydrocyanation.

Several factors could be responsible for the differences observed between amine vs ether photoreactions with DCA. Production of amino- and monocycanoanthracenes **8** and **9** by the Ohashi mechanism requires two events, protonation of the DCA anion radical and SET to hydroanthracenyl radical **34**, whose efficiencies might be dependent upon the nature of the original *n*-donor substrate. For example, if protonation of (or proton transfer to) DCA anion radical is competitive with desilylation and radical coupling, then the relative efficiencies of the Ohashi pathway would be dependent upon the rates of desilylation of the *n*-donor-derived cation radicals. One would expect that the desilylation rates would in turn depend inversely on the stability of the cation radicals and thus parallel the oxidation potentials of the parent ethers and amines. This conclusion is consistent with the ESR results of Sakurai³¹ which show qualitatively that the cation radical from TMSCH_2OMe is much less stable than that arising from its thio analogue, TMSCH_2SMe . While not included in the Sakurai study, the cation radical of silyl amine **3** is expected to undergo desilylation at an even slower rate. Perhaps more significant is the expected variation in the rates of SET to radical **33**, a process that must involve the α -substituted carbon radicals as electron donors (Scheme VII). It is known that α -amino radicals have low oxidation potentials.³² Thus, in comparison to their ether analogues, radicals of this type have the potential of participating in SET with hydroanthracenyl radical **33**. It should be noted that Lewis^{10b} has proposed a pathway of this type to rationalize the lack of adduct formation in the photochemistry of amines with 9-cyanophenanthrene³³ and that it is possible that the amine adduct **10** arises by bond formation in the ion pair **36**.

Production of the methylcyanoanthracene **7** from reactions of DCA with α -silyl amine **3** and Et_2NMe involves secondary photoreaction of the initially formed adduct **6**. A process of this type, probably involving an SET mechanism, has been detected before in Ohashi's study of amine photoadditions to dicyanobenzene.^{33b} Thus, the combined yields of **6** and **7** reflect the efficiency of adduct formation

(28) (a) To our knowledge, the pK_a of the hydro-dicyanoanthracenyl radical anion has not been measured. In addition, it is difficult to estimate this value by the Arnold thermochemical method (ref 28b). This issue has been addressed by other investigators (ref 28c,d). However, the pK_a s of conjugate acids of PhCN and $1,4\text{-(CN)}_2\text{Ph}$ anion radicals are 7 and ≤ 0 , respectively (ref 28g). The pK_a of the protonated DCA anion radical should be lower than this owing to greater delocalization in the anion radical. (b) Wayner, D. D. M.; Arnold, D. R. *Can. J. Chem.* 1985, 63, 871. (c) Mattes, S. C.; Farid, S. *J. Am. Chem. Soc.* 1986, 108, 7356. (d) Lewis, F. D.; Petisce, J. R. *Tetrahedron* 1986, 42, 6207. (e) The pK_a values for enone anion radicals in aqueous solution are ca. 10 (ref 28f). (f) Lillie, J.; Henglein, A. *Ber. Bunsen-Ges. Phys. Chem.* 1969, 73, 170. Hayon, E.; Iyata, T.; Lichtin, N. N.; Simic, M. *J. Phys. Chem.* 1972, 76, 2072. (g) Robinson, E. A.; Schulte-Frohlinde, H. *J. Chem. Soc., Faraday Trans. 1* 1973, 1, 707. However: Schested, K. *Ibid.* 1975, 3, 1211.

(29) Giese, B. *Radicals in Organic Synthesis Formation of Carbon–Carbon Bonds*; Baldwin, J. E., Organic Chemistry Series; Pergamon: Oxford, 1986; Vol. 5.

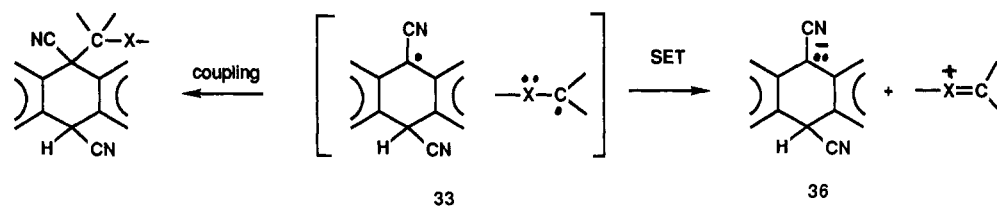
(30) Ohashi (ref 14) observed that **8** was produced only in aqueous MeCN solutions. This is not a requirement for **8** formation in the DCA–amine **3** or Et_2NMe systems. In addition, the Ohashi H_2O effect is unusual since one would have expected to observe more **9** as $[\text{H}_2\text{O}]$ increases.

