Photoaddition Reactions of Acenaphthylenedione with α-Silyl n-Electron Donors via Triplet Single Electron Transfer–Desilylation and Triplet Hydrogen Atom Abstraction Pathways

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Studies have been conducted to explore single electron transfer (SET) induced photoaddition reactions of acenaphthylenedione (ACND) with the n-electron donors $Et_2NCH_2SiMe_3$, n-$PrSCH_2SiMe_3$, $EtOCH_2SiMe_3$, $EtCO_2CH_2N(CH_2Ph)CH_2SiMe_3$, and $EtCO_2CH_2N(CH_2Ph)CH_3$. Photoaddition of α-silyl amine $Et_2NCH_2SiMe_3$ to ACND occurs in CH_3OH and CH_3CN to produce 2-hydroxy-2-[(diethylamino)methyl]acenaphthylen-1-one. In contrast, photoaddition of n-$PrSCH_2SiMe_3$ to ACND generates two photoadducts, 2-hydroxy-2-[(n-propylthio)methyl]acenaphthylen-1-one and 2-hydroxy-2-[(n-propylthio)(trimethylsilyl)methyl]acenaphthylen-1-one, along with a ACND photoreduction dimer. Photoaddition of $EtOCH_2SiMe_3$ to ACND produces two diastereomers of 2-hydroxy-2-[ethoxy(trimethylsilyl)methyl]acenaphthylen-1-one along with the reduction dimer. The formation of all photoproducts in these photoreactions is quenched by oxygen, indicating that the triplet of ACND is the reactive excited state. Based on a consideration of the oxidation potentials of the α-silyl n-electron donors, and the nature of photoproducts, mechanisms for these photoadditions involving triplet SET–desilylation and triplet H atom abstraction pathways are proposed. Photoaddition of $EtCO_2CH_2N(CH_2Ph)CH_2SiMe_3$ to ACND provides two major products, 2-hydroxy-2-[[N-benzyl-N-(carbethoxymethyl)amino]methyl]acenaphthylen-1-one and 2-hydroxy-2-[[N-benzyl-N-[(trimethylsilyl)methyl]amino]carbethoxymethyl]acenaphthylen-1-one along with several minor products. The formation of the major products via sequential SET–deprotonation pathways shows that the electron-withdrawing carbethoxy substituent serves to control the regioselectivity for deprotonation of the amine radical cation intermediate. Results obtained from the study of the photoaddition of the non-silicon-containing amino ester, $EtCO_2CH_2N(CH_2Ph)CH_3$, also demonstrate the effect of electron-withdrawing carbethoxy substituent on amine radical cation deprotonation regiochemistry.

Introduction

Our previous studies in the area of single electron transfer (SET) photochemistry using α-silyl electron donors led to the observation that photoinduced, sequential SET–desilylation pathways have the potential of serving as efficient and highly regioselective methods for carbon centered radical generation (Scheme Ia).[1] Further studies of photoaddition reactions occurring between the α-silyl amine **2** and conjugated cyclohexenones **1** revealed that SET–desilylation and SET–deprotonation pathways are competitive and that this competition can be governed by reaction conditions, especially the photoreaction medium, which control the preference for formation of solvent separated ion radical pairs (SSIRP) **3** and contact ion radical pair (CIRP) **4** (Scheme Ib)[2] and/or the basicity of the enone anion radical. Specifically, in aprotic media the intermediate CIRP **4** undergoes proton transfer of the acidic α-proton of the α-silyl amine radical cation to the oxy anion center in the cyclohexenone anion radical leading to trimethylsilyl-substituted adducts whereas in protic media the SIRP **3** undergoes desilylation to generate non-silicon-containing adducts. In more recent efforts probing intramolecular versions of this process, we have demonstrated that the regiochemistry for deprotonation of amine cation radicals is controlled by the kinetic acidity of the α-protons which in turn is governed by radical stabilizing substituents.[3]

In an effort to obtain further information about factors which can influence partitioning of α-silyl amine and related cation radicals between deprotonation and desilylation and to continue to explore for new photoinduced SET reactions of synthetic utility, we have investigated photoreactions of acenaphthylenedione (ACND) with the α-silyl n-electron donors, **5–7**. In addition, photoreactions of ACND with the glycine ester derivatives, **13** and **14**, were probed in order to determine the effect(s) of α-electron-withdrawing groups. Observations made in these studies have demonstrated that (1) ACND undergoes photoaddition reactions with the α-silyl n-electron donors **5–7** via two competing pathways involving triplet SET–desilylation and triplet α-hydrogen atom abstraction depending on the oxidation potential of the donor, (2) the SET-induced processes followed by **5** and **6** take place by exclusive desilylation of cation radical intermediates even in aprotic solvents, indicating that the ACND anion radical is nonbasic and this causes proton transfer from the corresponding cation radicals in the CIRP to be inefficient, and (3) the increase in α-proton acidity of amine cation radicals by an electron-withdrawing group causes regiocontrolled deprotonation to become competitive with desilylation in the SET photoreactions of ACND.

Results

α-Silyl Ether 7, α-Silyl Thioether 6, and α-Silyl Amine 5 Photoadditions to ACND. Photoaddition reactions of ACND and the α-silyl n-electron donors **5–7** were explored first. Preparative reactions were performed by irradiation of CH_3OH and CH_3CN solutions of ACND (ca. 8 mM) and **5–7** (ca. 16 mM) by using Pyrex-filtered light ($\lambda > 290$ nm). The nature of products generated and the gross chemical efficiencies were evaluated for the processes conducted at ACND conversions ranging from 55 to 80%. Product separations employed silica gel chromatographic

(1) (a) Ohga, K.; Yoon, U. C.; Mariano, P. S. *J. Org. Chem.* **1984**, *49*, 213. (b) Brumfield, M. A.; Quillen, S. L.; Yoon, U. C.; Mariano, P. S. *J. Am. Chem. Soc.* **1984**, *106*, 6855. (c) Hasegawa, E.; Brumfield, M. A.; Mariano, P. S.; Yoon, U. C. *J. Org. Chem.* **1988**, *53*, 5435.

(2) (a) Yoon, U. C.; Kim, J. U.; Hasegawa, E.; Mariano, P. S. *J. Am. Chem. Soc.* **1987**, *109*, 4421. (b) Hasegawa, E.; Xu, W.; Mariano, P. S.; Yoon, U. C.; Kim, J. U. *J. Am. Chem. Soc.* **1988**, *110*, 8099.

(3) Xu, W.; Jeon, Y. T.; Hasegawa, E.; Yoon, U. C.; Mariano, P. S. *J. Am. Chem. Soc.* **1989**, *111*, 406.

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Scheme I

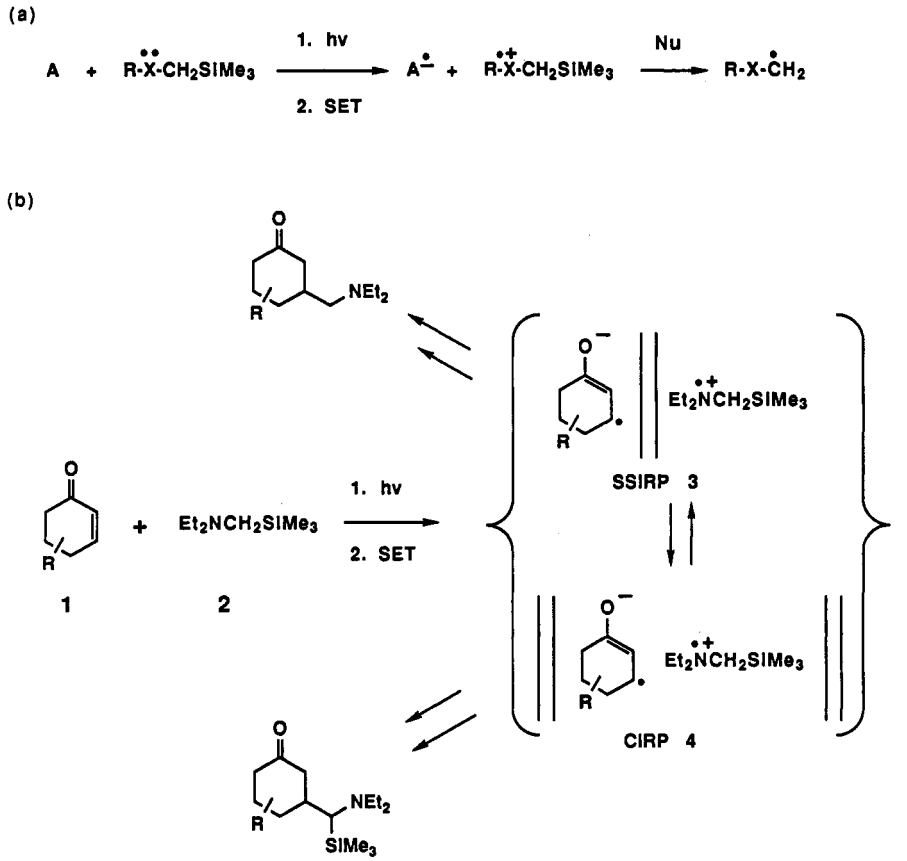
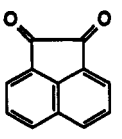


