

Electron-Transfer-Induced Photoadditions of the Silyl Amine $\text{Et}_2\text{NCH}_2\text{TMS}$ to α,β -Unsaturated Cyclohexenones. Dual Reaction Pathways Based on Ion-Pair-Selective Cation-Radical Chemistry

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Abstract: The photoaddition reactions of a series of conjugated cyclohexenones with the tertiary α -silyl amine $\text{Et}_2\text{NCH}_2\text{TMS}$ have been subjected to exploratory and mechanistic investigation. In general, photoadditions in these systems occur to generate in modest to good yields adducts resulting from carbon-carbon bonding between the enone β -carbons and amine silicon-substituted α -carbon. These processes lead to formation of TMS and non-TMS adducts corresponding to substitution by the enone grouping for hydrogen or the trimethylsilyl grouping in the amine. The polarity and protic nature of solvents used for these photoreactions appear to control the TMS to non-TMS adduct ratios, with the former being favored in low-polarity aprotic media (MeCN) and the latter in polar protic media (MeOH). A more detailed investigation of this phenomenon by using the photoadditions of 4,4-dimethylcyclohex-2-en-1-one with $\text{Et}_2\text{NCH}_2\text{TMS}$ has uncovered the source of this control. Accordingly the non-TMS to TMS adduct ratio in this system is found to be directly dependent upon the solvent polarity (E_T or AN values) and protic nature. Likewise, this ratio increases when the salts LiClO_4 and $n\text{-Bu}_4\text{NClO}_4$ are present in the photolysis solution. Protic acids bring about the same result. On the other hand, the proportion of TMS adduct in the product mixture is enhanced when amine concentration is increased or by the addition of $n\text{-Bu}_4\text{NOH}$. These effects are interpreted in terms of selective formation and chemical reaction of ion-pair intermediates. In aprotic solvents of low polarity, the solvent-separated ion pair (SSIP), generated by single electron transfer from $\text{Et}_2\text{NCH}_2\text{TMS}$ to the triplet excited state of the enone, rapidly collapses to a contact ion pair (CIP) comprised of the enone radical anion and amine radical cation. Rapid proton transfer in the CIP from the silicon-substituted α -carbon of the amine cation radical to oxygen of the enone anion radical produces the radical-pair precursor of the TMS adduct. However, in polar protic solvent and when protic acids or ionized salts are present, the SSIP dissociates to produce the free amine cation radical. This intermediate undergoes desilylation or deprotonation, forming radical precursors of the respective non-TMS and TMS adducts. While the desilylation process is preferred, deprotonation of the free amine cation radical becomes increasingly competitive when high concentrations of base, such as the amine or $n\text{-Bu}_4\text{NOH}$, are present in the medium. Adduct formation when α -amino radicals are produced in this way most probably involves conjugate addition to the ground-state enone. Support for this proposal is found in the observation that 9,10-dicyanoanthracene serves as an electron-transfer sensitizer for silyl amine additions to cyclohex-2-en-1-one and its 4,4-dimethyl analogue in MeCN.

The area of electron-transfer photochemistry has received intense study during the past decade¹ owing to a continuing interest in developing new excited-state organic processes and in understanding their mechanistic details. As the body of knowledge in this area has grown, it has become increasingly clear that a number of photoinduced, single-electron-transfer (SET) processes match the criteria required for synthetic utility.² A unique feature of excited-state transformations occurring by SET mechanisms is that the key reactive intermediates are ion and neutral radical species rather than the initially populated excited states. Consequently, a host of new reactions have been uncovered, the nature of which are governed by the chemical properties and reactivity profiles of these reactive intermediates. In addition, since ion radicals often serve as precursors of neutral radicals (by loss of nucleofugal or electrofugal groups), photoinduced SET can be used to promote common free-radical reactions such as coupling, addition, polymerization, etc.

In light of these facts, it is easy to see why investigations that focus on an understanding of the factors that control the chemistry of ion-radical intermediates generated by photo-SET routes continue to receive attention. Perhaps one of the most general reaction pathways probed in these systems is the fragmentation of radical cations leading to radical and cationic species.³ Of relevance to the research discussed below are reactions of this type in tertiary amine and α -trialkylsilyl cation-radical systems. A number of studies have demonstrated that radical cations derived by SET from tertiary amines undergo efficient and, in some cases, rapid proton loss and carbon-carbon bond cleavage at sites adjacent to nitrogen.⁴ Proton loss from simple unsymmetrical

tertiary amine cation radicals often occurs with modest to low regioselectivity to generate α -amino radicals. Examples of this are found in the studies by Lewis and his co-workers⁵ of stilbene-amine photoadditions.

Cation radicals generated by photoinduced-SET from α -trialkylsilyl-substituted donors are known to undergo selective desilylation to produce neutral, non-silicon-containing radicals, even when competitive deprotonation pathways are available. Observations supporting this conclusion have come from efforts probing the SET photochemistry of allyl-⁶ and benzylsilanes⁷ and

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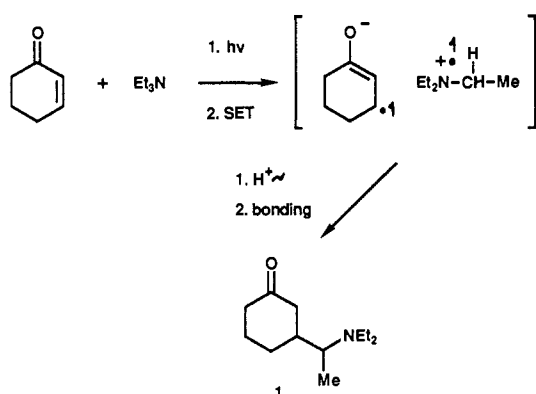
[†]Pusan National University.

Table I. Preparative Photochemical Reactions between α -Silyl Amine **2** and Cyclic Conjugated Enones

enone	solvent	[enone], mM	[2], mM	$h\nu$ time, h	conversion of Enone, %	product (yield, ^a %)
4	MeCN	60	60	2.5	60	6 (30)
4	MeOH	39	40	3.0	70	5 (30), 6 (4)
7	MeCN	40	60	3.5	60	8 (5), 9 (70)
7	MeOH	40	60	4.0	60	8 (60), 9 (30)
10	MeCN	40	60	19	20	11 (40), 12 (tr)
10	MeOH	40	60	12	25	11 (86)
13	MeCN	60	60	10	30	12 (35), 15 (tr)
						16 (25)
13	MeOH	60	60	6.5	51	12 (tr), 14 (40%)
						16 (tr)
17	MeCN or MeOH	40	50	1.5	80	18 (73%)

^aYields are based upon consumed enone. tr = trace.

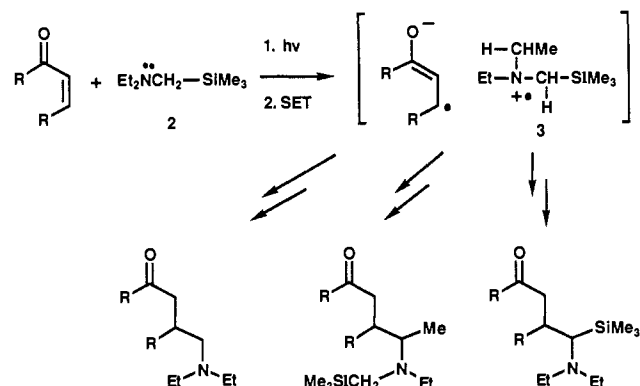
Scheme I



α -silyl ether and thioether systems.^{8,9} The results of a recent investigation of the photoinduced SET chemistry of an α -silyl amine with 9,10-dicyanoanthracene (DCA) exemplify this feature.⁹

These observations suggest that sequential SET–desilylation pathways have the potential of serving as efficient and highly regioselective methods for α -amino radical generation. Stimulated by this possibility and guided by a long-range goal to develop synthetically useful, photoinduced SET reactions, we have designed several programs to explore the scope, limitations, and applications of this methodology. Our initial efforts focused on a study of photoadditions of silyl amine **2** to α,β -unsaturated cyclic enones. The earlier, independent studies of Pienta,¹⁰ Cookson,¹¹ and Schuster¹² served as background for our investigations in this area. These workers had shown that triethylamine (TEA) undergoes photoaddition to conjugated enones (e.g., cyclohexenone) to produce β -adducts (e.g., **1**) (Scheme I). A general and gross mechanism¹³ for these processes can be constructed on the basis of observations made by the Pienta¹⁰ and Schuster¹² groups. The route, shown in Scheme I for reaction of cyclohexenone, involves SET from TEA to the triplet enone followed by proton transfer and radical coupling.

Scheme II



At the outset, we anticipated that photoadditions of silyl amine **2** to conjugated enones would follow similar SET mechanisms and that a variety of adducts could be generated via deprotonation or desilylation of the intermediate radical **3** (Scheme II). The selective operation of a sequential SET–desilylation pathway in these photoadditions (or for related photocyclizations)¹⁴ could have important implications. The most significant of these would be that processes of this type, where C–C bond formation occurs between centers with, in a classical sense, the same charge affinity,¹⁵ would serve as useful synthetic methods for the regiocontrolled construction of amine containing or N-heterocyclic compounds.

Finally, a study of enone–silyl amine SET photochemistry would enable an evaluation of another mechanistically and synthetically important issue. It is well-known that electron-rich radicals add smoothly to electron-deficient alkenes as part of overall addition and cyclization processes.¹⁶ α -Amino radicals produced by SET–desilylation or –deprotonation sequences are highly electron-rich species (high-energy SOMO) and, as a result, should add efficiently to conjugated enones, giving β adducts. Thus, an SET–photosensitized sequence for α -amino radical generation and addition (or cyclization) might be operable in reactions of silyl amine **2** with conjugated enones that are promoted by either direct irradiation of the carbonyl component or irradiation of electron-acceptor sensitizers.

In an earlier communication,¹⁷ the preliminary results of studies exploring the program outlined above were reported. Observations made in that study and in our continuing efforts have demonstrated

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(13) Pienta postulated the existence of a triplet excimer in this process.^{11a} However, Schuster¹² has shown that tertiary amines quench monomeric enone triplets.

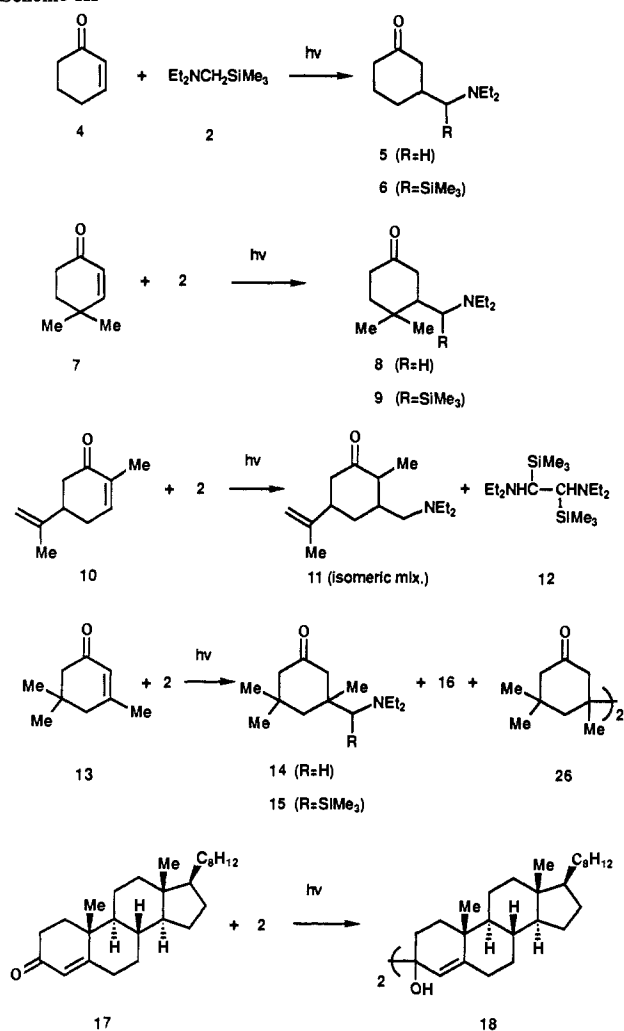
(14) In recent (unpublished) studies we have found that intramolecular silyl amine–enone systems undergo SET-induced photocyclization under direct and SET-sensitized conditions.

(15) Enone–amine additions of this type in charge affinity terms correspond formally to additions of β -keto anions to α -amino cations or of α -amino carbanions to enones. Thus, they represent partial umpolung of reactivity.

(16) Examples of this type of process are discussed in: Giese, B. *Radicals in Organic Synthesis*; Baldwin, J. E., Ed.; Organic Chemistry Series; Pergamon: Oxford, 1986; Vol. 5. Porter, N. A.; Magnin, P. R.; Wright, B. T. *J. Am. Chem. Soc.* **1986**, *108*, 2787.

