were obtained at 10 °C with use of a constant surface pressure of 25 dyn/cm. The improved transferability of **2** is presumed to reflect a stronger interlipid association in the polymeric state.

Dispersal of **1** in pure water (1.0 mg/mL) via vortex mixing produced a multilamellar dispersion exhibiting a main-phase transition (DSC) at ca. 26 °C (Figure 2), in agreement with temperature-dependent turbidity measurements.[3] The melting endotherm had a peak width at half-height of ca. 0.8 °C with ΔH = 5.1 ± 1.2 kcal mol^{-1} (four scans). In contrast, **2** exhibited a substantially broadened endotherm at 29 °C with a peak width of 5 °C and a ΔH of ca. 1.7 ± 0.5 kcal (lipid-mol)$^{-1}$ (three scans). The lower ΔH value of **2** appears to be compensated by a smaller ΔS, resulting in an overall increase in the transition temperature. Smaller values of ΔH and ΔS for **2** are a likely consequence of limited fluidity in the "liquid–crystalline" state and/or increased disorder in the gel state, due to the presence of the polydisulfide backbone. Bath sonication of these dispersions produced small vesicles having diameters ranging between 200 and 1000 Å (electron microscopy); dynamic light scattering revealed a similar size distribution.[3] Thin-layer chromatography confirmed the retention of the monomeric and polymeric states of **1** and **2**, respectively.

Space-filling models (CPK) of **2** suggest that the disulfide moiety, positioned α to the carbonyl groups, introduces a minimal perturbation in the packing behavior of the aliphatic chains. Results presented herein confirm this prediction and clearly demonstrate that spacer groups are not a prerequisite for forming tightly packed membranes from preformed polymers. This finding should stimulate further efforts in the design of new polymerizable surfactants. From the standpoint of membrane modeling, the feasibility of preparing polymeric phospholipid monolayers and bilayers directly from **2** should provide new opportunities for constructing unique "biological-like" membranes bearing highly sensitive components. Studies now in progress are aimed at exploring and exploiting these possibilities.

Acknowledgment. We are grateful to Robyn McMillan and Professor David Tirrell (University of Massachusetts) for assistance in obtaining the DSC data and for helpful discussions. We are also grateful to Professor John Baldeschwieler and Tracy Handel (California Institute of Technology) for informing us of their related efforts prior to publication.

Electron-Transfer Photochemistry of α-Silylamine–Cyclohexenone Systems. Medium Effects on Reaction Pathways Followed

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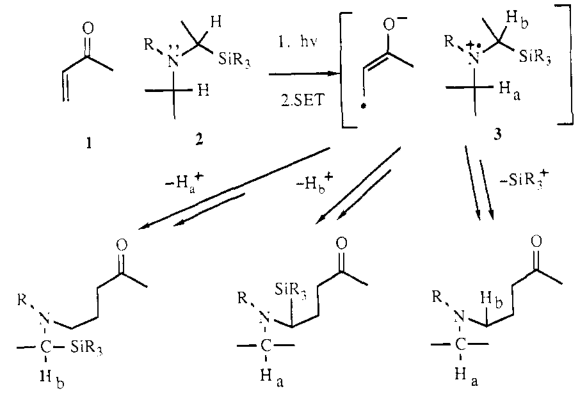
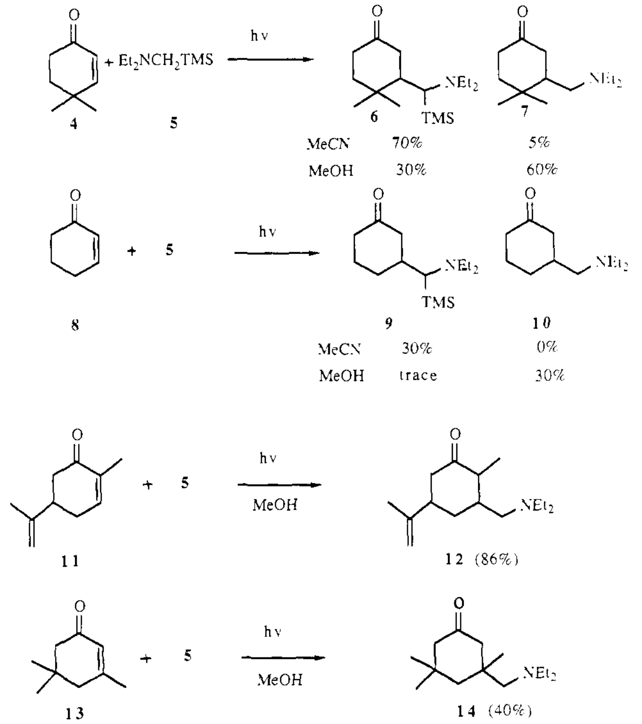
Previously, we demonstrated how photostimulated electron-transfer (SET) processes of α-trialkylsilyl-substituted electron donors can be employed to generate free radical systems.[1] Initial efforts focused on SET processes of iminium salts. Recently, we expanded this methodology to include arenecarbonitriles.[2] In this communication we report on the SET photochemistry of α,β-unsaturated cyclohexenones with an α-silyl tertiary amine donor. Earlier studies have shown that cation radicals derived from tertiary amines react via α-deprotonation and α-C–C bond cleavage,[3] and that α-silylamine cation radicals undergo α-C–Si bond rupture to produce α-amino radicals.[2] Also, tertiary amines are known to serve as electron donors to the triplet states of conjugated cyclohexenones. This process produces amine cation radicals[4] in pathways leading to adduct formation.[5]