(31) Kira, M.; Nakazawa, H.; Sakurai, H. *Chem. Lett.* 1986, 497.

(32) (a) Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* 1988, 110, 132. (b) Griller, D.; Lossing, F. P. *J. Am. Chem. Soc.* 1981, 103, 1586. (c) Buskey, J. J.; Castelhana, A. L.; Griller, D.; Lossing, F. P. *Ibid.* 1983, 105, 4701.

(33) (a) Of some importance related to this question are Ohashi's observations that Et_3N gives adducts with dicyanobenzenes. Here SET from the α -amino radical to the hydrobenzenyl radical might be slow owing to the expected lower $E_{1/2}^{\ominus}$ of the latter substance (ref 33b). (b) Ohashi, M.; Miyake, K.; Tsujimoto, K. *Bull. Chem. Soc. Jpn.* 1980, 53, 1683.

Scheme VII



arising by coupling of a DCA-derived radical to the α -amino radical, Et_2NCH_2 in these processes.

The low efficiency of adduct formation in the DCA α -silyl amine 3 photoreaction might also be due to a low rate for coupling of the α -amino radical, Et_2NCH_2 , to a DCA-derived radical. Steric (Et_2N vs EtO or EtS) or electronic (N-C a more electron rich radical than O-C or O-S) effects might play a role in this regard.

In order to determine whether long-lived Et_2NCH_2 radicals serve as intermediates, we conducted photoaddition of DCA with silyl amine 3 in the presence of two α,β -unsaturated ketones, 19 and 20, as trapping agents. We anticipated that the radical Et_2NCH_2 , generated by sequential SET-desilylation, would be reactive with electron-deficient olefins owing to its high-energy SOMO.³⁴ Termination of the reaction pathway leading to adduct formation could involve H-atom abstraction or sequential SET-proton transfer routes. In both reactions, silicon- and non-silicon-containing adducts (21, 22 and 23, 24 respectively) are produced in ratios that are a function of enone concentration. The enone-concentration effect is easily interpreted on the basis of the fact that under the reaction conditions (uranium filter) enones 19 and 20 are competitively absorbing light. Attempts to avoid this are frustrated by the low solubility of DCA. Furthermore, amine 3 is known¹⁹ to undergo photoaddition to enones 19 and 20 to produce 21–24 in which the silicon-containing adducts predominant (ca. 8:1). Thus, the product mixtures at [enone] = 0 more reflect results of DCA-sensitized routes. The fact that these mixtures are comprised mainly of non-silicon-containing adducts 23 and 24²¹ supports the conclusion drawn earlier that the radical cation derived from 3 undergoes preferential desilylation rather than deprotonation.

These results suggest that α -amino radicals formed by SET-sensitized methods undergo conjugate addition to the cyclohexenones, providing ultimately the addition products.³⁵ This methodology should be useful in the design of novel radical addition and cyclization processes and thus is being explored more thoroughly in our continuing efforts in this area.

Experimental Section

General Procedures. ¹H and ¹³C NMR spectra were recorded by using a Bruker WP-200 or AM-400 spectrometer and CDCl_3 solutions. Chemical shifts are reported in parts per million downfield from Me_4Si as the internal standard. For compounds containing Me_3Si groupings, CHCl_3 was used as an internal standard. ¹³C NMR resonances were assigned by use of the INEPT technique to determine numbers of attached hydrogens. IR spectra were recorded on a Perkin-Elmer 283 spectrometer. UV spectra were obtained on a Perkin-Elmer Lambda-5 spectrometer. A Perkin-Elmer MPF-44B fluorescence spectrometer equipped with a DCSU-1 correction unit was employed for fluorescence measurements. Mass spectra were recorded by using