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Scheme III



that (1) photoinduced SET additions of silyl amine **2** to cyclic conjugated enones represent modestly efficient C-C bond-forming processes, (2) a competition exists between reaction pathways formally involving α -deprotonation and desilylation of the intermediate amine cation radical **3**, (3) the relative efficiencies of these competitive pathways are governed by factors influencing the nature of reactive ion-pair intermediates, and (4) routes exist for adduct formation through conjugate addition of α -amino radicals to enones in both the direct and SET-sensitized processes. The results serving as the basis for these conclusions are presented below.

Results

Preparative Photoaddition Reactions. Qualitative aspects of photoaddition reactions of the α -silyl amine **2** and conjugated enones including the parent substance **4**, its 4,4-dimethyl analogue **7**, (-)-carvone (**10**), isophorone (**13**), and (+)-cholest-4-en-3-one (**17**) were explored initially. Preparative irradiations were conducted on MeCN and MeOH solutions of the amine **2** (ca. 40–60 mM) and enones (ca. 40–60 mM) by using Pyrex-filtered light ($\lambda > 290$ nm). The nature of products generated and the gross chemical efficiencies were evaluated for these processes, which were conducted at enone conversions ranging from 20 to 80%. Product separations employed chromatographic methods (Experimental Section). Product distributions (Scheme III) and yields along with reaction conditions used are recorded in Table I.

Several of the observations made in these studies warrant comment. Irradiation of MeCN solutions of cyclohex-2-en-1-one (**4**) in the presence of silyl amine **2** results in formation of the silicon-containing β -adduct **6** as the exclusive nitrogen-containing product. In contrast, adduct **5**, lacking silicon substitution, is generated by photoreaction of **4** and **2** in MeOH. The results of silyl amine **2** photoadditions to the cyclohexenone derivative **7** show

Table II. Representative ^{13}C NMR Chemical Shifts for Photoadducts and Related Cyclohexanones²¹

cyclohexanone	^{13}C NMR resonance, δ				
	C-2	C-3	C-4	C-5	C-6
cyclohexanone	40.7	26.8	24.1	26.8	40.7
3-methylcyclohexanone	49.1	33.0	32.5	24.5	40.1
3- <i>tert</i> -butylcyclohexanone	43.3	49.2	26.8	26.3	41.0
4,4-dimethylcyclohexanone	38.0	39.5	30.2	39.5	38.0
5	46.6	37.7	29.7	25.0	41.5
6	47.7	40.9	30.1	25.7	41.2
8	47.8	41.8	31.5		41.3
9	42.3	44.8	32.1	40.7	38.1
14	41.6	45.3	32.9	41.0	38.0
15	45.7	48.7	34.2	45.6	
	50.2	41.7	47.4	35.9	54.0
	52.0	46.1	46.6	35.9	54.0
	52.8	46.8	49.2	36.0	

similar trends. Accordingly, irradiation in MeCN provides the silicon-containing adduct **9** as the major product (70%) along with a minor quantity (5%) of its non-TMS analogue **8**. Product ratios are inverted for reaction in MeOH where **8** is generated in a 60% yield and the TMS-containing adduct **9** is formed in a 30% yield. Carvone (**10**) photoreactions with **2** produce the non-TMS adducts **11** in both MeCN (40%) and MeOH (86%). The silyl amine coupling product **12** is produced in trace quantities (<2%) only when this photochemical process is conducted in MeCN. The isophorone (**13**) α -silyl amine **2** photoprocess in MeCN. In this case, the silicon-containing β -adducts **15** represent a minor component (<2%) of the photoproduct mixture. On the other hand, irradiation of MeOH solutions of **13** and **2** results in formation of the non-TMS adduct **12** as a major product (40%) along with only trace quantities of **12** and **16**. Finally, irradiations of the cholestenone **17** in either MeOH or MeCN solutions containing silyl amine **2** (or triethylamine) lead to production of the pinacol dimer **18**. Nitrogen-containing β -adducts are not detected as products in any of the cholestenone photoreactions.

The silicon-containing photoadducts **6**, **9**, and **15** generated from reactions of **2** with the cyclohexenones **4**, **7**, and **13** are formed as inseparable mixtures of stereoisomers. GLC analysis of these substances indicates that the stereoisomers, differing in relative configuration at the adjacent C-3 and α -amino chiral centers, are produced in nearly equal quantities independent of reaction conditions (e.g., solvents and enone conversions). On the other hand, the silyl amine coupling product **12** and the known isophorone¹⁸ and cholestenone¹⁹ dimers **16** and **18** are generated as single stereoisomers of unassigned relative stereochemistry. Finally, the carvone, α -silyl amine adduct **11** is produced as a mixture of three stereoisomers in a 6:3:1 ratio. Stereochemical assignments to these species are discussed below.

Structural assignments to the amine-enone adducts were made by using spectroscopic data. Especially characteristic were the ^{13}C NMR resonances for key carbons (Table II) in the adducts, and assignments were aided by comparisons of ^{13}C NMR for related cyclohexanones.²⁰ For example, the ^{13}C NMR spectrum of **5** contains resonances at 41.5 and 46.6 ppm that correspond to the respective C-6 and C-2 ring carbons. The related carbons in cyclohexanone resonate at 41.9 ppm. The ca. 5 ppm downfield shift of C-2 in **5** compared to the parent ketone is due to the presence of the C-3 alkyl substituent. In addition, C-3 and C-4 of **5** resonate downfield of the corresponding carbons in the parent ketone while the resonance for C-5 at 25.1 ppm is nearly equivalent

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(20) It should be noted that Pienta's structural assignment of the TEA-cyclohexenone adduct as a β -adduct was supported by D_2O -exchange experiments.^{10a}

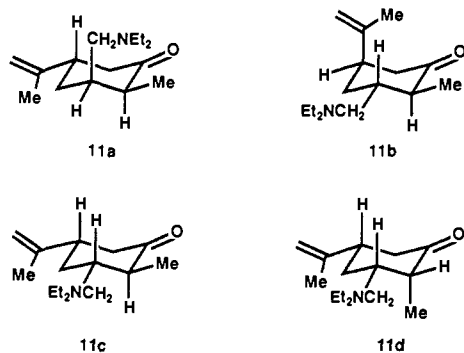
(21) Chemical shifts for the model cyclohexanones are taken from: Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Blomquist, A. T.; Wasserman, H., Eds.; Organic Chemistry Series; Academic: New York, 1972; Vol. 24.

Table III. Selected ^{13}C NMR Data for Carvone Adducts **11a-c**

adduct	^{13}C NMR chemical shift, ppm	
	CH_2NEt_2	C-2, CCH_3
11a	50.7	11.8
11b	57.0	15.0
11c	58.0	15.7

to that for the unsubstituted system. Similar variations of chemical shifts with C-3 alkyl substitutions are seen in the spectra of other 3-alkylcyclohexanones (Table II). All of these features are in complete accord with the β -adduct structure assigned to **5**. Analogous reasoning (see Table II) has been used to assign structures to the stereoisomers of silyl adducts **6**, **9**, and **15** as well as to the non-TMS adducts **8** and **14**.

Photoaddition of silyl amine to carvone (**10**) in MeOH occurs selectively at the conjugated π -bond and provides adduct **11** as a mixture of three stereoisomers (**11a-c**) in a ratio of 6:3:1. These



substances can be separated partially by chromatographic methods (see the Experimental Section). Tentative stereochemical assignments to these materials are based mainly on ^{13}C NMR data, epimerization reactions, and expectations arising from mechanistic considerations. Unfortunately, the application of ^1H NMR techniques focusing on coupling constant data is not possible since it is difficult to resolve key protons even in the high-field spectra of **11a-c**. The major isomers **11a** and **11b** are epimeric at C-2 since **11a** can be converted to a respective 41:59 equilibrium mixture of **11a** and **11b** by treatment with NaOH in EtOH. These substances are assigned as products of axial addition of the Et_2NCH_2 radical to **10** (or its anion radical, see below) having the *cis*,*trans* (**11a**) and *trans*,*trans* (**11b**) relative stereochemistries at C-2, C-3 and C-3, C-5. Indeed, radical additions to enones are expected to occur predominantly from the axial direction.²² Molecular mechanics calculations²³ suggest that the heats of formation for **11a** and **11b** are 16.0 and 15.6 kcal/mol, respectively, a result in accord with the measured equilibrium ratios of these epimers. Importantly, if the major adduct were the C-2 epimer pair **11c** and **11d**, a much larger ratio than 3:2 favoring the C-2 equatorial methyl epimer **11c** would have been expected.

Support for these stereochemical assignments and that of the minor adduct **11c** comes from inspection of characteristic ^{13}C NMR data (Table III). For example, the upfield chemical shift of the amino-substituted methylene carbon in **11a** as compared to the corresponding carbons in **11b** and **11c** (ca. 3.2–3.9 ppm) is expected on the basis of γ -gauche effects for axial carbon substituents in cyclohexane derivatives.²⁴ In addition, the C-2 methyl group in **11a** resonates upfield of the corresponding carbons in **11b** and **11c**. This behavior parallels shifts of methyl carbons in *cis*-2,3-dimethylcyclohexanone (16.2 and 16.5 ppm) and its *trans* isomer (20.5 and 19.2 ppm).²¹ Thus, it appears that the C-2

Table IV. Solvent Effects on Photoadduct **8** and **9** Production from Reaction of **7** with **2**

solvent	E_T	8:9
cyclohexane	31.2	0.05
CH_2Cl_2	41.1	0.10
MeCN	46.0	0.16
<i>t</i> -BuOH	43.9	0.01
<i>n</i> -BuOH	50.2	0.11
EtOH	51.9	0.64
MeOH	55.5	2.97
25% H_2O -MeCN		2.01
25% H_2O -MeOH		4.08
25% HCONH_2 -MeCN		1.78
40% HCONH_2 -MeCN		4.41

Table V. HClO_4 Effects on the Adduct Ratios from the Enone **7** Photoadditions with Silyl Amine **2**

$[\text{HClO}_4]$, M	8:9	$[\text{HClO}_4]$, M	8:9
0.000	0.16	0.043	0.37
0.011	0.27	0.110	0.74

methyl and C-3 aminomethyl groups in **11b** and **11c** adopt a *trans*-diequatorial orientation while those substituents in **11a** are oriented equatorial and axial, respectively.

Mechanistic Studies of Silyl Amine Photoadditions to 4,4-Dimethylcyclohexenone (7). The unusual effects of solvent on the nature of photoadducts (non-TMS- vs. TMS-containing products) generated in the photoadditions of α -silyl amine **2** to the cyclohexenones prompted further studies. At the outset, we envisaged several possible sources of this intriguing effect. Consequently, we have conducted reasonably thorough investigations using the 4,4-dimethylcyclohexenone (**7**) and silyl amine **2** photoaddition reaction which generates adducts **8** and **9**. This process was selected as the target for these efforts since it represented the most efficient reaction in the series studied and one that was amenable to analysis by GLC methods. The ratio of adducts (**8:9**) coming from these photoadditions conducted in (1) a number of solvents of differing polarity and protic nature, (2) solutions of varying amine **2**, added acid (HClO_4), and added base (*n*-Bu₄NOH) concentrations, and (3) solutions containing added salts (LiClO_4 and *n*-Bu₄NClO₄) were determined. Irradiations were performed with uranium glass-filtered light ($\lambda > 320$ nm). Secondary photoreactions of the cyclohexanone adducts do not occur under these conditions, and product ratios are unchanged over extended irradiation periods. In each case, concentrations of enone **7** (0.07 M) and amine **2** (0.21 M, except when **2** is varied) were kept constant.

The effects of solvent on the non-TMS to TMS adduct ratio (**8:9**) are shown by the results presented in Table IV. As can be seen by viewing these data, the **8:9** ratio increases, but not dramatically, as the polarity (E_T value) of aprotic solvents (cyclohexane, CH_2Cl_2 , MeCN) used for this photoaddition reaction increases. On the other hand, the **8:9** ratio changes dramatically with variations in the polarity of protic solvents. Accordingly, a 300-fold increase in **8:9** occurs upon changing the solvent for photoaddition from *tert*-butyl alcohol ($E_T = 43.9$) to methanol ($E_T = 55.5$). Moreover, when the highly polar substances H_2O and HCONH_2 are components of binary solvent systems for the **7** + **2** photoreaction, the **8:9** ratio is significantly enhanced. While the solvent effects noted in this study have important mechanistic implications discussed below, they also have a preparative significance. Thus, photoaddition of **2** to **7** in cyclohexane or *tert*-butyl alcohol leads to nearly exclusive (>95:5) production of the TMS adduct **9**. In contrast, the non-TMS adduct **8** is generated preferentially (84:16) in 40% HCONH_2 -MeCN.

The effects noted above suggest that both the polarity and protic nature of solvents can strongly influence the product ratio arising from photoaddition of silyl amine **2** to cyclohexenone **7**. In order to gain further information about this issue, the effects of medium acidity and ionic strength on the **8:9** ratio were explored. Irradiations of MeCN solutions of enone **7** containing silyl amine **2**

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(23) Calculations performed with Clark Still's Macromodel Program with an MM2 force field.

(24) For a discussion of the γ -gauche effect with representative examples see: Wehrli, F. W.; Wirthlin, T. *Interpretation of Carbon-13-NMR Spectra*; Heyden: London, 1976; pp 27–29.