These observations suggest that α,β-unsaturated ketones **1** and tertiary α-silylamines **2** could participate in electron-transfer-induced photoaddition reactions as outlined in Scheme I. Pathways

Scheme I



Scheme II



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(1) (a) Ohga, K.; Mariano, P. S. *J. Am. Chem. Soc.* **1982**, *104*, 617. (b) Ohga, K.; Yoon, U. C.; Mariano, P. S. *J. Org. Chem.* **1984**, *49*, 213. (c) Lan, A.; Quillen, S.; Heuckeroth, R. O.; Mariano, P. S. *J. Am. Chem. Soc.* **1984**, *106*, 6439. (d) Brumfield, M. A.; Quillen, S. L.; Yoon, U. C.; Mariano, P. S. *Ibid.* **1984**, *106*, 6855.

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Table I. Medium Effects on the 7:6 Adduct Ratio in Photoadditicn of the Silylamine **5** to Cyclohexenone **4**

solvent	E_T	pK_a	additive	7:6 ratio[a,b]
cyclohexane	31.2			0.05
CH_2Cl_2	41.1			0.10
MeCN	46.0			0.12
25% H_2O-MeCN				1.51
MeOH	55.5	16		1.65
25% H_2O-MeOH				2.30
EtOH	51.9	18		0.55
n-BuOH	50.2			0.11
t-BuOH[c]	43.9	19		0.01
MeCN			$LiClO_4$[d]	1.02
MeCN			$(n\text{-Bu})_4NClO_4$[d]	0.53
MeCN			CsF[e]	0.05

[a] Irradiations with uranium-glass filtered light ($\lambda > 320$ nm) with [**4**] = ca. 6.8×10^{-2} M and [**5**] = ca. 2.5×10^{-1} M. [b] Determined by GLC methods. [c] Containing 4% MeCN to prevent crystallization. [d] Salt concentrations were 0.26 M. [e] Saturated solutions of CsF in MeCN were used.

involving both deprotonation and desilylation of the amine cation radical **3** are possible. We anticipated that the sequential SET desilylation route would predominate based upon the reactivity of other α-silyl cation radicals.[1] If so, this would provide a method for regioselective α-amino radical formation from unsymmetric, tertiary amine cation radicals.[6]