Table I. Results of Photoadditions of α-Silyl n-Electron Donors 5–7 to ACND

electron donor	solvent	reaction time (h)	% conversion of ACND	product(s) (% yields)[a]
5	MeOH	1.0	80	8 (30)
5	MeCN	0.75	80	8 (23)
6	MeOH	3.5	75	9 (20), 12 (34)
6	MeCN	4.0	70	9 (17), 10 (19) 12 (37)
7	MeOH	5.0	60	11a (23), 11b (20) 12 (44)
7	MeCN	5.0	55	11a (21), 11b (19) 12 (31)

[a] Yields are based on consumed ACND.

methods (see the Experimental Section). Products distributions and yields along with the solvents used are summarized in Table I.



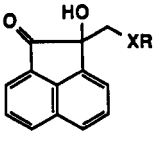
ACND

RX-CH2SiMe3

5 (RX=Et2N)

6 (RX=nPrS)

7 (RX=EtO)

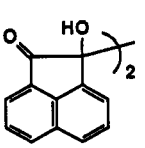


8 (RX=Et2N)

9 (RX=nPrS)

10 (RX=nPrS)

11 (RX=EtO)



12

Irradiation of ACND in the presence of α-silyl amine **5** in CH_3OH or CH_3CN results in formation of the non-silicon-containing adduct **8** as the exclusive nitrogen-containing product isolated. In contrast, only silicon-containing diastereomeric adducts **11** are generated in the photoreaction of ACND with the α-silyl ether **7** in both CH_3OH and CH_3CN. Finally, both the silicon-containing adduct **10** and non-silicon-containing adduct **9** are generated in photoreaction of ACND with α-silyl thioether **6** in CH_3CN. In the photoreactions of ACND with **6** and **7**, reduction dimer **12** is observed as one of the major products (31–44%) while none of dimer **12** is produced in the photoreaction of α-silyl amine **5** with ACND. The reduced dimer **12** was observed to undergo reversion to ACND during chromatographic separation or upon standing in air-saturated solutions.

Structural assignments to photoadducts **8–11** were made on the basis of characteristic spectroscopic data (see the Experimental Section). IR spectra of these photoadducts contain characteristic bands for hydroxyl groups at 3200–3600 cm^{-1} and carbonyl groups at 1720–1730 cm^{-1}. ^1H-NMR and ^{13}C-NMR spectra of photoadducts **8** and **9** show resonances which correspond to the respective (diethylamino)methyl and (*n*-propylthio)methyl groups. The photoadducts **10**, **11a**, and **11b** show singlets for nine hydrogens at −0.41 to −0.49 ppm in their ^1H-NMR spectra and at −1.7 to −2.2 ppm in their ^{13}C-NMR spectra corresponding to the trimethylsilyl groups.

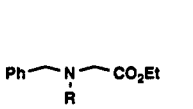
Photoadditions of *N*-Benzyl-*N*-alkylglycine Esters 13 and 14 to ACND. In order to examine the effect(s) of an electron-withdrawing carbethoxy group on the nature of amine photoadditions to ACND, photochemical reactions with the *N*-benzyl-*N*-alkylglycine ethyl esters **13** and **14** were explored. Preparative irradiations were conducted on CH_3OH, CH_3CN, and CH_2Cl_2 solutions of ACND (11 mM) and esters **13** and **14** (13 and 22 mM, respectively)

Table II. Results of Photoadditions of Glycine Esters 13 and 14 to ACND

glycine ester	solvent	reaction time (h)	% conversion of ACND	product(s) (% yields)[a]
13	MeOH	2.0	84	15 (20), 16 (57), 17 (2), 22 (3)
13	MeCN	2.0	70	15 (29), 16 (42), 17 (3), 19 (3), 22 (9), 23 (3)
13	CH_2Cl_2	2.0	75	15 (18), 16 (19), 17 (6), 19 (3), 22 (3), 23 (5)
14	MeOH	6.5	49	16 (23), 18 (23), 20 (22)
14	MeCN	2.0	71	16 (18), 18 (31), 20 (38)
14	CH_2Cl_2	0.5	49	16 (21), 18 (35), 20 (30)

[a] Yields are based on consumed ACND.

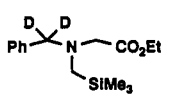
under conditions similar to those used in reactions with 5–7. The nature of products generated and the chemical yields were evaluated at ACND conversions ranging from 49 to 84%. Products were separated by chromatographic procedures (see the Experimental Section). Product yields along with the reaction solvents used are summarized in Table II.



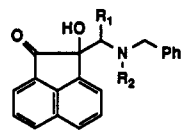
13 ($R=CH_2SiMe_3$)

14 ($R=Me$)

15 ($R=H$)



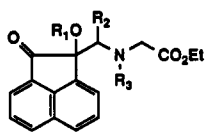
13-d



16 ($R_1=H$, $R_2=CH_2CO_2Et$)

17 ($R_1=CO_2Et$, $R_2=CH_2SiMe_3$)

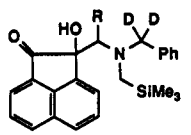
18 ($R_1=CO_2Et$, $R_2=Me$)



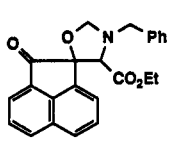
19 ($R_1=SiMe_3$, $R_2=H$, $R_3=CH_2Ph$)

20 ($R_1=R_2=H$, $R_3=CH_3$)

21 ($R_1=H$, $R_2=Ph$, $R_3=CH_2SiMe_3$)



17-d ($R=CO_2Et$)



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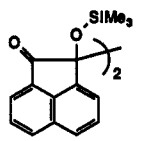


23

Irradiations of ACND in CH_3OH, CH_3CN, and CH_2Cl_2 containing the *N*-benzyl-*N*-[(trimethylsilyl)methyl]glycine ethyl ester (13) result in the formation of the non-silicon-containing photoadduct 16 as the major product, the yields increasing as the polarity (E_T value)[4] of the solvent ($CH_2Cl_2 < CH_3CN < CH_3OH$) increases. Irradiations in the aprotic solvents, CH_3CN or CH_2Cl_2, lead to formation of photoproducts 19 and 23 both of which contain a silyloxy group. Interestingly, 19 and 23 are not produced when photolysis of ACND and 13 is conducted in CH_3OH. The silicon-containing photoadduct 17 is formed as a minor product in the reactions of ACND and glycine ester 13 in all solvents. The oxazolidine 22, observed as an unexpected minor product (3–9%) from reaction of ACND with 13, appears to be produced by secondary photoinduced SET reaction of the initially formed silicon-containing photoadduct 17. The secondary amine 15 also forms in ca. 18–29% yields in these photoreactions.