Table VI. Salt Effects on Adduct Ratios in Photoadditions of Silyl Amine **2** to Cyclohexenone **7**

[LiClO ₄],		[<i>n</i> -Bu ₄ NClO ₄],			
M	solvent	8:9	M	solvent	8:9
0.000	MeCN	0.16	0.000	MeCN	0.16
0.023	MeCN	0.22	0.012	MeCN	0.21
0.050	MeCN	0.39	0.023	MeCN	0.23
0.063	MeCN	0.47	0.044	MeCN	0.24
0.130	MeCN	1.01	0.073	MeCN	0.21
0.200	MeCN	1.43	0.100	MeCN	0.21
0.300	MeCN	2.31	0.250	MeCN	0.28
0.400	MeCN	2.68	0.480	MeCN	0.40
0.130	MeCN and 0.13 M 18-crown-6	0.39	0.000	MeOH	2.97
			0.100	MeOH	3.41
0.000	MeOH	2.97	0.250	MeOH	3.53
0.100	MeOH	5.17			
0.250	MeOH	6.42			

and varying concentrations of HClO₄ were conducted. Perchloric acid at the highest concentration used (0.11 M) corresponds to 0.5 mol equiv with respect to silyl amine **2**. The ratios of adducts obtained in these processes are recorded in Table V. The results clearly demonstrate that the relative amount of non-TMS product **8** increases as HClO₄ concentration increases.

The effective polarity of media used for photoaddition of silyl amine **2** to enone **7** can be increased by the addition of salts. Because of this and as a result of our suspicion that photoproduct ratios are governed by factors influencing the nature of reactive ion-pair intermediates, the following experiments were conducted. The relative ratios of adducts **8** and **9** were determined for **2** + **7** reactions conducted in MeCN containing increasing concentrations of LiClO₄ and *n*-Bu₄NClO₄ in the range of ca. 0–0.5 M. The results from this study, recorded in Table VI, show quite convincingly that the 8:9 adduct ratio increases dramatically upon addition of LiClO₄. On the other hand, added *n*-Bu₄NClO₄ causes only slight increases in 8:9. The contrast between the effects of these salts on adduct ratios suggests that the metal cation, Li⁺, plays a major role. Evidence confirming this conclusion has come from observations showing that the LiClO₄ effect can be reversed when the metal cation, crown ether complexing agents, 18-crown-6 or 12-crown-4, are included (0.13 M) in photoreaction mixtures containing **2**, **7**, and LiClO₄ (0.13 M) (see Table VI). The salt effects are not restricted to photoadditions conducted in MeCN since the ratio 8:9 produced by reactions in MeOH increases upon addition of both LiClO₄ and *n*-Bu₄NClO₄ (Table VI). In addition, salts containing silophilic anions have variable effects on the nature of these photoadditions. For example, irradiation conducted on a CsF-saturated MeCN solution leads to production of **8** and **9** in a ratio equivalent to reactions conducted in the absence of this salt. However, 8:9 ratios are enhanced (6.37 and 5.62, respectively) when CsF and *n*-Bu₄NF are present at 0.10 M in the MeOH solutions of **2** and **7** being irradiated.

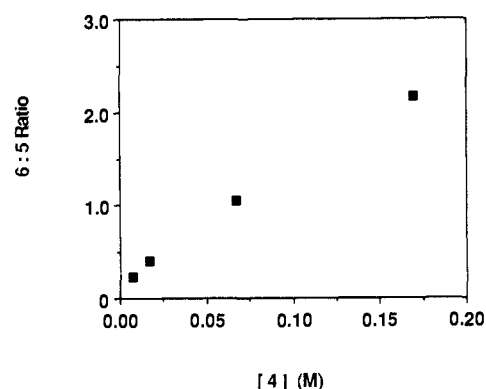
If SET mechanisms are operable in these processes, the relative efficiencies for formation of the non-TMS and TMS adducts, **8** and **9**, from addition of silyl amine **2** to cyclohexenone **7** must be governed by partitioning of the intermediate, amine-derived, cation radical **3**. Thus, desilylation of this species would lead ultimately to the non-TMS adduct **8** while deprotonation at the silicon-substituted carbon would produce TMS adduct **9**. The results presented thus far, when viewed in this way, show that protic polar solvents, metal cations, and acids have a pronounced effect upon this partitioning. In order to determine whether cation-radical deprotonation rates could be influenced by medium basicity, photoadditions of **2** to **7** were conducted in solutions containing varying concentrations of amine **2**. As the results in Table VII demonstrate, 8:9 ratios decrease when the amine concentration increases. Importantly, the magnitude of this effect is large for photoreactions occurring in the polar, protic solvent MeOH, lower for the less polar solvent EtOH, and least for the nonpolar solvent MeCN. Other added bases appear to bring about similar results. Thus, photoadditions of **2** to **7** conducted on MeCN solutions containing *n*-Bu₄NOH lead to adducts in which

Table VII. Adduct Formation from Irradiation of Cyclohexenone **7** in the Presence of Varying Silyl Amine **2** Concentrations

MeCN		EtOH		MeOH	
[2], M	8:9	[2], M	8:9	[2], M	8:9
0.083	0.27	0.068	1.62	0.04	6.51
0.096	0.36	0.098	1.64	0.11	3.50
0.17	0.17	0.14	0.99	0.14	3.16
0.21	0.16	0.21	0.64	0.21	2.97
0.24	0.19	0.25	0.69	0.28	2.35
0.49	0.11	0.37	0.52	0.65	1.94
0.56	0.12	0.46	0.64		
		0.56	0.52		

Table VIII. *n*-Bu₄NOH Effects on the 8:9 Adduct Ratios for Photoadditions of Silyl Amine **2** (0.21 M) to Cyclohexenone **7** in MeCN

[<i>n</i> -Bu ₄ NOH], M		[<i>n</i> -Bu ₄ NOH], M		[<i>n</i> -Bu ₄ NOH], M	
8:9	8:9	8:9	8:9	8:9	8:9
0.000	0.16	0.010	0.04	0.050	0.03
0.003	0.09	0.030	0.03	0.100	0.02

**Figure 1.** Plot of TMS to non-TMS adduct ratios (6:5) obtained from DCA-sensitized irradiation of cyclohexenone **4** in the presence of silyl amine **2** ([**2**] = 1.1 × 10⁻¹ M), as a function of enone **4** concentration.

the 8:9 ratios vary inversely with the concentration of the base (Table VIII).

9,10-Dicyanoanthracene SET Photosensitized Additions of Silyl Amine **2 to Cyclohexenones **4** and **7**.** Additional information about mechanistic features of the silyl amine photoadditions to the conjugated cyclohexenones has come from studies in which 9,10-dicyanoanthracene (DCA) is used to SET photosensitize reactions between amine **2** and enones **4** and **7**. These investigations have been conducted simultaneous with efforts⁹ probing DCA + **2** photoadditions in which we have found that DCA photoadds amine **2** by mechanisms involving formation of the intermediate α -amino radical Et₂NCH₂^{*} by a sequential SET-desilylation pathway. Electron-rich radicals of this type are known to add to simple alkenes²⁵ and unsaturated ketones.^{16,22} Consequently, we anticipated that Et₂NCH₂^{*} and related radicals would be reactive with electron-poor olefins like conjugated enones in their ground states. In order to demonstrate that reaction pathways of this type are possible, the α -amino radical Et₂NCH₂^{*} was generated by DCA photosensitization in solutions containing cyclohexenones **4** and **7**. Accordingly, irradiation of DCA with uranium glass-filtered light was conducted on MeCN solutions containing silyl amine **2** and cyclohexenone **4** or its dimethyl derivative **7**. Analysis of the basic product fractions showed that they contained the amine–enone adducts **5** and **6**, and **8** and **9**, respectively. Under the reaction conditions, DCA and the cyclohexenones both absorb light competitively. In order to determine the ratio of non-TMS- to TMS-containing adducts for the SET-sensitized processes alone, reactions were conducted with solutions of decreasing cyclohexenone concentrations. In addition, the effects of amine **2** on product distributions were probed by

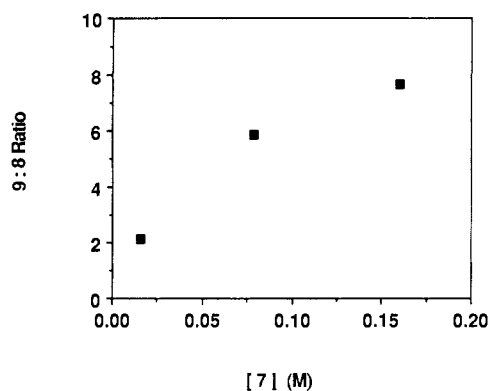


Figure 2. Plot of TMS to non-TMS adduct ratios (9:8) obtained from DCA-sensitized irradiation of cyclohexenone **7** in the presence of silylamine **2** ($[2] = 2.1 \times 10^{-1}$), as a function of enone **7** concentration.

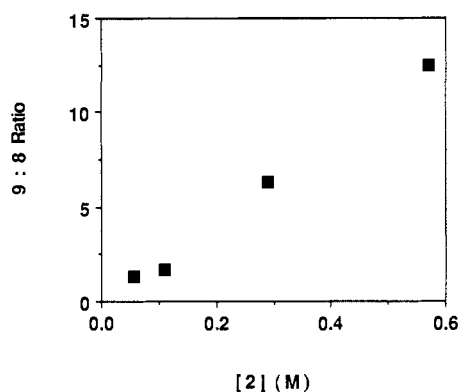


Figure 3. Plot of TMS to non-TMS adduct ratios (9:8) obtained from DCA-sensitized irradiation of cyclohexenone **7** ($[7] = 2.0 \times 10^{-2}$ M) in the presence of silyl amine **2** vs silyl amine concentration.

use of the **7** + **2** photoaddition with varying amine concentrations. The results of these experiments are summarized in Figures 1–3.

Discussion

Preliminary Considerations. The excited-state chemistry of conjugated cyclohexenones has played a prominent role in the development of a mechanistic understanding of organic photochemical reactions. Substances in this class undergo a number of excited-state reactions including rearrangements, cycloadditions, photoreductions, and photoinduced solvent additions. Comprehensive reviews, exemplified by those composed by Schuster,^{26a} Weedon,^{26b} and Chapman,^{26c} have summarized the results of key studies in this area. In general, the triplet states of cyclohexenones have been identified as reactive species in these reactions. A number of observations made in more recent investigations by Cookson, Schuster, and Pienta focusing on cyclohexenone–tertiary amine excited-state chemistry are pertinent to the results uncovered in our efforts. Cookson¹¹ was the first to show that irradiation of enones in the presence of tertiary amines results in the production of 1:1 adducts arising by C–C bond formation between the enone β -carbons and amine α -carbons. In a mechanistically comprehensive study with cyclohexenone and triethylamine (TEA), Pienta^{10a} observed that amine–enone adduct formation in MeCN occurs via a naphthalene-quenchable cyclohexenone triplet in competition with enone cyclodimerization and photoreduction. To rationalize enone concentration dependencies of reaction quantum yields, Pienta proposed that an enone triplet excimer is a common intermediate in these processes. In addition, a pathway involving single electron transfer (SET) from TEA to

this excimer was proposed to account for adduct and reduction product formation. A fast kinetic study of this process provided evidence to support an SET mechanism for these reactions but failed to contribute information about the intermediacy of a triplet excimer.^{10c} Pienta has also detected CIDNP in characteristic proton resonances associated with cyclohexenone and its 4,4-dimethyl derivative when MeCN solutions of these ketones are irradiated in the presence of DABCO. An analysis of the polarization results led Pienta to conclude that enones are formed in this system by reverse SET in ion-radical pairs rather than by reverse H atom transfer in neutral radical pairs.

In a parallel series of investigations, Schuster¹² found that DABCO in MeCN quenches the same triplet of 4,4-dimethylcyclohexenone that is responsible for cycloaddition of olefins, for the lumiketone-forming rearrangement, and for naphthalene quenching. This species, with a lifetime of 19 ns and a DABCO quenching rate constant of $2.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in MeCN, was identified as the relaxed π - π^* triplet of this enone.^{12,27} It should be noted that cyclohexenone π - π^* triplets are known to undergo photoreduction in isopropyl alcohol^{28a} and toluene photoadditions^{28b} via pathways involving β -H atom abstraction (see below). Schuster has offered solid evidence for the operation of SET pathways for amine quenching of enone triplets. Accordingly, the DABCO cation radical was detected by flash techniques when an acetonitrile solution of 4,4-dimethylcyclohexenone is irradiated in the presence of DABCO.