a Hitachi RMU-6E (low resolution) or a Kratos M50 (high resolution, Penn State Mass Spec Facility) instrument. Elemental analysis was performed by Dr. H. Kassler at the University of Maryland. Melting points were recorded by use of a Griffin Mel-Temp apparatus and are reported uncorrected. Analytical GLC (10% OV-101 packed, 6 ft \times 1/8 in. column) was performed with a Varian-940 (FID) chromatograph. Preparative TLC was conducted by using 20 \times 20 cm plates coated with Merck-EM type 60, GF-254 silica gel. Flash chromatography was performed with Merck-EM type 60 (230–400 mesh) silica gel. Drying of inorganic layers obtained following workup of reaction mixtures was performed with anhydrous Na_2SO_4 .

Preparative photochemical reactions were conducted by using an apparatus consisting of a 450-W Hanovia medium-pressure lamp (Ace) surrounded by a glass filter (for wavelength band selection) and within a quartz water-cooled well which was immersed in the photolysis solution. The photolysis solution was purged with N_2 both before and during irradiation.

9,10-Dicyanoanthracene was purchased from Eastman Kodak and recrystallized (CHCl_3) prior to use. The α -silyl ether 1¹² and α -silyl thioether 2¹³ were prepared by the reported methods. Diethylmethylamine, triethylamine, and morpholine were purchased (Aldrich) and distilled prior to use. MeCN employed in the photoreactions was spectrograde (Baker) and used without further purification.

***N*-[(Trimethylsilyl)methyl]-*N,N*-diethylamine (3).** A solution of diethylamine (117 mL, 1.1 mol) and (iodomethyl)-trimethylsilane (24.0 g, 0.1 mol) in 50 mL of anhydrous MeOH was stirred at reflux for 20 h, cooled, and diluted with 500 mL of pentane and 100 mL of 5% aqueous K_2CO_3 . The separated pentane layer was washed with water, dried, and concentrated by fractional distillation. The residue was distilled to yield the derived amine 3 (14.6 g, 83%, bp 146–148 °C): ¹H NMR 0.23 (s, 9 H), 1.13 (t, 6 H), 2.04 (s, 2 H), 2.57 (q, 4 H); ¹³C NMR 1.3 (Me_3Si), 11.5 (NCH_2CH_3), 44.7 (SiCH_2N), 50.2 (NCH_2); high-resolution mass spectrum, *m/e* 159.1643 ($\text{C}_8\text{H}_{21}\text{NSi}$ requires 159.1643).

Fluorescence Quenching. Quenching of 9,10-dicyanoanthracene fluorescence was carried out on solutions (4.38×10^{-5} M) in MeCN at 20 °C with excitation at 398 ± 2 nm. Fluorescence intensities were measured at five or more quencher concentrations. Slopes of Stern–Volmer plots were determined by least-squares techniques, and quenching rate constants were calculated on the basis of the known¹⁷ singlet lifetime of 9,10-dicyanoanthracene.

Photoadditions to 9,10-Dicyanoanthracene. Nitrogen-purged solutions of 9,10-dicyanoanthracene (152 mg, 0.66 mmol) in 180 mL of MeCN containing the following substrates were irradiated with flint glass filtered light ($\lambda > 290$ nm) for the time periods given below: the α -silyl ether 1 (397 mg, 2.99 mmol), the α -silyl thioether 2 (439 mg, 2.96 mmol), the α -silyl amine 3 (476 mg, 2.99 mmol), diethylmethylamine (20 mL, 0.17 mol), diethyl ether (50 mL, 0.48 mol), and THF (30 mL, 0.37 mol). The photolysates were then filtered to remove the unreacted anthracene. The filtrates were diluted with CHCl_3 , washed with saturated aqueous NaHCO_3 and water, dried, and concentrated in vacuo. The residues were subjected to either TLC or column chromatographic separations using the given solvent systems to give the products described below.