Irradiation of ACND in CH_3OH, CH_3CN, and CH_2Cl_2 solutions containing the *N*-benzyl-*N*-methylglycine ethyl ester (14) results in the formation of photoadducts 16, 18, and 20 as major products. The yields of products 16, 18, and 20 do not vary significantly with solvent polarity. However, the reaction efficiencies appear to increase as solvent polarity decreases, judged by the times required to bring about comparable conversions of ACND (see Table II). Noticeably, the yield of photoadduct 16 is lower in the reaction with *N*-methylglycine ester 14 as compared with *N*-[(trimethylsilyl)methyl]glycine ester 13. Moreover, photoadduct 18, forming via sequential deprotonation of the intermediate amine cation radical at the carbethoxy-substituted methylene carbon, is generated in larger yields than photoadduct 16, which arises by deprotonation at the methyl carbon. In addition to photoadduct 16 and 18, an unexpected photoadduct 20 which lacks a phenyl group is produced as a major product (22–38%) in all cases.

Structural assignments to the photoadducts were made by using characteristic spectroscopic data. ^{13}C-NMR spectra of photoadducts 16–20 and 22, for example, contain resonances at 76.9–86.6 ppm which correspond to the C-2 quaternary carbons. Their IR spectra contain two characteristic bands for the ketone and ester carbonyl groups at 1700–1755 cm^{-1} while those for photoadducts 16–18 and 20 possess strong bands for O–H stretching at 3200–3650 cm^{-1}. These spectroscopic features support the conclusion that photoadditions take place at the C-2 position of ACND. All of the other spectroscopic features including ^1H-NMR, ^{13}C-NMR, and high-resolution mass spectra of these substances are in complete accord with the assigned structures.

A special effort was made to remove ambiguity from the assignment of structure 17 rather than 21 to one of these photoadducts. These compounds are regioisomeric and their differentiation by analysis of ^1H-NMR and ^{13}C-NMR spectroscopic data is difficult owing to the similarities predicted for the benzylic and α-ester proton and carbon resonances. An unambiguous assignment of the structure to 17 was achieved by inspection of ^1H-NMR and ^{13}C-NMR spectra of the photoadduct 17-*d* obtained from photoreaction of the *N*-(benzyl-α,α-d_2)-*N*-[(trimethylsilyl)methyl]glycine ester (13-*d*) with ACND. Specifically, the ^1H-NMR spectrum of 17-*d* lacks resonances (AB quartet) at 3.72 and 4.18 ppm for the diastereotopic benzylic methylene protons in 17 and its ^{13}C-NMR spectrum in CD_3CN is missing the resonance at 61.2 ppm for benzyl methylene carbon of 17.

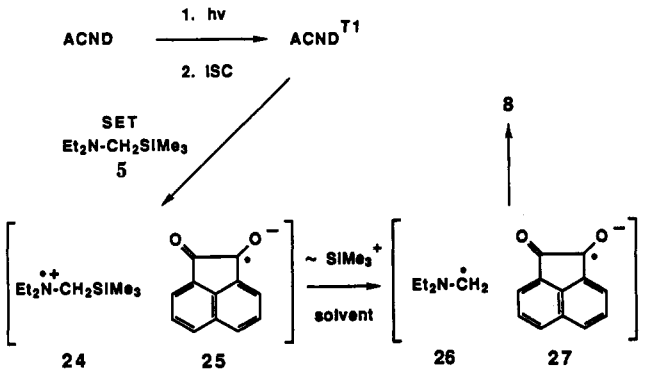
Discussion

Mechanism for Photoreactions of ACND with α-Silyl Amines. Photoreaction of ACND with the tertiary α-silyl amine 5 in both MeOH and MeCN results in exclusive[5] production of the non-TMS-containing adduct 8. These results are distinctly different from those found in our earlier studies of the photoadditions of α-silyl amines to conjugated cyclohexenones[2] and in more recent efforts probing silyl amine–cyclohexenone photocyclization reactions.[3] In these cases, non-TMS-containing adducts predominate only in those photoaddition (Scheme I) or

(4) Dimroth, K.; Reichardt, C.; Siepmann, T. S.; Bohlmann, F. *Ann.* **1963**, *661*, 1.

(5) Photoadduct 8 was observed as an exclusive product on tlc but the isolated yields are not high due to the photodecomposition of 8 during irradiations.

Scheme II



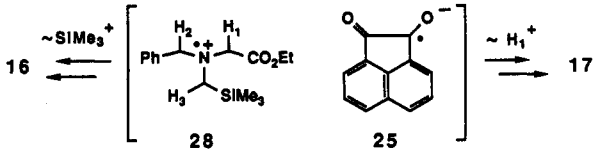
photocyclization reactions which occur in polar-protic solvents such as MeOH while TMS adducts are formed selectively or exclusively for reactions in less polar aprotic solvents like MeCN. This difference appears to be in accord with an SET mechanism for adduct 8 formation (see Scheme II) in the ACND + 5 process and with the anticipated basicity of the intermediate ACND radical anion 25.

Excitation of ACND should be followed by rapid intersystem crossing to produce the corresponding triplet excited state, ACND^{T1}. Earlier studies[6-8] have shown that ACND^{T1} is an efficiently formed, long lived (ca. 1 μs) species with an energy of ca. 50 kcal/mol. Electron transfer from the silyl amine 5 ($E_{1/2}(+)$ = ca. +0.4 V)[9a] to ACND^{T1} ($E_{1/2}{}^{T1}(-)$ = ca. +1.4 V)[10] is thermodynamically quite favorable (ΔG_{SET} = ca. −23 kcal/mol) and thus should be both rapid[11] and efficient ($k_{SET} > k_{decay}$) for the silyl amine concentration range (ca. 15 mM) used in our experiments. The oxygen quenching results presented above support the assignment of ACND^{T1} as the reactive excited state in this as well as the α-silyl ether and thioether reactions.[7]

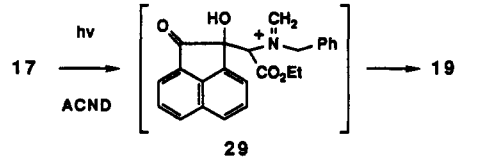
Electron transfer from 5 to ACND^{T1} results in the generation of the radical ion pair(s) 24 + 25 (CIRP and/or SSIRP). The pathway followed in the ensuing reaction of this pair is not dependent on solvent. Accordingly, desilylation of 24 by nucleophile-assisted displacement of the TMS group occurs in both MeOH and MeCN to produce exclusively the radical pair 26 + 27, the precursor of the observed adduct 8.

The contrasting nature of the reactions of ion radical pair(s) 24 + 25 (exclusive desilylation in MeCN) compared to 4 (predominant proton transfer in MeCN) correlates well with the expected basicities of the radical anion components. We have pointed out earlier[2] that proton transfer in 4 is driven by the high basicity of cyclohexenone anion radicals (pK_a of protonated species of ca. 10)[12] and acidity of tertiary amine cation radicals (pK_a ca. 7-8)[13] when paired in aprotic less polar solvents. In contrast, anion radicals derived from α-diketones and o-quinones such as ACND are much weaker bases (est. pK_a of conjugate acids ca. 5).[12] Consequently, proton transfer from 24 to 25 even in aprotic solvents should be thermodynamically (thus kinetically) unfavorable.