The results uncovered in our current efforts are accommodated by these mechanistic conclusions and those from a careful analysis of the intimate details of amine–aryl ketone photoinduced SET processes. Cohen²⁹ and Wagner,³⁰ on the basis of a host of independent observations, had concluded earlier that photoreactions in these systems are initiated by triplet-state charge/electron transfer. Peters has probed these processes through the use of picosecond laser techniques in investigations initially with TEA and benzophenone (BP)^{4d} and later with other tertiary amines.^{4f,31} This group concluded that SET from amines to triplet BP in MeCN occurs to produce solvent-separated ion pairs (SSIP). Collapse of SSIP to contact ion pairs (CIP) occurs in MeCN and nonprotic solvents of lower polarity (see below) and is followed by rapid proton transfer to produce α -amino and ketyl radical pairs. The rates of SET in these cases are large (ca. 10^9 – 10^{10} s^{-1}) even in solvents of low (C_6H_6) to modest (MeCN) polarity. Likewise, proton-transfer rates in CIP are exceptionally large (e.g., $7 \times 10^{10} \text{ s}^{-1}$ (25 °C) for Et_3N^{++} to Ph_2CO^*), and they vary inversely with solvent polarity. The high velocity of these proton transfers in spite of the fact that C–H bond cleavage is involved and $\text{p}K_a$ differences are not large is perhaps due to charge annihilation in nonpolar media (see below). Additional observations/interpretations by Peters suggest that (1) SSIP and CIP in these systems are in equilibrium ($K_{\text{eq}} \leq 5$) favoring CIP in MeCN,³¹ (2) salts such as NaClO_4 and LiClO_4 , which exist as SSIP in MeCN, participate in ion exchange with the amine cation–benzophenone anion radical SSIP (special salt effect),^{32,33} and (3) polar protic solvents like EtOH intercept the CIP via H bonding to the BP anion radical.

Pathways Involved in Cyclohexenone–Silyl Amine Photoadditions. Chemistry of Contact Ion Pairs. The results reviewed above serve as a useful framework for interpreting the findings of our efforts probing enone–silyl amine photoaddition processes. To summarize, we have found that two types of adducts are produced

(27) Schuster, D. I.; Greenberg, M. M.; Nunex, I. M.; Tucker, P. C. *J. Org. Chem.* **1983**, *48*, 2615.

(28) (a) Schuster, D. I.; Nunez, I. M.; Chan, C. B. *Tetrahedron Lett.* **1981**, 1187. Chan, C. B.; Schuster, D. I. *J. Am. Chem. Soc.* **1982**, *104*, 2928. (b) Bellus, D.; Kearns, D. R.; Schaffner, K. *Helv. Chim. Acta* **1969**, *52*, 971.

(29) Cohen, S. G.; Parola, A.; Parson, G. H. *Chem. Rev.* **1973**, *73*, 141. Guttenplan, J. B.; Cohen, S. G. *J. Am. Chem. Soc.* **1972**, *94*, 4040.

(30) Wagner, P. J. *Top. Curr. Chem.* **1976**, *66*, 1. Wagner, P. J.; Pruett, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 3669. Wagner, P. J.; Lam, A. H. *Ibid.* **1980**, *102*, 7566.

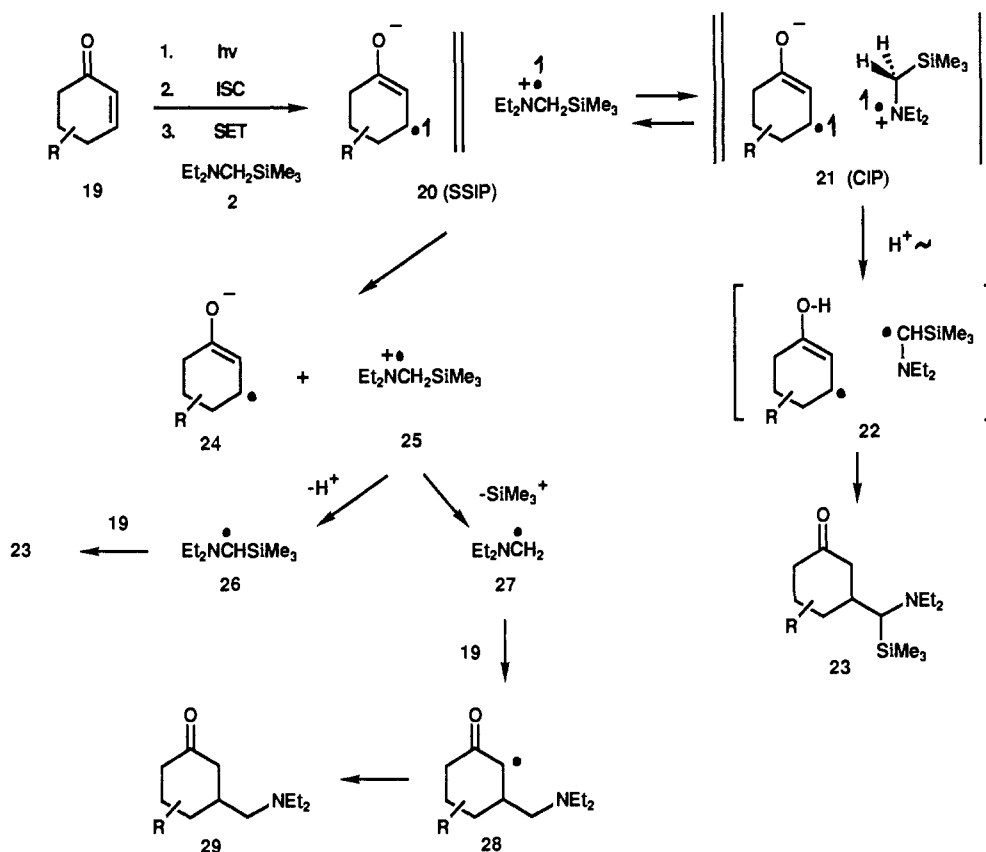
(31) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1981**, *103*, 6403.

(32) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1982**, *104*, 6542.

(33) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1983**, *105*, 4875.

(26) (a) Schuster, D. I. *Rearrangements in Ground and Excited States*; deMayo, P., Ed.; Organic Chemistry Series; Academic: New York, 1980; Vol. 42, 3. (b) Weedon, A. C. *Synthetic Organic Photochemistry*; Horspool, W. M., Ed.; Plenum: London, 1984; Chapter 2. (c) Chapman, O. L.; Weiss, D. S. *Molecular Photochemistry*; Chapman, O. L., Eds.; Marcel Dekker: New York, 1973; Vol. 3, Chapter 3.

Scheme IV



when cyclic enones are irradiated in the presence of the α -silyl tertiary amine Et₂NCH₂TMS. These adducts (referred to as TMS and non-TMS adducts) correspond to substitution of the enone moiety for a hydrogen or TMS group at the silicon-substituted carbon of the amine. The TMS to non-TMS adduct ratios are a sensitive function of the photoreaction conditions. TMS adducts predominate when irradiations are conducted in low-polarity, aprotic solvents while the proportion of non-TMS adducts generally increases in protic media of high polarity or when protic acids or the oxophilic metal cation Li⁺ is present.

These and other observations appear to suggest that the photochemistry of cyclohexenone-silyl amine systems is controlled by factors governing the nature and unique reactivity of intermediate ion radicals. A reaction sequence initiated by SET from silyl amine 2 to cyclohexenone triplet π - π^* states and involving the intermediacy of different enone anion and amine cation pairs is proposed to account for these results (Scheme IV). SET in these systems is predicted to be only slightly exothermic based upon an estimated oxidation potential of ca. 1 V for amine 2 and an enone reduction potential of -2.0 V and triplet energy of 70 kcal/mol.^{34,12b} Thus, we expect that the enone-amine radical SSIP 20 formed in this way would rapidly transform to the CIP in an equilibrium mixture favoring the CIP 21 in MeCN and solvents of lower polarity. Like the BP-amine systems, stabilization of the charged radicals is gained by their intimate contact rather than through solvation in low-polarity media.

Proton transfer in the CIP 21 should occur as rapidly as in the BP-amine CIP³⁵ and lead to generation of radical pair 22 which serves as the precursor of the TMS adduct 23. Of course, intersystem crossing providing singlet multiplicity in 22 must precede C-C bond formation. The selectivity for proton over SiMe₃ group transfer from the amine α -carbon to the oxyanion center in 21 is interesting since in the latter case a strong Si-O bond³⁶ would have been created. As a result, we have carefully inspected the

crude photolysates and have found no evidence for the existence of silyl enol ethers 30 that would have arisen from TMS transfer. Importantly, control experiments demonstrate that species of this type would have been stable under the reaction and workup conditions used. The H > TMS transfer selectivity in 21 could be a result of CIP conformational features. Observations by Peters^{4f} and Wagner³⁷ suggest that amine-ketone CIP exists in a highly oriented, tight structure. Based on this, CIP 21 should favor the distal orientation of the TMS substituent in a planar amine cation radical in order to maximize contact between the charged partners.

Another interesting issue concerns proton-transfer regiochemistry. The oxyanion center in enone anion radicals should be the site of highest negative charge density and one to which proton transfer should occur. Also, proton loss from the silicon-substituted carbon of the amine cation radical in 21 should be preferred owing to the greater thermodynamic/kinetic acidity of protons at this center. TMS substitution is known to have a pronounced effect on hydrocarbon acidities,³⁵ and electron-withdrawing groups are known to contribute in governing deprotonation regioselectivities of amine cation-stilbene anion-radical pairs.^{5,38} The influence in the TMS group in 21 is probably not of stereoelectronic origin, as is the case for alkyl substituents,^{5,38} since the TMS group is not appreciably larger than methyl.³⁹ In addition, the stereoelectronic effects are known to result in only modest degrees of regiocontrol. Thus, if purely stereoelectronic factors were governing acidity, deprotonation should also occur at the non-sili-

(35) The acidity of silicon-substituted hydrocarbons is discussed in a number of places. The discussion in Colvin's monograph³⁶ is informative.

(36) Colvin, E. *Silicon in Organic Synthesis*; Butterworths: London, 1981; Chapters 2 and 4.

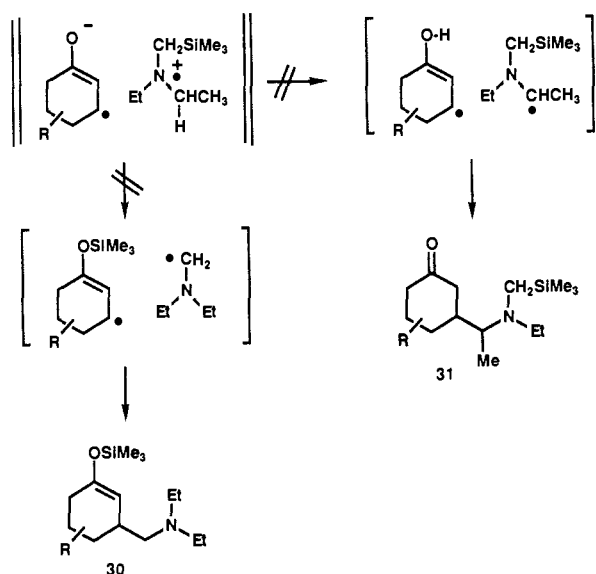
(37) Wagner, P. J.; Kempainen, A. E.; Jellinek, J. *J. Am. Chem. Soc.* 1972, 94, 7512.

(38) Lewis, F. D. *Acc. Chem. Res.* 1986, 19, 401.

(39) The effective size of the TMS group is smaller than anticipated owing to the fact that typical C-Si bond lengths are in the range of 1.9 vs 1.5 Å for the analogous C-C bonds.³⁶ *A* values for the TMS group that support this view have been measured: Kitching, W.; Olszowy, H. A.; Drew, G. M.; Adcock, W. *J. Org. Chem.* 1982, 47, 5153.

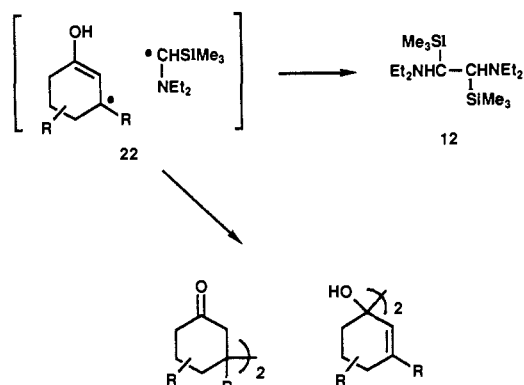
(34) (a) α -Silyl substitution causes an ca. 0.2–0.5 V reduction in the oxidation potential of amines^{34b} and related carbamates.⁴⁷ (b) Cooper, B. E.; Owen, W. *J. Organomet. Chem.* 1971, 29, 33.

con-substituted α -carbons, providing ultimately the TMS adducts **31**.