Silylmethyl ether 1 (10-h irradiation time, 5:3 CHCl_3 –hexane solvent for TLC) gave the adduct 4 (39%) and recovered 9,10-dicyanoanthracene (56%). Silylmethyl thioether 2 (10 h; TLC, 5:3 CHCl_3 –hexane) gave adduct 5 (58%) and the recovered anthracene (36%). Silylmethylamine 3 (10 h; TLC, 28:1 CHCl_3 – EtOAc) gave adduct 6 (10%), 9-cyano-10-aminoanthracene (8)¹⁴ (15%), and a mixture of 9-cyano-10-methylanthracene (7)¹⁵ (2%), 9-cyanoanthracene (9) (2%), and recovered dicyanoanthracene (50%). Diethylmethylamine (24 h; silica gel flash chromatography,

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(35) (a) Other examples of photoinduced, conjugate additions of radicals to enones have been described (ref 35b). (b) Benko, Z.; Fraser-Reid, B.; Mariano, P. S.; Beckwith, A. L. J. *J. Org. Chem.* 1988, 53, 2066. Porter, N. A.; Magnin, D. R.; Wright, B. T. *J. Am. Chem. Soc.* 1986, 108, 2787.

CHCl_3) gave adduct 6 (2%) and products 7¹⁵ (3%), 9 (1%), and 8 (35%) along with recovered dicyanoanthracene (15%). Diethyl ether (45 h; silica gel flash chromatography, 1:1 CHCl_3 -hexane) gave adduct 11 (86%) and recovered dicyanoanthracene (8%). THF (24 h; silica gel flash chromatography, 5:2 CHCl_3 -hexane) gave adduct 12 (86%) and recovered dicyanoanthracene (14%).

Spectroscopic data for 6: ^1H NMR 1.05 (t, 6 H, $J = 7$ Hz), 2.59 (q, 4 H, $J = 7$ Hz), 4.50 (s, 2 H), 7.58 (m, 2 H), 7.68 (m, 2 H), 8.43 (m, 2 H), 8.64 (m, 2 H); ^{13}C NMR 11.8 (CH_3), 46.7 (CH_2Me), 50.3 (CH_2NEt_2), 105.9 (C-9), 117.5 (CN), 125.8, 126.0, 126.2, 128.3, 130.6, 132.8, 138.8; IR (CHCl_3) 2970, 2880, 2800, 2222, 1445, 1390, 1360, 1290, 1180, 1120, 1070, 650, 640, 610 cm^{-1} ; UV (CH_3CN) λ_{max} (nm) 351 (sh, ϵ 3750), 369 (7310), 389 (9360), 409 (7920); mass spectrum, m/e (relative intensity) 288 (M^+ , 24), 273 (6), 259 (2), 216 (100), 202 (2), 86 (10), 72 (17); high-resolution mass spectrum, m/e 288.1624 ($\text{C}_{20}\text{H}_{20}\text{N}_2$ requires 288.1626).

Generation of Anthrones 14-17. A benzene (6 mL) solution of photoadduct 4 (75 mg, 0.26 mmol) and morpholine (0.22 mL, 0.25 mmol) was stirred at 75 °C for 24 h. Concentration of the solution in vacuo gave a residue, which was dissolved in CHCl_3 . This solution was washed with saturated aqueous NaHCO_3 and water, dried, and concentrated in vacuo, giving a residue, which was subjected to TLC separation (CHCl_3), yielding 44 mg (61%) of the anthrone 15 (mp, 121-122 °C, hexane) and 13 mg (22%) of 9,10-dicyanoanthracene. Spectroscopic data for 15: ^1H NMR 0.96 (t, 3 H, $J = 7$ Hz), 3.21 (q, 2 H, $J = 7$ Hz), 3.67 (s, 2 H), 7.58 (m, 2 H), 7.72 (m, 2 H), 7.92 (m, 2 H), 8.31 (m, 2 H); ^{13}C NMR 14.5 (CH_3), 47.0 (C-10), 68.0 (CH_2Me), 81.2 (CH_2OEt), 120.0 (CN), 127.8, 128.0, 129.2, 131.2, 133.4, 136.9, 182.4 (C=O); IR (CHCl_3) 2980, 2860, 2240, 1670, 1600, 1460, 1320, 1110, 930, 690 cm^{-1} ; UV (CH_3CN) λ_{max} (nm) 268 (ϵ 17000), 345 (87), 360 (sh, 76), 376 (33); mass spectrum, m/e (relative intensity) 277 (M^+ , 5), 247 (6), 219 (73), 218 (45), 190 (46), 59 (100), 31 (44).