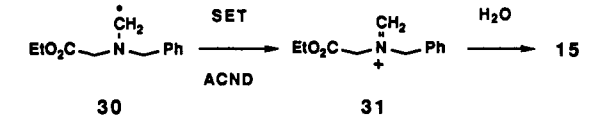
Photoaddition of the silylglycine ester 13 to ACND leads to formation of the non-TMS adduct 16 mainly along with lesser quantities of the TMS adduct 17 and oxazolidine 22, a product derived from secondary photoreaction of 17 (see below). Moreover, the ratio of 16 to 17 + 22 descreases when the polarity and protic nature of the medium decreases (e.g., MeOH, 11.4; MeCN, 3.5; CH_2Cl_2, 2.1). These results are consistent with a reaction pathway promoted by SET from 13 ($E_{1/2}(+)$ = ca. 0.7 V)[14] to ACND^{T1} giving the radical ion pair 28 + 25. Proton transfer between 28 and 25 is now competitive with desilylation. This is most probably due to the effect of the α-ester substituent in 28 which enhances the acidity of the amine cation radicals.[15,16]



The origins of the other products formed in the reaction of silylglycine 13 with ACND are interesting. The production of oxazolidine 19 is best understood in terms of a secondary ACND promoted photoreaction of the primary adduct 17. Thus, sequential SET–desilylation–SET would



transform 17 to an iminium cation 29 which is the likely precursor of the oxazolidine. The secondary amine 15, generated in significant quantities in the 13 + ACND photoreaction, results from an oxidative dealkylation pathway that we[3] and others[17] have identified previously. In it, the intermediate α-amino radical 30, a strong reducing agent ($E_{1/2}(+)$ = ca. −1 V),[18] is oxidized by ACND to give a hydrolytically unstable formaldiminium ion. In contrast, it is difficult to imagine, much more to propose, a reasonable mechanism for formation of the desphenyl product 20 in reaction of the N-methylglycine 14 with ACND.



(6) Fang, T.-S.; Singer, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 6278.
(7) Koo, J.-Y.; Schuster, G. B. *J. Org. Chem.* **1979**, *44*, 847.
(8) Kuboyama, A.; Yake, S. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2475.
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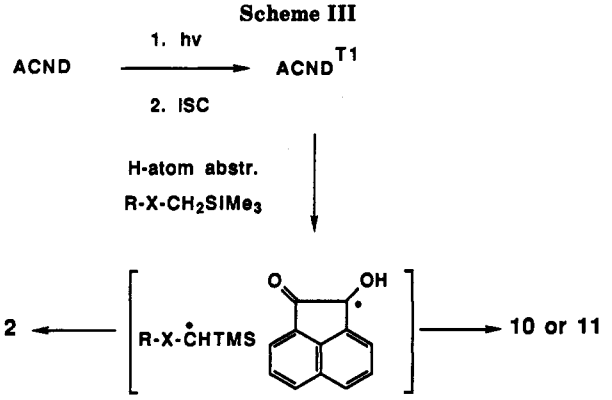
(10) (a) The ground-state reduction potential of ACND is −0.84 V (ref 10b) and the triplet excited state reduction potential can be calculated from the triplet energy ($E_{0,0}{}^{T1}$) and this potential ($E_{1/2}(-)$) by the following $E_{1/2}{}^{T1}(-) = E_{0,0}{}^{T1} + E_{1/2}(-)$. (b) *Function of Quinones in Energy Conserving Systems*; Trumpower, B. L., Ed.; Academic Press: New York, 1982; p 31.
(11) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.
(12) Heyon, E.; Ibata, T.; Lichtin, N. N.; Simic, M. *J. Phys. Chem.* **1972**, *76*, 2072.
(13) Das, S.; vonSonntag, C. *Z. Naturforsch.* **1986**, *416*, 505.
(14) Polarographic measurements (vs Ag/AgCl, 0.1 M $CaClO_4$, acetone) on the electron donors 5, 13, and 14 showed that the oxidation potentials for the glycine esters, 13 and 14, are higher by ca. 0.25 V than that of amine 5.
(15) (a) Lewis, F. D. *Acc. Chem. Res.* **1986**, *19*, 401. (b) Xu, W.; Mariano, P. S. *J. Am. Chem. Soc.* **1991**, *113*, 1431.
(16) It is not clear why adducts resulting from deprotonation at the benzylic center in 28 (i.e., H_2) are not formed in this process and why in the reaction of the N-methyl analogue 14 adducts resulting from deprotonation at the methyl center in the intermediate cation radical are produced. These questions are pertinent in light of the substituent effects noted earlier[15] on tertiary amine α-CH cation radical kinetic acidities.
(17) See, for instance: Bartholomew, R. F.; Davidson, R. S.; Howell, M. J. *J. Chem. Soc. C* **1971**, 2804. Bhattacharyya, K.; Das, P. K. *J. Phys. Chem.* **1986**, *90*, 3987. Cohen, S. G.; Chao, H. M.; Stein, N. *J. Am. Chem. Soc.* **1969**, *90*, 521.
(18) Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132.
(19) See, for instance: Rubin, M. B.; Zwitkowits, P. *J. Org. Chem.* **1964**, *29*, 2362; *Tetrahedron Lett.* **1965**, 2453.

Scheme III



Mechanisms for Photoreactions of ACND with the α-Silyl Ethers and Thioethers. Several significant differences exist between the ACND photoreactions with the silyl amines **5** and **13** and those with the silyl thioether **6** and silyl ether **7**. Firstly, based on a qualitative analysis of the photoreaction times required to bring about the same conversions to products, photoreaction of ACND with **5** is more efficient than with **6** or **7**. Moreover, large quantities of the TMS-containing adduct **10** are formed in the reaction of **6** with ACND in MeCN, and TMS-containing product **11** is produced as the sole adduct in photoaddition of **7** to ACND. These clear differences reflect a change in reaction mechanism in proceeding from the silyl amine **5**, which is a good electron donor ($E_{1/2}(+)$ = ca. +0.4 V),[9a] to the more difficulty oxidized thioether **6** ($E_{1/2}(+)$ = ca. 1.3 V)[9b,c,d] and ether **7** ($E_{1/2}(+)$ = ca. 1.9 V).[9d] Clearly, unlike with the amine systems, SET from the ether or thioether to $ACND^{T1}$ should be much less favorable (ΔG_{SET} = ca. +12 and −2 kcal/mol, respectively). Like other ketones, *o*-quinones are known to participate in triplet H atom abstraction reactions with good H atom donors.[20] Thus, reaction of ACND with the silyl ether **7** most likely follows an H atom abstraction pathway (Scheme III) leading to production of the diastereomeric, TMS adducts **11** along with the photoreduction dimer **12**. The high degree of regioselectivity for this process (Me_3Si-C-H > CH_3-C-H) is perhaps consistent with the slightly smaller bond dissociation energies of silicon substituted C–H bonds.[20] In a similar fashion, the thioether–ACND photoreaction likely occurs by both SET and H atom abstraction mechanisms.

Experimental Section

General Procedures. ^{1}H-NMR and ^{13}C-NMR spectra were recorded by using 60-, 200-, and 400-MHz spectrometers. ^{13}C-NMR resonances were assigned by use of the INEPT technique to the determine number of attached hydrogens. Preparative photochemical reactions were conducted with an apparatus consisting of a 450-W medium-pressure mercury vapor lamp surrounded by a Pyrex filter in a water-cooled quartz immersion well surrounded by the solution being irradiated. The photolysis solutions were purged with nitrogen both before and during irradiations, and solvent used for photolysis was removed under reduced pressure after reactions. Preparative TLC was performed on 20 × 20 cm plates coated with silica gel PF_{254}. Column chromatography was performed with Merck silica gel 60. Low- and high-resolution mass spectrometric analyses were performed using EI (70 eV). Drying of organic layers obtained by workup of reaction mixtures was performed by standing over anhydrous sodium sulfate. *N*-[(Trimethylsilyl)methyl]-*N*,*N*-diethylamine (**5**),[2] (trimethylsilyl)methyl *n*-propyl thioether (**6**),[21] (trimethylsilyl)methyl ethyl ether (**7**)[21] and *N*-benzyl-*N*-[(trimethylsilyl)methyl]amine[22] were prepared by the reported methods. All new compounds characterized in this work were judged to be >90% pure by ^{1}H- and ^{13}C-NMR analysis. Photoproducts **10**, **12**, **17**, **18**, and **21–23** were obtained as single diastereomers.[23]