We anticipate that the rate of proton transfer in CIP **21**, when formed in MeCN, should be in the region of 10^9 s^{-1} as found for the BP-amine CIP. A thermodynamic driving force reflected in the relative pK_a values of the amine cation and ketyl (protonated enone anion radical) radicals should contribute in making proton transfer rapid. By use of pulse radiolysis techniques, Hayon⁴⁰ and Lilie⁴¹ have independently determined that the pK_a of ketyl radicals arising from methyl vinyl ketone and BP in water are 10.1 and 9.3, respectively. Thus, conjugated enone-derived anion radicals are slightly stronger bases than the BP anion radical. Sonntag,⁴² employing pulse radiolysis, has measured a pK_a (H_2O) of 8 for the trimethylamine cation radical. If the relative (not absolute) magnitudes of these acidity constants remain the same in less polar solvents like MeCN and if the TMS group further reduces the pK_a of $2^{+\cdot}$, then proton transfer in **21** should be more facile than in the BP-amine systems probed by Peters.^{43,44}

Product formation by this pathway occurs in the radical pair **22**, and the TMS adduct **23** is delivered as a mixture of stereoisomers, with little if any stereoselectivity. However when radical coupling in **22** is inhibited by steric factors arising from β -alkyl substitution, cage collapse can become competitive leading to eventual production of the TMS-amine dimer **12** and enone-derived pinacols and diketones (and perhaps reduction products).



Formation and Chemistry of Free Silyl Amine Cation Radicals. Partitioning of the enone-silyl amine SSIP **20** to CIP **21** vs free ion radicals (FI) **24** + **25** (Scheme IV) should be influenced by medium effects that allow alternative modes of ion stabilization. In protic, highly polar solvents such as MeOH or H_2O , stabi-

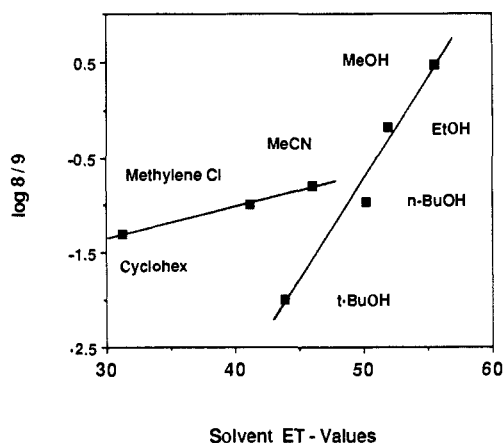


Figure 4. $\log(8/9)$ vs solvent E_T values. Data come from irradiation of solutions of cyclohexenone **7** and silyl amine **2**.

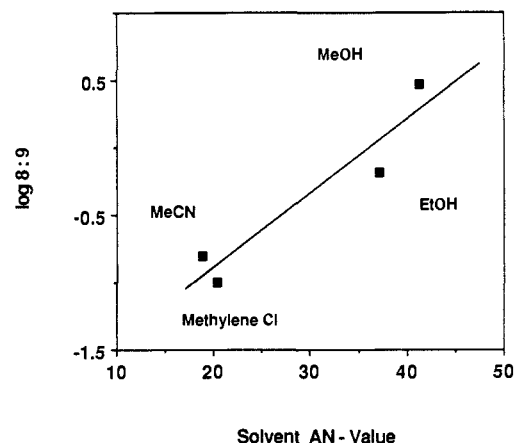


Figure 5. $\log(8/9)$ vs Gutman AN values of solvents. Data come from irradiation of solutions of cyclohexenone **7** and silyl amine **2**.

zation of enone radical anions **24** can occur via hydrogen-bonding interactions.⁴³ Likewise, the donor nature of hydroxylic solvents and formamide will lead to their stabilization of the amine cation radicals **25**. As a result, photoprocesses in these solvents should be dominated by the chemistry of enone and amine radical FI. Indeed, we have seen trends in the nature of photoadducts that seem to parallel this expected behavior. As shown in Figure 4, the ratio of non-TMS adduct **8** to TMS adduct **9** arising from photolysis of enone **7** increasingly favors **8** as the solvent polarity, as judged by E_T values,⁴⁴ increases. The effects seen are more pronounced in the series of alcohols where the **8:9** ratio varies with pK_a , a measure of hydrogen-bonding potential. In addition, inclusion of H_2O or formamide in acetonitrile solutions of **7** results in a preference for formation of the non-TMS adduct **8** (Table IV). Perhaps a superior parameter for judging the ability of a solvent to stabilize charged species is the acceptor (AN) and donor (DN) numbers summarized by Gutman.⁴⁵ Indeed, the good correlation seen between $\log[8/9]$ and Gutman AN values (Figure 5) of several solvents is another indicator of the different chemistry seen depending upon the nature of radical ion-pair intermediates. It should be noted here that alcohols and water ($pK_a \sim 15-18$) are insufficiently acidic to protonate enone radicals (pK_a (conjugate acids) 10).

The solvent effects reviewed above, which are in some cases sufficiently potent to cause reversal of the major adducts produced,

(40) Hayon, E.; Ibat, J.; Lichtin, N. N.; Simic, M. *J. Phys. Chem.* **1972**, *76*, 2072.

(41) Lilie, J.; Henglein, A. *Ber. Bunsenges. Phys. Chem.* **1969**, *73*, 170.

(42) Das, S.; von Sonntag, C. *Z. Naturforsch.* **1986**, *416*, 505.

(43) Peters³² has presented results showing that the effect of the protic solvent EtOH on BP-amine systems is through induction of CIP collapse through hydrogen bonding to the BP radical anion. This result is counterintuitive since hydrogen-bonding interactions should have been present in SSIP and enhanced in FI.

(44) Dimroth, K.; Reichardt, C.; Siepmann, T.; Bohlmann, E. *Justus Liebig's Ann. Chem.* **1963**, *661*, 1.

(45) Gutman, V. *The Donor-Acceptor Approach to Molecular Interactions*; Plenum: London, 1978; Chapter 2.

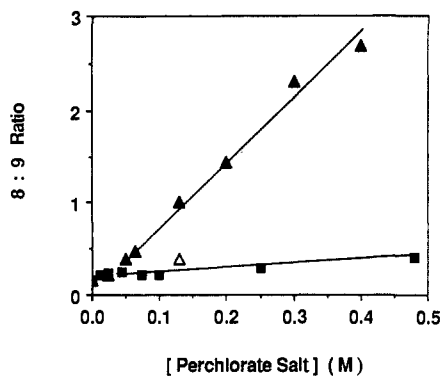


Figure 6. Non-TMS to TMS adduct ratios (8:9) obtained by irradiation of MeCN solutions of enone **7** and silyl amine **2** in the presence of varying concentrations of LiClO_4 (\blacktriangle) and $n\text{-Bu}_4\text{NClO}_4$ (\blacksquare). Point Δ corresponds to reaction with $[\text{LiClO}_4] = 0.13 \text{ M}$ and $[\text{18-crown-6}] = 0.13 \text{ M}$.

can be understood on the basis of selectivities in the formation and chemistry of ion-pair intermediates. The amine cation radical **25** as a solvated free ion should be capable of undergoing desilylation to produce the α -amino radical **27**. This reaction mode should predominate when **25** is formed in the absence of a strongly basic, intimate partner (see below). A number of other photochemical and electrochemical efforts have provided results supporting this proposal. For example, cation radicals of sulfur⁴⁶ and carbamate⁴⁷ analogues of **2** formed electrochemically undergo desilylation. Likewise, photo-SET generation of oxygen and sulfur analogues of cation radical **25** in the presence of weakly basic partners leads to exclusive desilylation.^{8,9} The photoaddition of amine **2** to 9,10-dicyanoanthracene serves to exemplify this; only the non-TMS adduct **33** is produced.⁹ The absence of proton transfer in **32** is most likely the result of the expected⁴⁸ low basicity of the DCA anion radical.

The distribution of enone-amine ion radicals among the ion-pair states can be influenced by other factors. For example, the ammonium cation of **2** should be a strong enough acid ($\text{p}K_a \sim 11$) to protonate the enone anion radical **24** as part of SSIP or CIP. This should result in generation of the amine cation radical **25** and hydroxyallyl radical. The increase in the amount of non-TMS adduct **8** observed upon addition of increasing quantities of HClO_4 can be accounted for in this fashion (Table V) if the chemistry of **25** as an FI is dominated by desilylation.

As discussed earlier, salt effects are known to play a role in determining preferred ion-pair states of photogenerated radical ions. In light of this, the salt effects observed on the 8:9 ratios add further evidence to support our proposals about mechanisms and factors governing chemoselectivity in silyl amine-enone photoaddition processes. The presence of both LiClO_4 and $n\text{-Bu}_4\text{NClO}_4$ appears to alter the 8:9 photoadduct ratios resulting from irradiation of **7** in MeCN (Figure 6). The effect is much more dramatic with LiClO_4 , a substance existing as a SSIP in MeCN.⁵¹ The lithium cation is a much stronger acceptor than is $n\text{-Bu}_4\text{N}^+$ in interactions with oxyanion donors.⁴⁵ Thus, LiClO_4 should be more capable of intercepting the enone-amine SSIP **20** and transforming it to the free amine ion radical **25** and Li-complexed enone anion radical. The lithium-specific nature

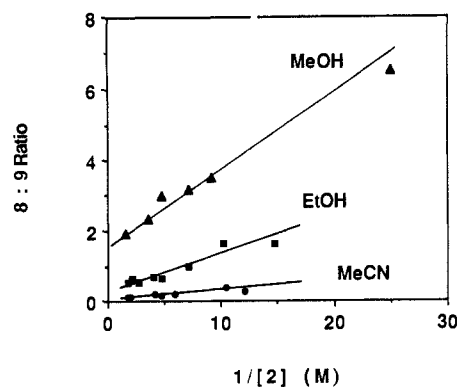


Figure 7. Plots of 8:9 adduct ratios obtained from irradiation of cyclohexenone **7** in the presence of varying concentrations of silyl amine **2** and in MeOH (\blacktriangle), EtOH (\blacksquare), and MeCN (\bullet).

of this salt effect is confirmed by the reversal noted upon addition of the complexing agents 18-crown-6 and 12-crown-4.⁵²

Chemistry of the Free Silyl Amine Cation Radical. The chemistry of the nonpaired amine cation radical **25** will govern the nature of photoprocesses occurring in highly polar-protic solvents and under conditions of high Li salt and acid concentrations. While desilylation is expected to be the major pathway followed in reaction of **25**, its acid-base chemistry may contribute when this species is produced in a basic environment. Evidence has been gained to support the proposal that **25** can partition to both α -amino radicals **27** and **26** (Scheme IV) by desilylation and deprotonation, respectively. This conclusion, discussed below, is based upon the reasonable assumption that radicals **26** and **27** serve as respective precursors of the TMS and non-TMS adducts (e.g., **9** and **8**).

The results from studies probing the amine **2** concentration dependence of the adduct ratio 8:9 in MeOH, EtOH, and MeCN are illustrative. As the plots in Figure 7 show, the relative amount of TMS adduct **9** increases as silyl amine **2** concentration is increased. The magnitude of this effect is greatly dependent upon the solvent ($\text{MeOH} > \text{EtOH} > \text{MeCN}$). To understand these results, the basic nature of amine **2** must be considered. Sonntag⁴² has shown on the basis of pulse radiolysis experiments that the $\text{p}K_a(\text{H}_2\text{O})$ of trimethylamine cation radical is ca. 8 and that proton transfer from this species to trimethylamine occurs rapidly (ca. $7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$). We expect **25** to be more acidic than the Me_3N cation radical owing to the α -silyl effect. Consequently, amine **2** should be sufficiently basic to rapidly deprotonate cation radical **25** when the latter is produced as a free ion. In this way, the effect of amine concentration on partitioning to **8** and **9** via radicals **27** and **26** should be greater when a larger fraction of the photoaddition process is occurring via free ion rather than CIP intermediates. The amplification seen on proceeding from MeCN to MeOH can be understood in this context. Moreover, in the extreme where all reaction proceeds via partitioning of FI **25** to **26** and **27**, a plot of 8:9 vs $1/[2]$ should be linear. Indeed this is what is observed for the reaction of **7** with **2** in MeOH.

It is important to mention here that Nelsen and his co-workers have concluded on the basis of thermochemical data that proton transfer should be less favorable than H atom transfer as a general pathway for α -amino radical production in amine-amine cation-radical reactions.⁵³ A Hofmann-Löffler-Freytag⁵⁴ mechanism of this type could also rationalize our amine concentration effects if the regiochemistry of H atom abstraction by **25** from **2** were the same as for deprotonation of **25** by **2**. It has been reported, however, that the difference between the C-H bond dissociation energies of comparable trialkylsilyl- and alkyl-substituted systems is small (e.g., $D(\text{Me}_3\text{SiCH}_2 - \text{H}) = 99.2 \text{ kcal/mol}$ and $D(\text{CH}_3\text{CH}_2 - \text{H}) = 98 \text{ kcal/mol}$).⁵⁵ Thus, it is difficult to

(46) Yoshida, J.; Isoe, S. *Chem. Lett.* **1987**, 631.

(47) Yoshida, J.; Isoe, S. *Tetrahedron Lett.* **1987**, 6621.

(48) The low kinetic and thermodynamic basicity of the DCA and other cyano aromatic anion radicals has been discussed by Lewis.⁴⁹ The $\text{p}K_a$ of the conjugate acids of the PhCN and 1,4-CN₂Ph anion radicals are 7 and ≤ 0 , respectively.⁵⁰ The $\text{p}K_a$ of the protonated DCA anion radicals should be lower than this owing the greater delocalization in this species, which is reflected in its relatively high reduction potential as compared to PhCN and 1,4-CN₂Ph.