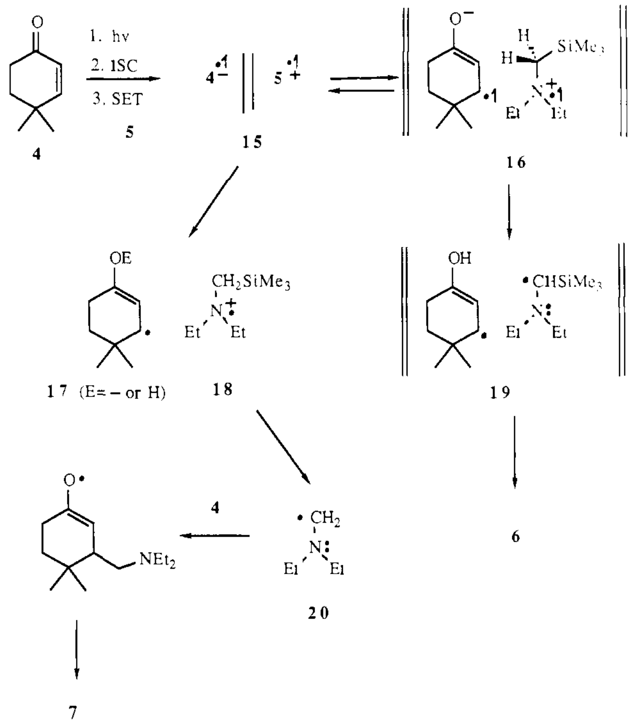
These ideas have been explored in studies of photoaddition reactions of several cyclohexenone derivatives with the tertiary amine $Et_2NCH_2Si(CH_3)_3$ (**5**). We have uncovered results which show that a competition exists between deprotonation and desilylation of cation radicals related to **3**, which is controlled by the nature of the photoreaction medium. These results and their interpretation in terms of the nature of ion radical intermediates are discussed below.

Our initial studies focused on preparative aspects of the photoadditon reactions of the α-silylamine **5** with several cyclohexenone derivatives. The results are outlined in Scheme II. In summary, we noted that two types of adducts are produced when the enones (4×10^{-2} M) are irradiated ($\lambda > 300$ nm) in either MeCN or MeOH solutions containing the amine **5** (6×10^{-2} M). In the case of enones **4** and **8**, the predominant product changes from the trimethylsilyl adducts **6** and **9** to the non-silyl adducts **7** and **10** when the solvent is varied from MeCN to MeOH. Also, only the non-silyl adducts **12** and **14** are produced when carvone (**11**) and isophorone (**13**) are irradiated in MeOH solution containing **5**.

The intriguing differences seen in these processes were probed by use of the enone **4** and amine **5** and reaction conditions in which the medium polarity (E_T values), protic nature (pK_a), and ionic strength and character were varied. As the data in Table I show, the **7**:**6** ratio varies directly and reasonably uniformly with the E_T, pK_a, and ionic strength properties of the medium. This ratio rises by nearly 100-fold when the solvent is changed from cyclohexane to MeOH. A similar effect is seen when photoreactions are conducted in alcohol solvents of varying polarity and acidity. Addition of water to the MeCN photolysis solution results in a large (10-fold) increase in the **7**:**6** ratio. Likewise, added salts such as $LiClO_4$ and $(n\text{-Bu})_4NClO_4$ that increase ionic strength enhance the chemoselectivity of the process favoring the non-silyl adduct **7**. Significantly, CsF has virtually no effect on the **7**:**6** ratio.

The above results demonstrate that the α-silylamine photoadditions to cyclohexenones represent reasonably efficient carbon–carbon bond-forming processes. However, the medium effects observed represent the most interesting aspect of the study. The mechanism outlined in Scheme III appears to best rationalize these observations. Electron transfer between the amine **5** and triplet enone (e.g., **4**)[4,5] results in generation of the solvent-separated ion pair (SSIP) **15**, which can transform to the contact ion pair (CIP) **16** or free ion radicals **17** and **18**. This sequence is known to be operable in related triplet benzophenone tertiary amine electron-transfer processes.[8] Both Mataga[9] and Peters[10] have shown that in media of high polarity or ionic strength, or when the "special salt effect" is operable, contact and solvent-separated ion pair equilibria favor SSIP formation, and free radical ion generation is likely.