***N*-Benzyl-*N*-alkylglycine Esters 13 and 14.** To a solution of *N*-benzyl-*N*-[(trimethylsilyl)methyl]amine (6.79 g, 35.2 mmol) or *N*-(benzylmethyl)amine (4.26 g, 35.2 mmol) in 25 mL of CH_3CN was added dropwise ethyl α-bromoacetate (4.64 g, 27.8 mmol). The solution was stirred at 0 °C for 3 h, and 7 N aqueous NaOH solution (30 mL) was added. The mixture was extracted with ether, and the ethereal extracts were concentrated in vacuo giving a residue which was subjected to column chromatographic separation (*n*-hexane/CH_2Cl_2, 1:1) to yield 6.8 g (88.5%) of *N*-benzyl-*N*-[(trimethylsilyl)methyl]glycine ethyl ester (**13**) and 5.3 g (92.1%) of *N*-benzyl-*N*-methylglycine ethyl ester (**14**).[24]

13: ^{1}H-NMR (CCl_4) 0.32 (s, 9 H), 1.39 (t, 3 H, J = 7 Hz, $CO_2CH_2CH_3$), 2.47 (s, 2 H, CH_2SiMe_3), 3.43 (s, 2 H, NCH_2CO_2), 3.96 (s, 2 H, $PhCH_2N$), 4.27 (q, 2 H, J = 7 Hz, $CO_2CH_2CH_3$), 7.40 (br s, 5 H, $C_6H_5CH_2$); ^{13}C-NMR ($CDCl_3$) −1.5 (Me_3Si), 14.3 (CH_3), 45.7 ($TMSCH_2N$), 57.1 (OCH_2), 59.9 ($PhCH_2N$), 61.5 ($COCH_2N$), 126.9, 128.2, and 128.8 (aromatic CH), 139.5 (aromatic C), 171.4 (C=O); MS *m*/*z* (rel intensity) 279 (M^+, 2), 206 (47), 160 (13), 91 (100), 73 (12); high-resolution MS *m*/*z* 279.1655 ($C_{15}H_{25}NO_2Si$ requires 279.1653).

14: ^{1}H-NMR ($CDCl_3$) 1.25 (t, 3 H, J = 7 Hz, $CO_2CH_2CH_3$), 2.35 (s, 3 H, NCH_3), 3.65 (s, 2 H, NCH_2CO_2), 4.15 (q, 2 H, J = 7 Hz, $CO_2CH_2CH_3$), 7.15 (br s, 5 H, $C_6H_5CH_2$).

Irradiation of ACND with *N*-[(Trimethylsilyl)methyl]-*N*,*N*-diethylamine (5) in CH_3OH and CH_3CN. A solution of acenaphthylenedione (ACND) (300 mg, 1.65 mmol) and $Me_3SiCH_2NEt_2$ (**5**) (523 mg, 3.29 mmol) in 200 mL of CH_3OH or CH_3CN was irradiated under N_2 purging for 1 h or 45 min, respectively, resulting in ca. 80% conversion of ACND. After removal of solvent, the residue was subjected to preparative TLC (2.5% CH_3OH in CH_2Cl_2) to yield 103 mg (30%) and 80 mg (23%), respectively, of photoadduct **8** as an oil.

8: ^{1}H-NMR ($CDCl_3$) 1.02 (t, 6 H, J = 7.1 Hz, $N(CH_2CH_3)_2$), 2.70 (q, 4 H, J = 7.1 Hz, $N(CH_2CH_3)_2$), 2.89 and 2.91 (2 s, diastereotopic, NCH_2), 7.56–8.10 (m, 6 H, aromatic); IR (neat) 3600–3200 (OH), 1725 cm^{-1} (C=O); ^{13}C-NMR ($CDCl_3$) 12.0 (NCH_2CH_3), 48.4 (NCH_2CH_3), 60.5 (CH_2N), 89.2 (C-2), 120.1, 121.5, 125.0, 128.2 and 131.4 (CH, aromatic), 128.7, 130.5, 132.5, 141.1 and 141.7 (C, aromatic), 206.3 (C=O); MS *m*/*z* (rel intensity) 268 (M^+ − H, 4), 267 (11), 253 (4), 198 (45), 196 (80), 183 (29), 168 (11), 154 (100), 126 (93); high-resolution MS *m*/*z* 268.1338 ($C_{17}H_{18}O_2N$ − H requires 268.1338).

Irradiation of ACND with (Trimethylsilyl)methyl *n*-Propyl Thioether (6) in CH_3OH. A solution of acenaphthylenedione (400 mg, 2.2 mmol) and $Me_3SiCH_2SCH_2CH_2CH_3$ (**6**) (710 mg, 4.38 mmol) in 200 mL of CH_3OH was irradiated for 3.5 h, resulting in ca. 75% conversion of ACND. After solvent removal and crystallization of the residue from *n*-hexane/$CHCl_3$ (1:2, v/v) 102 mg (34%) of photoreduction dimer **12** was obtained. The concentrated mother liquors were subjected to preparative TLC (1% CH_3OH in CH_2Cl_2) to yield 90 mg (20%) of photoproduct **9** as an oil.

9: ^{1}H-NMR ($CDCl_3$) 0.84 (t, 3 H, J = 7.3 Hz, $SCH_2CH_2CH_3$), 1.46 (sext, 2 H, J = 7.3 Hz, $SCH_2CH_2CH_3$), 2.34 (t, 2 H, J = 7.3 Hz, $SCH_2CH_2CH_3$), 3.01 (d, 1 H, J = 13.5 Hz, diastereotopic CH_2S), 3.25 (d, 1 H, J = 13.5 Hz, diastereotopic CH_2S), 3.42 (s, 1 H, OH), 7.61–8.13 (m, 6 H, aromatic); IR (neat) 3650–3200 (OH), 1720 cm^{-1} (C=O); ^{13}C-NMR ($CDCl_3$) 13.1 ($SCH_2CH_2CH_3$), 22.8 ($SCH_2CH_2CH_3$), 36.3 ($C(OH)CH_2S$), 40.0 ($SCH_2CH_2CH_3$), 79.0 (C-2), 120.8, 122.1, 125.6, 128.3, 128.7, and 131.9 (CH, aromatic), 130.6, 131.0, 139.0, and 141.8 (C, aromatic), 204.2 (C=O); MS *m*/*z* (rel intensity) 272 (M^+, 6), 255 (M^+ − OH, 5), 196 (100), 183 (66),

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(22) Padwa, A.; Dent, W. *Org. Synth.* **1988**, *67*, 133.

(23) NMR and TLC analysis of the crude photolysates did not reveal the presence of the other diastereomers of these substances. The relative stereochemistries at the two chiral centers in the single diastereomers obtained were not assigned.

(24) Kim, J.-M.; Cho, I.-S.; Mariano, P. S. *J. Org. Chem.* **1991**, *56*, 4943.

168 (10); high-resolution MS m/z 272.0871 ($C_{16}H_{16}O_2S$ requires 272.0871).

12: ^{1}H-NMR (DMSO-d_6) 7.05–7.20 (m, 2 H, aromatic), 7.40–7.55 (m, 2 H, aromatic), 7.65–7.80 (m, 4 H, aromatic), 7.90–8.00 (m, aromatic), 8.15–8.25 (m, 2 H, aromatic); IR (KBr) 3400 (OH); ^{13}C-NMR (DMSO-d_6) 82.8 (COH), 121.6, 123.6, 126.2, 128.8, 130.8, 132.1, 132.2, 137.9, 142.3, 203.3 (C=O); MS m/z (rel intensity) 364 (M^+ – 2H, 41), 331 (81), 324 (32), 301 (40).