(49) Lewis, F. D.; Petisce, J. R. *Tetrahedron* **1986**, *42*, 6207.

(50) Robinson, E. A.; Schulte-Fronhlinde, H. *J. Chem. Soc., Faraday Trans. 1* **1973**, *1*, 707. Holzman, J.; Schested, K. *Ibid.* **1975**, *3*, 1211.

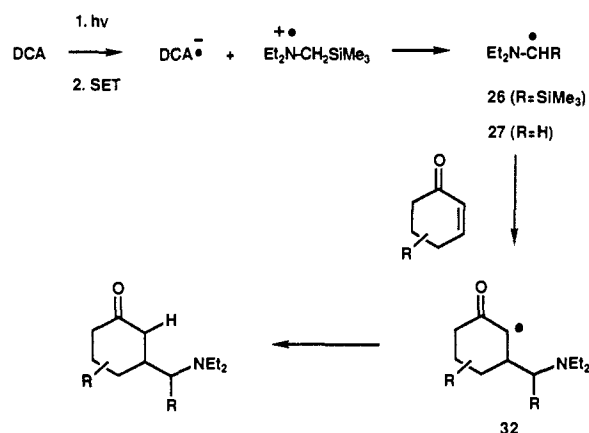
(51) Cohen, Y. M.; Hardy, P. R.; Roach, E. T.; Popov, A. J. *J. Phys. Chem.* **1975**, *79*, 80. Maciel, G. E.; Hancock, J. K.; Lafferty, L. F.; Mueller, P. A.; Musher, W. K. *Inorg. Chem.* **1966**, *5*, 554.

(52) Smetana, A. J.; Popov, A. I. *J. Solution Chem.* **1980**, *9*, 183.

(53) Nelsen, S. F.; Ippoliti, J. T. *J. Am. Chem. Soc.* **1986**, *108*, 4879.

(54) Chow, Y. L.; Danen, W. C.; Nelsen, S. F.; Rosenblatt, D. H. *Chem. Rev.* **1978**, *78*, 243.

Scheme V



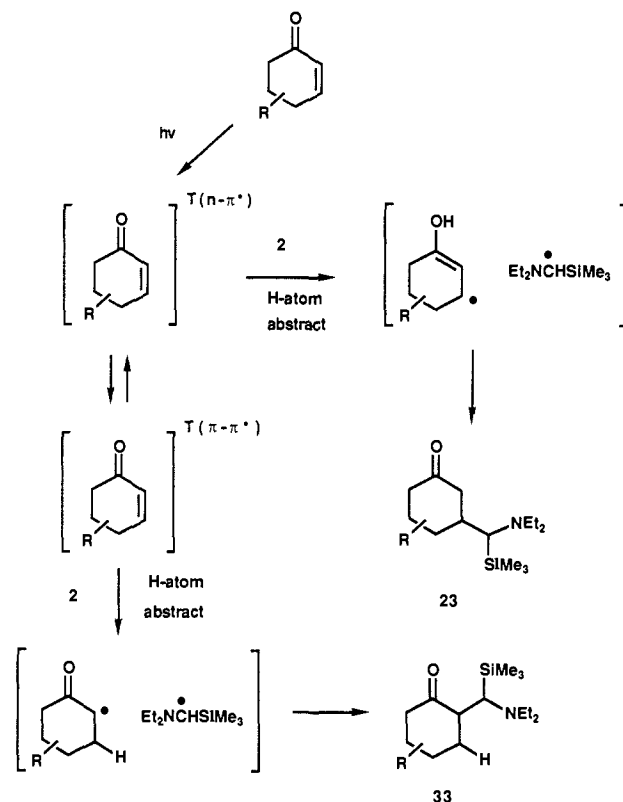
rationalize why adducts arising via the α -amino radical are not produced in these processes if the H atom rather than proton-transfer routes are involved.⁵⁶ In addition, an effect quite similar to that displayed by **2** is seen when *n*-Bu₄NOH is the addend. Accordingly, the 8:9 ratio falls with increasing *n*-Bu₄NOH concentration for reactions in MeCN (see Table VIII).^{57a} This result should be viewed in light of the fact that additions of *n*-Bu₄NClO₄ cause an opposite response in the 8:9 ratio.

It appears that partitioning of amine cation radical **25** to α -amino radicals **26** and **27** can also be influenced by silophiles. While CsF in MeCN does not cause changes in the 8:9 ratio, the presence of this salt or *n*-Bu₄NF in MeOH solutions of **7** and amine **2** results in an increase in the 8:9 photoadduct ratio. The larger effect of *n*-Bu₄NF as compared with *n*-Bu₄NClO₄ suggests that the silophilicity of F⁻ is the factor responsible for these changes, which are most probably a result of partitioning of **25** to **26** and **27**. The absence of a CsF effect in MeCN could very well be due to the absence of complete dissociation of this salt (contact ion pair) in the low-polarity solvent.^{57b}

Mechanism for Adduct Formation. Formation of amine-enone adducts in processes that proceed by proton transfer in CIP most likely occurs by carbon-carbon bond formation in radical pair **22** (Scheme IV). However, in cases where α -amino radicals **26** and **27** are generated from free cation radical **25**, adduct formation by radical coupling seems less likely. The probability for out-of-cage reaction of α -amino and enone anion radicals should be low since the concentrations of both species would be low. On the other hand, as electron-rich radicals, **26** and **27** should be reactive with conjugated enones present at high concentrations. Conjugate additions of electron-rich radicals to enones are known to be facile processes,^{16,22,25} and FMO reasoning suggests that α -amino radicals should be highly reactive in this regard.

Evidence gained from SET-photosensitization studies supports the postulate that conjugate-radical addition pathways are responsible for adduct formation in reactions occurring through free-ion radical intermediates. In parallel efforts we have shown that 9,10-dicyanoanthracene serves as a singlet-state electron acceptor in reaction with silyl amine **2**.⁹ In this case, a non-TMS adduct is produced exclusively by an SET sequence in which α -amino radical **27** is produced by desilylation of cation radical **25**. Consequently, this procedure serves as an independent method for synthesis of α -amino radicals. Thus, when irradiation of MeCN

Scheme VI



solutions of DCA is conducted in the presence of silyl amine **2** and cyclohexenones **4** and **7** under the condition where DCA absorbs most of the incident light, amine-enone adducts **5** and **6** and **8** and **9** are produced (Figures 1 and 2). The mechanism proposed for this DCA SET-sensitized addition is outlined in Scheme V. Importantly, the non-TMS adducts **5** and **8** predominate in these processes since the intermediate radical cation **25** that serves as a precursor of the photoadduct is not paired with a strongly basic partner.⁴⁸ The influence of amine concentration on the 9:8 adduct ratio (Figure 3) gives further evidence to the proposal that **25** can undergo both desilylation (major) and deprotonation (minor), the latter pathway becoming more favorable as amine concentration increases.

A final point warranting brief comment concerns steps responsible for termination of the DCA-sensitized additions of **2** to **4** and **7**. Conjugate addition of α -amino radicals to enone produces oxoallyl radicals **32** that can transform to ground-state product by pathways involving SET from the DCA anion radical followed by protonation or hydrogen abstraction from solvent. At this point in our studies, data have not been accumulated on this point. Thus, the issue remains open.

Consideration of Alternate Mechanisms. It is clear that any discussion of enone-silyl amine reactions not considering hydrogen atom abstraction mechanisms for TMS adduct formation would be incomplete. Accordingly, an alternative pathway for production of TMS adducts involves initial H atom abstraction by an enone triplet from the silicon-substituted α -carbon of **2** (Scheme VI). The enone triplet would be required to employ oxygen or the α -carbon as the site for this H atom abstraction, and in Scheme VI oxygen abstraction in an $n-\pi^*$ triplet is portrayed. In the absence of other considerations, mechanisms of this type have several attractive features. For example, the solvent effects could be rationalized on the basis of interactions that lead to energetic ordering of $\pi-\pi^*$ and $n-\pi^*$ triplets.²⁶ Accordingly, in polar protic solvents, $n-\pi^*$ enone triplet could be of higher energy and thus TMS adducts arising by H atom abstraction would be minimized. Similar reasoning could be used to explain the acid and lithium cation effects. Moreover, Dauben⁵⁸ and Chapman⁵⁹ have identified

(55) (a) Dancaster, A. M.; Walsh, R. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 2908. For a review see: Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246. (b) However, it is difficult to evaluate the contribution of captodative effects^{55c} on this system. (c) Viehe, H. G.; Janousek, z.; Merenyi, R. *Acc. Chem. Res.* **1985**, *18*, 148.

(56) We are not sure about how substituents would control regioselectivities in Hofmann-Löffler-Freytag processes of amine cation radicals.^{55b} Thus, our conclusion remains somewhat tentative on this point.

(57) (a) Irradiation of **7** in MeOH containing *n*-Bu₄NOH leads to very high 8:9 ratios. This result is surprising in light of the outcome of the MeCN experiments and is not easily rationalized. However, in MeOH *n*-Bu₄NOH may be a better silophile than a base. (b) A reviewer has suggested that since fluoride ion is highly basic in nonprotic solvents, addition of CsF can cause an increase in the rates of both desilylation and deprotonation.

(58) Dauben, W. G.; Spitzer, W. A.; Kellogg, M. S. *J. Am. Chem. Soc.* **1971**, *93*, 3674.

two reactive triplet states ($n-\pi^*$ and $\pi-\pi^*$) of cyclohexenones on the basis of differential solvent and triplet quenching effects on rearrangement and cycloaddition processes. Importantly, these groups have shown that triplet quenchers such as naphthalene and di-*tert*-butyl nitroxide in concentration ranges of ca. 0–0.1 M cause significant changes in the distributions of products derived from $n-\pi^*$ and $\pi-\pi^*$ triplet states.

Several lines of evidence agree against the operation of $n-\pi^*$, H atom abstraction in the pathways leading to TMS adduct formation. As mentioned earlier, Schuster^{12,27} and Pienta¹⁰ have provided convincing evidence for the intervention of a cyclohexenone $\pi-\pi^*$ triplet in tertiary amine quenching in MeCN, a solvent in which TMS adduct formation predominates. Moreover, SET mechanisms for this triplet quenching are firmly supported by CIDNP and flash spectroscopy experiments. In addition, if $\pi-\pi^*$ triplets of the enones were to react via H atom abstraction, α -adducts **33** arising by β -abstraction should have been produced. This expectation comes from efforts by Schuster^{28a} and Schaffner,^{28b} the combined results of which lead to the conclusion that $\pi-\pi^*$ triplet enones undergo β -H atoms abstraction in pathways leading to photoreduction and photoaddition. Also, the amine concentration effects observed in our studies would be difficult to rationalize if non-TMS and TMS adducts come from different triplets by respective SET and H-abstraction routes.⁶⁰ In this regard, we have found that the non-TMS to TMS adduct ratio (8:9) from reaction of 4,4-dimethylcyclohexenone (**7**) with silyl amine **2** in MeCN is not decreased by the addition of the triplet quencher naphthalene at concentrations in the range 0–0.11 M, which should²⁷ result in quenching of ca. 50% of the reactive triplets. Thus, if **8** and **9** arise from $\pi-\pi^*$ and $n-\pi^*$ triplets, respectively, with different lifetimes,^{58,59} then naphthalene quenching would have brought about variations in the 8:9 ratio. Finally, the expected similarity of bond dissociation energies for the α -CH bonds in the ethyl and (trimethylsilyl)methyl groups on nitrogen in **2** (see above) would be inconsistent with the high degrees of regioselectivity seen if H atom abstraction mechanisms were responsible for TMS adduct formation.

Implications of These Results. The results presented above are significant from both a synthetic and mechanistic perspective. Silyl amine photoadditions to cyclohexenones represent reasonably efficient methods for carbon–carbon bond formation. The chemoselectivity of these processes (TMS vs non-TMS products) can be controlled by the choice of reaction conditions. This is exemplified by reaction of 4,4-dimethylcyclohexenone (**7**) with silyl amine **2** where in cyclohexane the TMS adduct **9** is produced nearly exclusively (95:5) and yet in methanolic LiClO₄ (0.25 M) the non-TMS adduct **8** predominates (86:14). In addition, SET-sensitized methods for α -amino radical generation and conjugate addition to enone have been uncovered. This technique will be useful in the development of procedures for N-heterocycle synthesis based on radical cyclization sequences.¹⁴ Perhaps the greatest significance of these investigations lies in their demonstration of ion-pair-dependent chemistry in the SET photochemistry of donor–acceptor pairs. While not unique,⁶¹ phenomena of this type are rare and perhaps useful in probing the intimate details of other SET processes.

Experimental Section

General Procedures. ¹H NMR and ¹³C NMR spectra were recorded by using a Bruker WP-200 or AM-400 spectrometer and CDCl₃ solutions. Chemical shifts are reported in parts per million relative to Me₄Si as the internal standard. For compounds containing Me₃Si groupings,

(59) Chapman, O. L.; Koch, T. H.; Klein, F.; Nelsen, P. J.; Brown, E. L. *J. Am. Chem. Soc.* **1968**, *90*, 1658.