Anal. Calcd for $\text{C}_{18}\text{H}_{15}\text{NO}_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 78.12; H, 5.33; N, 4.96.

A benzene (12 mL) solution of adduct 5 (140 mg, 0.46 mmol) and morpholine (0.44 mL, 0.51 mmol) was stirred at reflux for 45 h. Workup and purification by the procedure outlined above gave 28 mg (21%) of anthrone 14 (mp, 109.5-110 °C, hexane) and 63 mg (60%) of 9,10-dicyanoanthracene. Spectroscopic data for 14: ^1H NMR 0.83 (t, 3 H, $J = 7$ Hz), 1.62 (q, 2 H, $J = 7$ Hz), 3.28 (s, 2 H), 7.59 (m, 2 H), 7.71 (m, 2 H), 7.91 (m, 2 H), 8.35 (m, 2 H); ^{13}C NMR 14.2 (CH_3), 27.8 (CH_2Me), 46.2 (C-10), 51.6 (CH_2SEt), 120.7 (CN), 127.2, 127.7, 129.3, 131.9, 133.5, 137.7, 182.1 (C=O); IR (CHCl_3) 2960, 2920, 2240, 1675, 1600, 1460, 1320, 1290, 930, 680 cm^{-1} ; UV (CH_3CN) λ_{max} (nm) 266 (ϵ 15600), 358 (sh, 82); mass spectrum, m/e (relative intensity) 293 (M^+ , 2), 218 (4), 75 (100), 47 (29).

Anal. Calcd for $\text{C}_{18}\text{H}_{15}\text{NOS}$: C, 73.69; H, 5.15; N, 4.77. Found: C, 73.38; H, 5.08; N, 4.68.

An acetonitrile (8 mL) solution of adduct 11 (120 mg, 0.40 mmol) and Et_3N (2 mL, 14.3 mmol) was stirred at 20 °C for 40 h. Workup as described above followed by column chromatography on silica gel (CHCl_3 -hexane) afforded 76 mg (66%) of anthrone 16 (mp, 116.5-117.5 °C, DME-hexane) and 9 mg (10%) of 9,10-dicyanoanthracene. Spectroscopic data for 16: ^1H NMR 0.93 (m, 6 H, CH_3), 2.96 (m, 1 H), 3.28 (m, 1 H), 3.69 (q, 1 H, $J = 6$ Hz, 7.57 (m, 2 H), 7.69 (m, 2 H), 7.87 (m, 1 H), 7.97 (m, 1 H), 8.27 (m, 2 H); ^{13}C NMR 14.8 (CH_3), 15.9 (CH_3), 51.3 (C-10), 66.9 (CH_2Me), 83.9 (CHOEt), 120.3 (CN), 127.1, 127.5, 128.1, 128.2, 128.9, 129.0, 132.3, 132.5, 132.7, 132.9, 136.7, 183.0 (C=O); IR (CHCl_3) 2970, 2880, 2240, 1660, 1600, 1450, 1380, 1310, 1300, 1260, 1100, 930, 690 cm^{-1} ; UV (CH_3CN) λ_{max} (nm) 269 (ϵ 15500), 346

(104), 358 (sh, 93), 376 (40); mass spectrum, m/e (relative intensity) 291 (M^+ , 0.03), 246 (2), 219 (69), 218 (19), 190 (35), 73 (79), 45 (100); high-resolution mass spectrum, m/e 291.1263 ($\text{C}_{19}\text{H}_{12}\text{NO}_2$ requires 291.1260).