Irradiation of ACND with (Trimethylsilyl)methyl *n*-Propyl Thioether (6) in CH_3CN. A solution of acenaphthylenedione (400 mg, 2.2 mmol) and $Me_3SiCH_2SCH_2CH_2CH_3$ (**6**) (710 mg, 4.38 mmol) in 200 mL of CH_3CN was irradiated for 4 h, resulting in ca. 70% conversion of ACND. After solvent removal crystallization of the residue from *n*-hexane/$CHCl_3$ (1:2 v/v) provided 104 mg (37%) of the photoreduction dimer **12**. The concentrated mother liquors were subjected to preparative TLC (1% CH_3OH in CH_2Cl_2) to yield 70 mg (17%) of photoproduct **9** and 100 mg (19%) of photoproduct **10** both as oils.

10: ^{1}H-NMR ($CDCl_3$) –0.47 (s, 9 H, $Si(CH_3)_3$), 1.02 (t, 3 H, J = 7.4 Hz, $SCH_2CH_2CH_3$), 1.70 (sext, 2 H, J = 7.4 Hz, $SCH_2CH_2CH_3$), 2.63 (s, 1 H, SCHSi), 2.76 (t, 2 H, J = 7.4 Hz, $SCH_2CH_2CH_3$), 5.27 (s, 1 H, OH), 7.57–8.13 (m, 6 H, aromatic); IR (neat) 3600–3200 (OH), 1730 cm^{-1} (C=O); ^{13}C-NMR ($CDCl_3$) –1.7 ($Si(CH_3)_3$), 13.4 ($SCH_2CH_2CH_3$), 23.2 ($SCH_2CH_2CH_3$), 40.1 ($SCH_2CH_2CH_3$), 43.2 (SiCHC), 80.4 (C-2), 120.0, 121.7, 125.4, 128.3, 128.6 and 131.9 (CH, aromatic), 130.8, 131.8, 140.5, 141.0 (C, aromatic), 203.5 (C=O); MS m/z (rel intensity) 327 (M^+ – OH, 100), 269 (35), 255 (78), 237 (16), 197 (24), 181 (89), 161 (52); high-resolution MS m/z 344.1266 ($C_{19}H_{24}O_2SSi$ requires 344.1267).

Irradiation of ACND with (Trimethylsilyl)methyl Ethyl Ether (7) in CH_3OH. A solution of acenaphthylenedione (300 mg, 1.65 mmol) and $Me_3SiCH_2OCH_2CH_3$ (**7**) (440 mg, 3.33 mmol) in 200 mL of CH_3OH was irradiated for 5 h, resulting in ca. 60% conversion of ACND. After solvent removal, crystallization of the residue from *n*-hexane/$CHCl_3$ (1:2, v/v) afforded 80 mg (44%) of photoreduction dimer **12**. The concentrated mother liquors were subjected to column chromatography (CH_2Cl_2) to yield the diastereomeric photoproducts **11a** (R_f = 0.7; 70 mg, 23%) and **11b** (R_f = 0.8; 62 mg, 20%), respectively, both as oils.

11a: ^{1}H-NMR ($CDCl_3$) –0.41 (s, 9 H, $Si(CH_3)_3$), 1.24 (t, 3 H, J = 7 Hz, OCH_2CH_3), 3.49 (s, 1 H, methine), 3.53–3.82 (m, 2 H, OCH_2CH_3), 3.95 (br s, 1 H, OH), 7.61–8.13 (m, 6 H, aromatic); IR (neat) 3650–3200 (OH), 1720 cm^{-1} (C=O); ^{13}C-NMR ($CDCl_3$) –2.2 ($Si(CH_3)_3$), 15.8 (OCH_2CH_3), 71.3 (OCH_2CH_3), 80.1 (CHSi), 81.3 (C-2), 121.1, 121.8, 125.7, 128.5, 128.6, and 131.6 (CH, aromatic), 130.6, 132.6, 138.3, and 141.7 (C, aromatic) 204.5 (C=O); MS m/z (rel intensity) 327 (M^+, 5), 299 (M^+ – CH_3, 12), 269 (34), 253 (70), 240 (25), 224 (25), 196 (32), 181 (14), 167 (20), 131 (65), 103 (100); high-resolution MS m/z 314.1329 ($C_{18}H_{22}O_3Si$ requires 314.1338).

11b: ^{1}H-NMR ($CDCl_3$) –0.49 (s, 9 H, $Si(CH_3)_3$), 1.26 (t, 3 H, J = 7 Hz, OCH_2CH_3), 3.21 (br s, 1 H, OH), 3.57 (s, 1 H, methine), 3.62–4.05 (m, 2 H, OCH_2CH_3), 7.62–8.16 (m, 6 H, aromatic); IR (neat) 3600–3200 (OH), 1720 cm^{-1} (C=O); ^{13}C-NMR ($CDCl_3$) –2.5 ($Si(CH_3)_3$), 16.1 (OCH_2CH_3), 71.3 (OCH_2CH_3), 77.4 (CHSi), 82.7 (C-2), 121.9, 122.6, 125.2, 128.2, 128.8, and 132.0 (CH, aromatic), 130.6, 131.7, 139.3, and 141.6 (C, aromatic), 203.5, (C=O); MS m/z (rel intensity) 314 (M^+, 5), 299 (M^+ – CH_3, 15), 269 (35), 253 (24), 240 (5), 224 (9), 196 (16), 167 (14), 131 (68), 103 (100); high-resolution MS m/z 314.1320 ($C_{18}H_{22}O_3Si$ requires 314.1338).

Irradiation of ACND with (Trimethylsilyl)methyl Ethyl Ether (7) in CH_3CN. A solution of acenaphthylenedione (300 mg, 1.65 mmol) and $Me_3SiCH_2OCH_2CH_3$ (**7**) (440 mg, 3.33 mmol) in 200 mL of CH_3CN was irradiated for 5 h, resulting in ca. 55% conversion of ACND. After solvent removal, crystallization of the residue from *n*-hexane/$CHCl_3$ (1:2, v/v) afforded 50 mg (31%) of photoreduction dimer **12**. The concentrated mother liquors were subjected to column chromatography (CH_2Cl_2) to yield 60 mg (21%) of **11a** and 53 mg (19%) of **11b**.

Irradiation of ACND with the α-Silyl n-Electron Donors 5–7 in the Presence of Oxygen. Solutions of acenaphthylenedione (200 mg, 1.1 mmol) and $Me_3SiCH_2N(CH_2CH_3)_2$ (**5**) (870 mg, 5.48 mmol), $Me_3SiCH_2SCH_2CH_2CH_3$ (**6**) (890 mg, 5.48 mmol), and $Me_3SiCH_2OCH_2CH_3$ (**7**) (724 mg, 5.48 mmol) in 120 mL of CH_3CN were irradiated under oxygen, purging for 0.5 h with **5** and for 2 h with **6** and **7**. Analysis for product formation was performed by TLC (CH_2Cl_2). The formation of photoproduct **8** in the photoreaction with **5** was observed to be considerably quenched. The formation of products **9**, **10**, and **12** in the photoreaction of **6** and of products **11a**, **11b**, and **12** in the photoreaction of **7** was observed to be completely quenched.

Irradiation of ACND with *N*-Benzyl-*N*-[(trimethylsilyl)methyl]glycine Ethyl Ester (13) in CH_3OH. A solution of acenaphthylenedione (400 mg, 2.2 mmol) and $Me_3SiCH_2N(CH_2Ph)CH_2CO_2CH_2CH_3$ (**13**) (736 mg, 2.64 mmol) in 200 mL of CH_3OH was irradiated for 4 h, resulting in ca. 84% conversion of ACND. The residue obtained after solvent removal was subjected to column chromatography to yield 100 mg of a fraction (CH_2Cl_2) containing **17** and **22** (fraction 1), (CH_2Cl_2/AcOEt, 10:1 v/v) 410 mg (57%) of **16** as a crystalline solid (mp 132–133 °C), and (CH_2Cl_2/AcOEt, 5:1 v/v) 100 mg (20%) of the secondary amine **15**.[22] Fraction 1 was subjected to preparative TLC (*n*-hexane/AcOEt, 3/1) to give 20 mg (2%) of **17** as an oil and 20 mg (3%) of **22** as a crystalline solid (mp 127–128 °C).