(60) One could have rationalized the increase in TMS adduct **9** with increases in [**2**] by considering that **9** arises from interaction of **2** with a shorter lived $n-\pi^*$ triplet and **8** from a longer lived $\pi-\pi^*$ triplet. However, if this were the case, it would be difficult to comprehend why the effect of increasing [**2**] would be larger in MeOH where a smaller contribution of the $n-\pi^*$ state to the overall process would be occurring. Also, the effects of [**2**] seen in the DCA-sensitized process supports the SET mechanism conclusion.

(61) For an example of an elegant study of another ion-pair-selective SET photochemical process see: Sankararaman, S.; Haney, W. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 7824 and references therein.

CHCl₃ 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. Mass spectra were recorded by using a Hitachi RMU-6E (low resolution) or a Kratos M 50 (high resolution, Pennsylvania State Mass Spec Facility) instrument. Melting points were recorded by use of a Griffin Mel-Temp apparatus and are reported uncorrected. Analytical GLC (10% OV-101 packed, 10 ft × 1/8 in. column) was performed with a Varian-940 (FID) chromatograph. Preparative TLC was conducted with 20 × 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 organic layers obtained following workup of reaction mixtures was performed with anhydrous Na₂SO₄.

Preparative photochemical reactions were conducted in an apparatus consisting of a 450-W Hanovia medium-pressure mercury lamp (ACE) surrounded by a glass filter (for wavelength band selection) and within a quartz, water-cooled well immersed in the photolysis solution. The photolysis solution was purged with N₂ both before and during irradiation.

The cyclohexenones were purchased from Aldrich and distilled before use. α -Silyl amine **2** was prepared by the reported method.⁹ Bu₄NOH, Bu₄NF, CsF, and LiClO₄ were purchased from Aldrich. Bu₄NClO₄ was purchased from Eastman Kodak. Crown ethers were purchased from Aldrich. The solvents in photoreactions were spectrograde or reagent grade: MeCN (Baker or Mallinckrodt, spectrograde), MeOH (Baker or Mallinckrodt, spectrograde), EtOH (Warner-Graham, anhydrous), cyclohexane (Aldrich, spectrograde), CH₂Cl₂ (Baker, spectrograde), *n*-BuOH (Fisher Scientific), *t*-BuOH (Baker). 9,10-Dicyanoanthracene was purchased from Eastman Kodak and recrystallized (CHCl₃) prior to use.

Preparative Photoreactions of Cyclohexenones and α -Silyl Amine **2**.

The general procedures used in the preparative photoreactivities between the cyclohexenones and α -silyl amine **2** were as follows. MeCN or MeOH solutions containing the appropriate cyclohexenone and **2** were irradiated with Pyrex or Flint glass filtered light. Cyclohexenone conversions were monitored by GLC (except for cholestenone). The residues obtained by concentration of the photolysates were dissolved in ether and extracted with 5% aqueous HCl. The basified (10% aqueous NaOH to pH 14) aqueous extracts were extracted with CHCl₃. The CHCl₃ extracts were dried and concentrated in vacuo, giving residues that were subjected to chromatographic (TLC or column) separation, providing products (Scheme III) in the yields given in Table I.

Irradiation of 2-Cyclohexen-1-one (4**) and α -Silyl Amine **2**.** A solution of **4** (693 mg, 7.21 mmol) and 1.145 g (7.19 mmol) of **2** in 120 mL of MeCN was irradiated for 2.5 h (60% conversion of **4**) to give after workup, column chromatography (CHCl₃), and TLC (1.5% MeOH–CHCl₃) 560 mg (30%) of TMS adduct **6**. GLC analysis of **6** indicates that it is an ca. 1:1 mixture of two stereoisomers.

A solution of **4** (454 mg, 4.72 mmol) and **2** (763 mg, 4.79 mmol) in 120 mL of MeOH was irradiated for 3 h (70% conversion of **4**) to give after workup and TLC (2% MeOH–CHCl₃) 24 mg (4%) of TMS adduct **6** (ca. 1:1 mixture of stereoisomers) and 182 mg (30%) of the non-TMS adduct **5**.

5: ¹H NMR 0.91 (t, 6 H, NCH₂CH₃), 1.15–1.35 (m, 1 H), 1.48–1.65 (m, 1 H), 1.80–2.05 (m, 5 H), 2.10–2.30 (m, 4 H), 2.41 (q, 4 H, NCH₂CH₃); ¹³C NMR 11.5 (NCH₂CH₃), 25.0 (C-5), 29.0 (C-4), 37.7 (C-3), 41.5 (C-6), 46.6 (C-2), 47.4 (NCH₂CH₃), 60.0 (CH₂N), 211.8 (C=O); IR (neat) 2950, 2900, 1720, 1400, 1360, 1320, 1260, 760 cm⁻¹; MS, *m/e* (relative intensity) 183 (M⁺, 14), 168 (1), 87 (6), 86 (100), 72 (11); high-resolution MS, *m/e* 183.1624 (C₁₁H₂₁NO requires 183.1623).

6: ¹H NMR 0.10 (two s, 9 H, SiMe₃), 0.92 (two t, 6 H, NCH₂CH₃), 1.40–1.80 (m, 3 H), 1.90–2.65 (m, 11 H); ¹³C NMR 1.0 and 1.1 (SiMe₃), 15.3 (NCH₂CH₃), 25.7 (C-5), 30.1 and 31.5 (C-4), 41.2 and 41.3 (C-6), 40.9 and 41.8 (C-3), 47.7 and 47.8 (C-2), 48.6 (NCH₂CH₃), 59.5 (CHTMS), 212.3 and 212.5 (C-1); IR (neat) 2950, 2900, 1710, 1400, 1260, 760 cm⁻¹; MS, *m/e* (relative intensity) 255 (M⁺, 0.3), 254 (2), 182 (100), 158 (33), 130 (8), 75 (34), 73 (27); high-resolution MS, *m/e* 255.1994 (C₁₄H₂₉NOS requires 255.1989).

Irradiation of 4,4-Dimethyl-2-cyclohexen-1-one (7**) and α -Silyl Amine **2**.** A solution of 744 mg (5.99 mmol) of **7** and 1.431 g (8.98 mmol) of **2** in 150 mL of MeCN was irradiated for 3.5 h (60% conversion of **7**). Workup and TLC (2% MeOH–CHCl₃) separation afforded 723 mg (70%) of TMS adduct **9** (ca. 1:1 mixture of stereoisomers) and 38 mg (5%) of non-TMS adduct **8**.

A solution containing the same quantities of **7** and **2** as above in 150 mL of MeOH, irradiated for 4 h (60% conversion of **7**), gave after TLC separation 300 mg (30%) of TMS adduct **9** and 455 mg (60%) of non-TMS adduct **8**.

8: ^1H NMR 0.95 (t, 6 H, NCH_2CH_3), 1.00 (s, 3 H, Me), 1.05 (s, 3 H, Me), 1.55–1.70 (m, 3 H), 2.07 (m, 2 H), 2.20–2.55 (m, 7 H), 2.62 (m, 1 H); ^{13}C NMR 11.9 (NCH_2CH_3), 19.8 (C-4 Me), 28.7 (C-4 Me), 32.1 (C-4), 38.1 (C-6), 40.7 (C-5), 42.3 (C-2), 44.8 (C-3), 47.4 (NCH_2CH_3), 54.8 (CH_2N), 211.9 (C=O); IR (neat) 2950, 2900, 1715, 1400, 1360, 1320, 1230, 760 cm^{-1} ; MS, m/e (relative intensity) 211 (M^+ , 0.3), 139 (0.3), 138 (1), 124 (1), 86 (100); high-resolution MS, m/e 211.1940 ($\text{C}_{13}\text{H}_{25}\text{NO}$ requires 211.1936).

9: ^1H NMR 0.10 (two s, 9 H, SiMe_3), 0.90–1.00 (two t and two s, 9 H, NCH_2CH_3 and Me), 1.04 and 1.15 (s, 3 H, Me), 1.45–1.75 (m, 3 H), 2.00–2.85 (m, 9 H); ^{13}C NMR 0.9 and 1.3 (SiMe_3), 14.6 and 14.7 (NCH_2CH_3), 20.9 and 21.0 (C-4Me), 29.4 and 29.9 (C-4Me), 32.9 and 34.2 (C-4), 38.0 (C-6), 41.0 and 45.6 (C-5), 41.6 and 45.7 (C-2), 45.3 and 48.7 (C-3), 50.0 (NCH_2CH_3), 52.2 and 56.3 (CHTMS), 211.8 and 213.1 (C=O); IR (neat) 2950, 2900, 1715, 1400, 1360, 1300, 1230, 850, 760 cm^{-1} ; MS, m/e (relative intensity) 283 (M^+ , 2), 268 (6), 210 (100), 158 (74), 130 (7), 112 (10), 73 (32); high-resolution MS; m/e 283.2328 ($\text{C}_{16}\text{H}_{33}\text{NOSi}$ requires 283.2331).

Irradiation of (R)-(-)-Carvone (10) and α -Silyl Amine 2. A solution of 900 mg (5.99 mmol) of 10 and 1.431 g (8.98 mmol) of 2 in 150 mL of MeCN was irradiated for 19 h (20% conversion of 10) to give after workup and TLC (2.5% MeOH- CHCl_3) 74 mg (40%) of non-TMS adduct 11 (see below) and trace quantities of the bis(trimethylsilyl)amine dimer 12.

Irradiation of MeOH (150 mL) solutions of 10 and 2 in the same concentration as above for 12 h (95% conversion of 10) gave 307 mg (86%) of non-TMS adducts 11 comprised of a mixture of three stereoisomers. The ratio of these isomers was determined by ^1H NMR integration methods to be 6:3:1 for 11a:11b:11c. Careful separation of these isomers by Florisil (1.3 EtOAc-hexane) and silica gel (1:1 EtOAc-hexane), chromatographic methods resulted in pure samples of 11a and 11b and a sample enriched (ca. 60%) in 11c.

11 (mixture of stereoisomers): IR (neat) 2960, 2850, 1720, 1650, 1460, 1380, 1205, 1080, 980 cm^{-1} ; MS, m/e (relative intensity) 237 (M^+ , 2), 87 (6), 86 (100), 72 (13); high-resolution MS, m/e 237.2099 ($\text{C}_{15}\text{H}_{27}\text{NO}$ requires 237.2093).

11a: ^1H NMR 0.95 (t, $J = 7.1$ Hz, 6 H, NCH_2CH_3), 1.01 (d, $J = 6.9$ Hz, 3 H, C-2 Me), 1.59 (ddd, $J = 12.4, 12.4, 3.8$ Hz, 1 H, H-4 ax), 1.73 ns, 3 H, $\ll\text{dgdCCH}_3$, 2.07 (dd, $J = 12.4, 12.4$ Hz, 1 H), 2.17 (ddd, $J = 12.4$, ca. 1, 1 Hz, 1 H, H-4 eq), 2.2–2.6 (m, 8 H), 2.41 (dd, $J = 12.4, 4.4$ Hz, 1 H), 2.67 (dq, $J = 6.9, 5.2$ Hz, 1 H, H-2 ax), 4.70 (s, 1 H, =CH), 4.75 (s, 1 H, =CH); ^{13}C NMR 11.6 (NCH_2CH_3), 11.8 (C-2 Me), 20.8 (=CCH₃), 32.4 (C-4), 39.1 (C-3), 41.2 (C-5), 46.1 (C-6), 47.3 (NCH_2CH_3), 47.7 (C-2), 50.7 (CH_2N), 109.7 (=CH₂), 147.8 (=C), 213.1 (C=O).

11b: ^1H NMR 0.96 (t, $J = 7.1$ Hz, 6 H, NCH_2CH_3), 1.13 (d, $J = 6.9$ Hz, 3 H, C-2 Me), 1.7 (d, $J = 0.5$ Hz, =CCH₃), 1.73–1.81 (m, 1 H), 2.01–2.09 (m, 1 H), 2.19 (dq, $J = 6.9, 6.0$ Hz, 1 H, H-2 ax), 2.24–2.44 (m, 6 H), 2.46–2.68 (m, 4 H), 4.66 (d, $J = 0.5$ Hz, 1 H, =CH), 4.77 (s, 1 H, =CH); ^{13}C NMR 11.9 (NCH_2CH_3), 15.0 (C-2 Me), 21.2 (=CCH₃), 30.0 (C-4), 39.3 (C-3), 40.5 (C-5), 43.6 (C-6), 47.5 (NCH_2CH_3), 47.9 (C-2), 57.0 (CH_2N), 110.6 (=CH₂), 147.4 (C=), 214.2 (C=O).

11c (obtained on mixture of 11c and 11b) by subtraction methods): ^1H NMR 0.95 (t, $J = 6.8$ Hz, 6 H, NCH_2CH_3), 1.03 (d, $J = 7.3$ Hz, 3 H, C-2Me), 1.61–1.68 (m, 1 H), 1.71 (s, 3 H, =CCH₃), 1.95–2.56 (m, 12 H), 4.73 (s, 1 H, =CH) 4.74 (s, H, =CH); ^{13}C NMR 11.8 (NCH_2CH_3), 15.7 (C-2 Me), 20.4 (=CCH₃), 36.2 (C-4), 43.9 (C-3), 44.9 (C-5), 46.8 (C-6), 47.7 (NCH_2CH_3), 48.4 (C-2), 58.0 (CH_2N), 109.5 (=CH₂), 147.7 (=C), 212.5 (C=O).