An acetonitrile (8 mL) solution of adduct 12 (110 mg, 0.37 mmol) and Et_3N (2 mL, 14.3 mmol) was stirred at 20 °C for 40 h. The reaction mixture was subjected to the workup procedure described above. Purification by silica gel column chromatography (CHCl_3 -hexane) gave 85 mg (80%) of anthrone 17 (mp 112.5-113 °C, DME-hexane) and 5 mg (6%) of 9,10-dicyanoanthracene. Spectroscopic data for 17: ^1H NMR 1.07 (m, 1 H), 1.57 (m, 3 H), 3.43 (m, 1 H), 3.64 (m, 1 H), 4.25 (m, 1 H), 7.58 (m, 2 H), 7.70 (m, 2 H), 7.96 (m, 2 H), 8.28 (m, 2 H); ^{13}C NMR 25.2 (β -THF), 50.4 (C-10), 70.0 (α -THF), 88.0 (α' -THF), 120.0 (CN), 127.4, 127.8, 128.0, 128.2, 129.1, 131.8, 132.2, 133.1, 136.2, 136.3, 182.8 (C=O); IR (CHCl_3) 2960, 2880, 2240, 1670, 1600, 1450, 1320, 1270, 1080, 1060, 930, 690 cm^{-1} ; UV (CH_3CN) λ_{max} (nm) 268 (ϵ 15500), 346 (101), 358 (sh, 91), 376 (39); mass spectrum, m/e (relative intensity) 289 (M^+ , 0.1), 219 (75), 218 (15), 190 (30), 71 (100), 43 (53); high-resolution mass spectrum, m/e 289.1102 ($\text{C}_{19}\text{H}_{16}\text{NO}_2$ requires 289.1103).

Formation of Anthracene 13 by Dehydrocyanation of 5.

A nitrogen-purged 14% aqueous CH_3CN (14 mL) solution of adduct 5 (154 mg, 0.51 mmol) and 350 mg (0.25 mol) of K_2CO_3 was stirred at 20 °C for 6 h and then filtered to give 122 mg (87%) of the crystalline anthracene 13 (mp, 174.5-175.5 °C, CH_3CN). Spectroscopic data for 13: ^1H NMR 1.35 (t, 3 H, $J = 7$ Hz), 2.70 (q, 2 H, $J = 7$ Hz), 4.73 (s, 2 H), 7.67 (m, 4 H), 8.42 (m, 4 H); ^{13}C NMR 14.7 (CH_3), 27.5 (CH_2Me), 28.6 (CH_2SEt), 106.1 (C-9), 117.2 (CN), 125.0, 126.2, 126.8, 128.4, 129.1, 133.0, 137.3; IR (CHCl_3) 2970, 2920, 2210, 1620, 1560, 1445, 1370, 1285, 1265, 1170, 630 cm^{-1} ; UV (CH_3CN) λ_{max} (nm) 413 (ϵ 11200), 392 (12800), 371 (9820), 352 (sh, 4750); mass spectrum, m/e (relative intensity) 277 (M^+ , 68), 216 (100); high-resolution mass spectrum, m/e 277.0930 ($\text{C}_{18}\text{H}_{15}\text{NS}$ requires 277.0925).

Photoconversion of Adduct 6 to Adduct 7. Acetonitrile solutions (6 mL) of adduct 6 (6 mg, 0.02 mmol) with and without the α -silyl amine 3 (25 mg, 0.15 mmol) were simultaneously irradiated with flint glass filtered light for 2 h. The photolysates were concentrated in vacuo, and the residue obtained was analyzed by ^1H NMR. Conversion of 6 to 7 was 100% when irradiation was conducted in the presence of amine 3 and 35% from irradiation in the absence of 3.

Deuterium Labeling Experiments. Acetonitrile (6 mL) solutions of 9,10-dicyanoanthracene (15 mg, 0.07 mmol), and the α -silyl thioether 2 (57 mg, 0.38 mmol) containing either D_2O (0.2 mL) or H_2O (0.2 mL) were irradiated with uranium glass filtered light ($\lambda > 320$ nm) for 10 h. The photolysates were filtered to remove unreacted 9,10-dicyanoanthracene. To the filtrates were added 0.2 mL of H_2O (for the D_2O - CH_3CN reaction) or 0.2 mL of D_2O (for the H_2O - CH_3CN reaction). The solutions were allowed to stand for 10 h and extracted with CHCl_3 . The CHCl_3 extracts were dried and concentrated in vacuo, giving residues, which were analyzed by ^1H NMR (resonances at 5.26 and 5.46 ppm for H-10 integrated relative to CH_2S resonances). The percent monodeuterium incorporation at C-10 in the adduct 5 was determined to be 44% for the D_2O - CH_3CN reaction followed by H_2O addition and 13% for the H_2O - CH_3CN reaction followed by D_2O addition.

Acknowledgment. This research was supported by a grant from the National Science Foundation (PSM) (CHE-09589) and a joint NSF-KOSEF Cooperative Research Grant (INT-8416512).