15:[22] ^{1}H-NMR (CCl_4) 1.25 (t, 3 H, J = 7.2 Hz, $CO_2CH_2CH_3$), 1.92 (s, 1 H, NH), 3.40 (s, 2 H, CH_2CO), 3.80 (s, 2 H, $PhCH_2N$), 4.20 (q, 2 H, J = 7.2 Hz, $CO_2CH_2CH_3$), 7.32 (s, 5 H, C_6H_5); IR (KBr) 3250–3100 (NH), 1740 cm^{-1} (C=O).

16: ^{1}H-NMR ($CDCl_3$) 1.05 (t, 3 H, J = 7 Hz, CH_2CH_3), 3.05–3.20 (m, 2 H, CH_2CO_2), 3.15 and 3.25 (2 d, J = 10 Hz, CH_2N), 3.65 (s, 2 H, benzylic), 3.95 (q, 2 H, J = 7 Hz, CH_2CH_3), 4.55 (s, 1 H, OH), 6.77–7.05 (m, 5 H, C_6H_5), 7.40–7.95 (m, 6 H, aromatic); IR (KBr) 3500–3200 (OH), 1730 and 1700 cm^{-1} (C=O); ^{13}C-NMR ($CDCl_3$) 14.1 (OCH_2CH_3), 54.8 (CH_2), 59.7 (CH_2), 60.4 (CH_2), 61.6 (CH_2), 79.0 (C-2), 120.5, 121.6, 125.2, 127.1, 128.2, 128.2, 128.7, and 131.5 (CH, aromatic), 130.5, 131.4, 138.2, 139.8 and 141.9 (C, aromatic), 171.7 (ester C=O), 205.8 (C=O); MS m/z (rel intensity) 390 (M^+, 2), 344 (M^+ – OCH_2CH_3, 3), 206 (10), 200 (15), 194 (41), 182 (58), 154 (36), 126 (65), 120 (57), 106 (35), 91 (100); high-resolution MS (Cl) m/z 390.1679 (M + H^+, $C_{24}H_{24}NO_4$ requires 390.1886).

17: ^{1}H-NMR ($CDCl_3$) 0.19 (s, 9 H, $Si(CH_3)_3$), 1.00 (t, 3 H, J = 7.1 Hz, OCH_2CH_3), 2.22 (d, 1 H, J = 14.4 Hz, $CH_2Si(CH_3)_3$), 2.86 (d, 1 H, J = 14.4 Hz, $CH_2Si(CH_3)_3$), 3.72 (d, 1 H, J = 12.2 Hz, CH_2Ph), 3.90–4.04 (m, 3 H, OCH_2CH_3), 4.13 (s, 1 H, CH), 4.18 (d, 1 H, J = 12.2 Hz, CH_2Ph), 5.55 (br s, 1 H, OH), 6.99–7.01 and 7.40–7.43 (m, 5 H, phenyl), 7.48–7.91 (m, 5 H, acenaphthyl); ^{13}C-NMR ($CDCl_3$) –1.4 ($Si(CH_3)_3$), 14.0 (OCH_2CH_3), 44.2 ($CH_2Si(CH_3)_3$), 60.8 (two peaks overlapped, CH_2Ph and $CO_2CH_2CH_3$), 69.6 (CH), 76.9 (C-2), 120.2, 121.0, 125.4, 127.9, 128.2, 128.4, 128.6, 130.0, and 130.7 (CH, aromatic), 130.4, 132.7, 138.0, 139.8, and 142.0 (C, aromatic), 169.4 (ester C=O), 204.3 (C=O); IR (KBr) 3300–3600 (OH), 1710 and 1740 cm^{-1} (C=O); ^{13}C-NMR (CD_3CN) –1.5 ($Si(CH_3)_3$), 14.5 (OCH_2CH_3), 45.1 ($CH_2Si(CH_3)_3$), 61.2 (CH_2Ph), 61.6 (OCH_2CH_3), 70.7 (CH), 78.6 (C-2), 121.7, 122.3, 126.5, 128.4, 129.3, 129.5, 130.7, and 131.9 (CH aromatic), 131.5, 133.4, 139.3, 140.4, and 142.8 (C, aromatic), 170.2 (ester C=O), 205.1 (C=O); MS (CI) m/z (rel intensity) 462 (M + H^+, 33), 446 (M^+ – CH_3, 3), 388 (M^+ – $CO_2CH_2CH_3$, 5), 284 (4), 280 (18), 279 (48), 278 (M^+ – acenaphthenyl, 100); high-resolution MS (CI) m/z 462.2101 (M + H^+, $C_{27}H_{32}NO_4Si$ requires 462.2100).

22: ^{1}H-NMR ($CDCl_3$) 0.28 (t, 3 H, J = 7.1 Hz, $CO_2CH_2CH_3$), 3.43–3.57 (m, 2 H, $CO_2CH_2CH_3$), 3.91 (d, 1 H, J = 13.0 Hz, CH_2Ph), 4.08 (s, 1 H, $NCHCO_2CH_2CH_3$), 4.44 (d, 1 H, J = 13.0 Hz, CH_2Ph), 4.75 (d, 1 H, J = 3.7 Hz, OCH_2N), 5.05 (d, 1 H, J = 3.7 Hz, OCH_2N), 7.28–8.14 (m, 11 H, aromatic); IR (KBr) 1730 and 1755 cm^{-1} (two, C=O); ^{13}C-NMR ($CDCl_3$) 13.0 (OCH_2CH_3), 56.9 (CH_2Ph), 60.3 (OCH_2CH_3), 71.4 ($NCHCO_2$), 86.6 (C-2), 89.3 (OCH_2N), 121.8, 122.1, 125.8, 127.5, 128.2, 128.5, 128.7, 128.9, and 131.8 (CH, aromatic), 130.5, 131.2, 136.6, 138.2, 142.6 (C, aromatic), 168.7 (ester C=O), 201.7 (C=O); MS m/z (rel intensity) 387 (M^+, 1), 314 (M^+ – $CO_2CH_2CH_3$, 14), 205 (19), 198 (25), 196 (16), 182 (26), 154 (90), 126 (100); high-resolution MS m/z 387.147058 ($C_{24}H_{21}NO_4$ requires 387.147035).

Irradiation of ACND with *N*-Benzyl-*N*-[(trimethylsilyl)methyl]glycine Ethyl Ester (13) in CH_3CN. A solution of acenaphthylenedione (400 mg, 2.2 mmol) and $Me_3SiCH_2N(CH_2Ph)CH_2CO_2CH_2CH_3$ (**13**) (736 mg, 2.64 mmol) in 200 mL of CH_3CN was irradiated for 2 h, resulting in ca. 70% conversion of ACND. After solvent removal the residue was subjected to column chromatography giving (*n*-hexane/CH_2Cl_2, 1:1, v/v) 80 mg of a mixture of **19** and **23** (fraction 1), (CH_2Cl_2) 120 mg of a

mixture of 17 and 22 (fraction 2), (CH_2Cl_2/AcOEt, 10:1, v/v) 250 mg (42%) of 16, and (CH_2Cl_2/AcOEt, 5:1, v/v) 150 mg (29%) of 15.[22] Fraction 1 was subjected preparative TLC (*n*-hexane/ether, 1/2) to give 20 mg (3%) of 19 and 11 mg (3%) of 23 both as crystalline solids (mp 144–146 °C and mp 130–132 °C, respectively). Further purification of fraction 2 by preparative TLC (*n*-hexane/AcOEt, 3/1) gave 20 mg (3%) of 17 and 55 mg (9%) of 22 both as oils.