12: ^1H NMR 0.10 (s, 18 H, SiMe_3), 0.99 (t, $J = 7.0$ Hz, 12 H, NCH_2CH_3), 2.55–2.74 (m, 10 H, NCH_2 and NCHTMS); ^{13}C NMR 2.72 (SiMe_3), 15.4 (NCH_2CH_3), 48.6 (CCH_2CH_3), 59.2 (NCHTMS); IR (CHCl_3) 2940, 2830, 1450, 1380, 1240, 1150, 1120, 850, 835 cm^{-1} ; MS, m/e (relative intensity) 158 (half of M^+ , 100); high-resolution MS, m/e 158.1365 (half of m^+ is $\text{C}_8\text{H}_{20}\text{NSi}$ and requires 158.1365).

Epimerization of Carvone Adduct 11a to 11b. A solution of carvone adduct 11a (17 mg, 0.07 mmol) in 12 mL of 0.075 M ethanolic NaOH was stirred at 20 °C for 20 min and concentrated in vacuo, giving a residue shown by ^{13}C NMR spectroscopy to consist of a mixture of 11a and 11b in ca. 41:59 ratio. Conducting this epimerization process for longer time periods (e.g. 50 min) led to mixtures of 11a and 11b in the same (2:3) ratio.

Irradiation of Isophorone (13) and α -Silyl Amine 2. A solution of 13 (995 mg, 7.20 mmol) and 2 (1.145 g (7.1 mmol)) in 120 mL of MeCN was irradiated for 10 h (30% conversion of 13). A CHCl_3 solution of the concentrated photolysate was extracted with 5% aqueous HCl, dried, and concentrated in vacuo to give a residue that was subjected to TLC (0.1% MeOH- CHCl_3) separation, providing the isophorone dimer 16 (250 mg, 25%; mp 160–162 °C (EtOC-ether), lit.¹⁸ mp 163 °C). The aqueous

acid extract was made basic (pH 14) and extracted with CHCl_3 . Concentration of the CHCl_3 extract gave a residue that upon TLC (2% MeOH- CHCl_3) separation provided 150 mg (35%) of the silyl amine dimer 12 and trace quantities of what appears to be a stereoisomeric mixture of the silicon-containing adducts 15.

Irradiation of MeOH (150 mL) solutions of 13 and 2 at the same concentrations as above for 6.5 h (51% conversion of 13) gave after workup and TLC (2% MeOH- CHCl_3) separation of 330 mg (40%) of the non-TMS adduct 14. The α -silyl amine dimer 12 and isophorone dimer 16 were also detected in the crude photolysate.

14: ^1H NMR 0.92 (s, 3 H, Me), 0.95 (t, $J = 7.1$ Hz, 6 H, NCH_2CH_3), 1.01 (s, 3 H, Me), 1.04 (s, 3 H, Me), 1.25 (ddd, $J = 14.0, 1.8, 1.6$ Hz, 1 H, H-4 eq), 1.77 (d, $J = 14.0$ Hz, 1 H, H-4 ax), 1.86 (dd, $J = 12.8, 1.8, 1.6$ Hz, 1 H, H-2 eq), 2.05 (d, $J = 13.8$ Hz, 1 H, NCH), 2.01 (dd, $J = 13.0, 1.7, 1.8$ Hz, 1 H, H-6 eq), 2.20 (d, $J = 13.0$ Hz, 1 H, H-6 ax), 2.23 (d, $J = 13.8$ Hz, 1 H, NCH), 2.4 (d, $J = 12.8$ Hz, 1 H, H-2 ax), 2.52 (q, $J = 7.1$ Hz, 4 H, NCH_2CH_3); ^{13}C NMR 12.0 (NCH_2CH_3), 25.6 (C-5 Me), 29.3 (C-5 Me), 34.2 (C-3 Me), 35.9 (C-5), 41.7 (C-3), 47.4 (C-4), 49.2 (NCH_2CH_3), 50.2 (C-2), 654.0 (C-6), 67.5 (CH_2N), 213.6 (C=O); IR (neat) 2950, 2900, 1720, 1460, 1380, 1260, 1060 cm^{-1} ; MS, m/e (relative intensity) 225 (M^+ , 4), 224 (8), 210 (2), 168 (4), 139 (6), 131 (58), 130 (20), 119 (79), 113 (15), 86 (100), 72 (12); high-resolution MS, m/e 225.2093 ($\text{C}_{14}\text{H}_{27}\text{NO}$ requires 225.2093).

15: ^1H NMR 0.16 and 0.17 (two s, 9 H, SiMe_3), 1.00–1.06 (m, 15 H), 1.23–2.31 and 3.03–3.13 (m, 7 H), 2.56–2.90 (m, 4 H); ^{13}C NMR 3.8 and 3.6 (SiMe_3), 16.8 (NCH_2CH_3), 25.1 and 26.3 (C-5 Me), 28.5 and 29.2 (C-5 Me), 35.1 and 35.2 (C-3 Me), 35.9 and 36.0 (C-5), 46.1 and 46.8 (C-3), 46.6 and 49.2 (C-4), 50.2 and 51.3 (NCH_2CH_3), 52.0 and 52.8 (C-2), 54.0 (C-6), 68.4 and 68.9 (NCHTMS), 214.4 and 214.6 (C=O); MS, m/e (relative intensity) 297 (M^+ , 1), 224 (44), 158 (100), 130 (5), 73 (17); high-resolution MS, m/e 224.2029 ($\text{C}_{14}\text{H}_{26}\text{NO}$, M^+ – TMS, requires 224.2014).

Irradiation of (+)-4-Cholesten-3-one (17) and α -Silyl Amine 2. Irradiation of a solution of cholestenone (17; 2.31 g, 6.02 mmol) and 2 (1.43 g, 7.50 mmol) in 150 mL of MeCN for 1.5 h (80% conversion of 17) gave a photolysate containing a solid precipitate. The residue obtained by filtration contained 1.70 g (73%) of the pinacol 18 (mp 202–205 °C (CHCl_3 -MeOH), lit. mp 200–205 °C,^{19a} 200 °C,^{19b} 225–227 °C^{19c}). This substance was also obtained by irradiation of MeOH solutions of 17 and 2 and by irradiation of MeCN solutions of 17 and Et_3N . The pinacol 18 was not produced when 17 was irradiated in MeCN solutions not containing 2 or Et_3N .

General Procedures for Determining the Effects of Reaction Conditions on Formation of Adducts 8 and 9 from Irradiation of 4,4-Dimethylcyclohex-2-en-1-one (7) and α -Silyl Amine 2. In general, solutions of enone 7 (7.0×10^{-2} M) and amine 2 (2.1×10^{-1} M) in the specified solvent containing required additives in 1-cm-diameter quartz tubes were simultaneously irradiated in a merry-go-round apparatus by use of uranium glass filtered light. To the crude photolysates was added the internal GLC standards 1,4-dimethoxybenzene. GLC analysis at 100–110 °C was performed to determine the percent conversion of enone and at 150–160 °C to determine the 8 to 9 ratio. Measurements of 8:9 ratios were performed on photolysates corresponding to <60% conversion. However, the 8:9 ratios were found to be unchanged as a function of percent conversions smaller than 60%. In cases where additives interfered with GLC analysis, an acid extraction procedure was followed. Solutions (CHCl_3) of concentrated photolysates were extracted with 1 M aqueous HCl. The basified (1 M aqueous NaOH, pH 14) aqueous layers were extracted with CHCl_3 . The concentrated CHCl_3 extracts were dried and concentrated in vacuo, giving residues that were analyzed by GLC to determine 8:9 ratios. The product ratios as a function of solvent, $[\text{HClO}_4]$, [2], $[\text{n-Bu}_4\text{NOH}]$, $[\text{n-Bu}_4\text{NF}]$, $[\text{CsF}]$, $[\text{LiClO}_4]$, and $[\text{n-Bu}_4\text{NClO}_4]$ are provided in tables and figures recorded in Results.

Since 8:9 ratios are in some cases very sensitive to variations in solvent purity and moisture content, a method for standardization of data based upon controls was developed. Photoreactions of 7 (7.0×10^{-2} M) and 2 (2.1×10^{-1} M) provided average 8:9 ratios of 0.16 to 0.06 in MeCN, 0.64 ± 0.10 in EtOH, and 2.97 ± 1.32 in MeOH. For experiments conducted in these solvents containing varied additives, control irradiations without additives were run simultaneously. The measured 8:9 ratios were then converted to standardized ratios by multiplying by a factor required to adjust the ratio of the control to the average given above. In practice, this standardization method does not affect variations in 8:9 ratios as a function of a single additive but merely allows comparison of results for different additives.

9,10-Dicyanoanthracene Electron-Transfer-Photosensitized Photoadditions of α -Silyl Amine 2 to Cyclohexenones 4 and 7. Solutions of enones 4 and 7, silyl amine 2, and 9,10-dicyanoanthracene (10 mg, saturated solutions), in 4 mL of MeCN were irradiated simultaneously in a merry-go-round apparatus with uranium glass filtered light. Filtration of the

photolysate to remove DCA gave filtrates that were subjected to the acid extraction technique described above, providing amine-containing fractions that were analyzed by GLC to determine the 5:6 and 8:9 adduct ratios. The results of experiments in which [enone] and [silyl amine] were varied are provided in Results (see Figures 1-3).

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A Strategy for Intermolecular Diels-Alder Cycloaddition to Enamides[†]

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Abstract: A strategy for the net Diels-Alder addition of conjugated dienes to enamides is proposed and exemplified. The strategy is based upon cation radical cyclobutanation of *N*-methyl-*N*-vinylacetamide (MVA) to give *N*-(2-alkenylcyclobutyl)-*N*-methylacetamides. The secondary amines resulting from hydrolysis of the latter are then subjected to an aminyl anion assisted vinylcyclobutane rearrangement, giving the Diels-Alder adduct. The mechanism and stereoselectivity of the addition and rearrangement reactions are elucidated, and the synthetic advantages of the indirect Diels-Alder sequence are stressed.

The intermolecular Diels-Alder cycloaddition of enamides and other electron-rich alkenes to conjugated dienes is a potentially valuable synthetic operation which has been mechanistically blocked by the low cycloaddition reactivity of such electron-rich dienophiles. In the intramolecular domain, however, the feasibility of diene/enamide cycloadditions has already been demonstrated and exploited in the context of alkaloid synthesis.¹⁻⁵ Recent observations of cation radical Diels-Alder additions of vinyl ethers and vinyl sulfides to dienes suggests a novel catalytic approach to this challenging methodological problem.⁶ However, the fact that Diels-Alder periselectivity in these cycloadditions is largely confined to cyclic dienes appears to impose serious practical limitations upon this strategy.⁷ The present paper reports an effective synthetic procedure for net intermolecular Diels-Alder addition of enamides to a variety of dienes which retains a cation radical strategy (specifically, cyclobutanation) coupled to a novel and efficient heteroatom anion assisted vinylcyclobutane rearrangement.

Historical Precedents. Cation radical cyclobutanation has undergone rapid development since the discovery of the efficient cation radical chain cyclodimerization of *N*-vinylcarbazole by metal ions and by photosensitized electron transfer (PET).⁸⁻¹¹ The cyclodimerizations of other electron-rich alkenes, such as phenyl vinyl ether,¹²⁻¹⁴ and of styrene-like conjugated systems, such as indenenes,^{12,15-19} have since been observed and studied intensively. Although most of the efficient cation radical cyclobutanations reported have been cyclodimerizations, several cross additions have also been observed.¹² More recently, the catalysis of some of these cycloadditions and cyclodimerizations by tris(4-bromophenyl)-aminium hexachloroantimonate (in dichloromethane at 0 °C) has been reported and the stereospecificity of the aminium salt catalyzed cyclodimerizations of (*E*)- and (*Z*)-anethole established.²⁰ A detailed kinetic study of the aminium salt catalyzed cyclodimerization of (*E*)-anethole has been carried out, revealing an activation energy of only 0.8 kcal/mol for the cycloaddition step.²¹ Both the aminium salt and the PET methods have been used to study the cycloadditions of a variety of electron-rich alkenes and styrenes to conjugated dienes.^{6,7} As noted previously, dienes which are not rigidly *s*-cis tend to exhibit at least modest cyclobutane,

as opposed to Diels-Alder, periselectivity.⁷

The vinylcyclobutane rearrangement, a second element of the synthetic strategy, has been studied extensively,²² and the development of an oxyanion assisted version has added additional utility to the reaction.²³⁻²⁶ Prior to this work, an aminyl anion assisted vinylcyclobutane rearrangement had not been observed, but an aminyl anion assisted 1,3-shift has been found in a bicyclic system.²⁷

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