19: ^{1}H-NMR ($CDCl_3$) –0.20 (s, 9 H, $Si(CH_3)_3$), 1.18 (t, 3 H, J = 7.1 Hz, OCH_2CH_3), 2.79 (d, 1 H, J = 17.9 Hz, CH_2CO_2), 3.04 (d, 1 H, J = 17.9 Hz, CH_2CO_2), 3.38 (d, 1 H, J = 13.2 Hz), 3.45 and 3.56 (2 H, AB quartet, J = 14.1 Hz), 3.68 (d, 1 H, J = 13.2 Hz), 6.35–6.39 (m, 2 H, phenyl), 6.87–6.99 (m, 3 H, phenyl), 7.58–8.12 (m, 6 H, acenaphthyl); IR (KBr) 1730 cm^{-1} (C=O); ^{13}C-NMR ($CDCl_3$) 1.5 ($Si(CH_3)_3$), 14.3 (OCH_2CH_3), 53.7 (CH_2), 58.9 (CH_2), 60.0 (CH_2), 63.0 (CH_2), 81.8 (C-2), 121.0, 121.3, 125.2, 126.6, 127.8, 128.1, 128.3, 128.5, and 131.3 (CH, aromatic), 130.6, 132.4, 138.7, 140.5, and 142.0 (C, aromatic), 171.6 (ester C=O), 206.6 (C=O). Physical properties of photoadduct 19 were identical to those of authentic sample 19 obtained by O-silylation of isolated photoproduct 16 (hexamethyldisilazane, MeCN, 80 °C, 12 h, 84%).

23: ^{1}H-NMR ($CDCl_3$) –0.33 (s, 18 H, 2 $Si(CH_3)_3$), 7.58–7.70 (m, 8 H, aromatic), 7.88–7.93 (m, 2 H, aromatic), 8.04–8.08 (m, 2 H, aromatic); IR (KBr), 1725 cm^{-1} (C=O); ^{13}C-NMR ($CDCl_3$) 1.1 ($Si(CH_3)_3$), 85.3 (C-2), 120.7, 123.9, 125.4, 127.7, 127.8 and 131.3 (CH, aromatic), 130.3, 132.0, 137.4 and 142.0 (C, aromatic), 201.5 (C=O); MS m/z (rel intensity) 495 ($M^+ - CH_3$, 1), 386 (0.6), 347 (1), 328 (19), 255 (91), 240 (10), 210 (5), 198 (10), 154 (13), 126 (13), 73 (100); high-resolution MS m/z 255.08413 ($M^+/2$) ($M^+/2$, $C_{15}H_{15}O_2Si$ requires 255.08413).

Irradiation of ACND with *N*-Benzyl-*N*-[(trimethylsilyl)methyl]glycine Ethyl Ester (13) in CH_2Cl_2. A solution of acenaphthylenedione (400 mg, 2.2 mmol) and $Me_3SiCH_2N(CH_2Ph)CH_2CO_2CH_2CH_3$ (13) (740 mg, 2.65 mmol) in 200 mL of CH_2Cl_2 was irradiated for 2 h, resulting in ca. 75% conversion of ACND. After solvent removal the residue was subjected to column chromatography, giving (*n*-hexane/CH_2Cl_2, 1:1, v/v) 70 mg of a mixture containing 19 and 23 (fraction 1), (CH_2Cl_2) 100 mg of a mixture containing 17 and 22 (fraction 2), (CH_2Cl_2/AcOEt, 10:1, v/v) 120 mg (19%) of 16, and (CH_2Cl_2/AcOEt, 5:1, v/v) 90 mg (18%) of 15.[22] Fraction 1 was subjected to preparative TLC (*n*-hexane/ether, 10/1) to give 20 mg (3%) of 19 and 19 mg (5%) of 23. Fraction 2 was subjected to preparative TLC (*n*-hexane/AcOEt, 3/1), giving 45 mg (6%) of 17 and 20 mg (3%) of 22.

Irradiation of ACND with *N*-Benzyl-*N*-methylglycine Ethyl Ester (14) in CH_3OH, CH_3CN, and CH_2Cl_2. A solution of acenaphthylenedione (400 mg, 2.2 mmol) and $CH_3N(CH_2Ph)CH_2CO_2CH_2CH_3$ (14) (910 mg, 4.4 mmol) in 200 mL of CH_3OH was irradiated for 6.5 h, resulting in 49% conversion of ACND. After solvent removal the residue was subjected to column chromatography (2% CH_3OH in CH_2Cl_2) to give 96 mg (23%) of 18 (as a crystalline solid, mp 85–86 °C), 95 mg (23%) of 16, and 73 mg (22%) of 20 (as a crystalline solid, mp 79–80 °C), respectively.

18: ^{1}H-NMR ($CDCl_3$) 1.03 (t, 3 H, J = 7.1 Hz, OCH_2CH_3), 2.30 (s, 3 H, NCH_3), 3.59 (d, 1 H, J = 12.7 Hz, CH_2Ph), 3.83 (d, 1 H, J = 12.7 Hz, CH_2Ph), 3.91–4.08 (m, 2 H, OCH_2CH_3), 4.11 (s, 1 H, CH), 5.20 (br s, 1 H, OH), 6.99–7.18 (m, 5 H, C_6H_5), 7.38–8.00 (m, 6 H, acenaphthyl); IR (KBr) 3620–3400 (OH), 1720 and 1745 cm^{-1} (two C=O); ^{13}C-NMR ($CDCl_3$) 14.1 (OCH_2CH_3), 40.2 (NCH_3), 61.0 ($PhCH_2$), 61.2 (OCH_2CH_3), 71.5 (CH), 78.0 (C-2), 121.2, 121.4, 125.7, 127.4, 128.2, 128.3, 128.5, and 129.0 (CH aromatic), 130.0, 131.0, 132.4, 138.1, 139.0, and 142.5 (C, aromatic), 170.0 (ester C=O), 203.7 (C=O); MS (Cl) m/z (rel intensity) 390 ($M + H^+$, 37), 389 (M^+, 3), 388 ($M^+ - H$, 11), 316 ($M^+ - CO_2CH_2CH_3$, 13), 298 ($M^+ - CH_2Ph$, 3), 207 (94), 206 (M^+ – acenaphthyl, 100), 196 (13), 183 (32), 182 (44), 154 (67), 134 (45), 127 (32), 126 (100); high-resolution MS (Cl) m/z 390.1690 ($M + H^+$, $C_{24}H_{24}NO_4$ requires 390.1705).

20: ^{1}H-NMR ($CDCl_3$) 1.23 (t, 3 H, J = 7.2 Hz, OCH_2CH_3), 2.45 (s, 3 H, NCH_3), 3.04 (d, 1 H, J = 14.4 Hz, CH_2N), 3.19 (d, 1 H, J = 14.4 Hz, CH_2N), 3.40 (s, 2 H, NCH_2CO_2), 4.13 (q, 2 H, J = 7.2 Hz, OCH_2CH_3), 7.62–8.10 (m, 6 H, acenaphthyl); IR (KBr) 3450–3600 (OH), 1705 and 1740 cm^{-1} (two C=O); ^{13}C-NMR ($CDCl_3$) 14.2 (OCH_2CH_3), 44.6 (NCH_3), 59.6 (CH_2), 60.6 (CH_2), 62.6 (CH_2), 78.7 (C-2), 120.6, 121.7, 125.2, 128.3, 128.7, and 131.6 (CH, aromatic), 130.5, 131.1, 139.8, and 141.7 (C, aromatic), 171.5 (ester C=O), 205.7 (C=O); MS (Cl) m/z (rel intensity) 314 ($M + H^+$, 100), 297 ($M^+ - CH_3$, 7), 268 (2), 240 (1); high-resolution MS (Cl) m/z 314.1392 ($M + H^+$, $C_{18}H_{20}NO_4$ requires 314.1392).

Similar irradiations in CH_3CN and CH_2Cl_2 yielded products 16, 18, and 20. Irradiation times, percent conversions, and products (yield) were as follows; 2 h, 71%, 16 (18%), 18 (31%), 20 (38%) in CH_3CN; 0.5 h, 49%, 16 (21%), 18 (35%), 20 (30%) in CH_2Cl_2.

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Supplementary Material Available: ^{1}H and ^{13}C NMR spectra of new compounds described in the Experimental Section (30 pages). This material is contained in many 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.