Scheme III



In solvents of low polarity, the CIP **16** formation should be strongly favored. Regioselective proton transfer occurs in **16** from the amine cation radical to the oxy anion center producing the radical pair **19**. This is analogous to the results of Peters[8] and Mataga[11] showing that proton transfer occurs in the CIP of the $Ph_2C{=}O/R_3N$ ion radical system. The selectivity for proton rather than trimethylsilyl group transfer in **16** is likely a result of steric effects, which are minimized by the conformation shown. Also, the methylene protons adjacent to silicon in **16** should be more acidic.[12] This factor, which is known to influence cation radical deprotonation regiochemistry,[6] leads to selective generation of radical pair **19** and ultimately trimethylsilyl-adduct **6**.

In contrast, proton transfer between ion radicals should not be favorable in the SSIP **15** or free species **17** and **18**. Instead, desilylation (either with solvent as a nucleophile or liberating a short-lived silenium cation) occurs to give the α-amino radical **20**. Coupling to the enone radical anion or its protonated form would be inefficient. Instead, conjugate addition of the nucleophilic radical **20** to the enone present in higher concentration could occur to form eventually the non-silyl adduct **7**. Support for this proposal is provided by studies which show that the addition of amine **5** to cyclohexenones **4** and **8** can be SET-sensitized by using 9,10-dicyanoanthracene (DCA).[2] Irradiation of DCA in MeCN containing low concentrations[13] of either **4** or **8** leads to near

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(6) Lewis, F. D.; Ho, T. I. *J. Am. Chem. Soc.* **1980**, *102*, 1751. Lewis, F. D. Ho, T. I.; Simpson, J. J. *J. Org. Chem.* **1981**, *46*, 1077.

(7) (a) All new substances possessed satisfactory spectroscopic data. (b) The trimethylsilyl adducts **6** and **9** were produced as a ca. 1:1 mixture of diastereomers. (c) Adduct **12** is a mixture of three stereoisomers with one as major.

(8) (a) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1981**, *103*, 6403. (b) Simon, J. D.; Peters, K. S. *Ibid.* **1982**, *104*, 6542.

(9) Masuhara, H.; Mataga, N. *Acc. Chem. Res.* **1981**, *14*,, 312.

(10) (a) Simon, J D.; Peters, K. S. *J. Am. Chem. Soc.* **1982**, *104*, 6142. (b) Simon, J. D.; Peters, K. S. *Ibid.* **1983**, *105*, 4875.

(11) Arimitsu, S.; Masuhara, H.; Mataga, N.; Tsubomura, A. *J. Phys. Chem.* **1975**, *79*, 1255.

(12) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981; Chapter 4.

exclusive production of the non-silyl adducts **7** and **10**. Thus, the α-amino radical **20**, formed by SET to DCA followed by desilylation, does indeed add to enones.

Desilylation of the amine cation radical **18** represents the more typical behavior of α-silyl cation radicals.[1] Thus, it appears that desilylation is more efficient than deprotonation unless these species are in contact ion pairs with basic partners (e.g., enone radical anions).[14] In a general sense, the medium effects can be understood in terms of the base strength of the enone radical anions. Thus, while solvent polarity, protic nature, and ionic strength will govern efficiencies of CIP formation, they also influence the pK_b of the enone anion radicals.

In summary, we have uncovered interesting medium effects on silylamine-cyclohexenone SET photoaddition reactions. An interpretation in terms of differential reactivity of CIP and SSIP or free ion radical intermediates is proposed. It will be interesting to see if this phenomenon is general and if it can be used as a diagnostic tool in the study of other photoelectron-transfer processes.

Acknowledgment. Financial support for this research was provided by the National Science Foundation (CHE-86-09589) for P.S.M. and by the Korea Science and Engineering Foundation for U.C.Y. A joint KOSEF-NSF Cooperative Research Grant provided travel funds.

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(13) Competitive light absorption occurs at high enone concentrations.

(14) Application of Arnold's method[14b] suggests that the enone radical anion is more basic than that of DCA, reflective mainly of the reduction potential differences for the neutral precursors (e.g., $E_{1/2}(-)$ values for enone are ca. −2.6 V while those for DCA are −0.89 V). (b) Wayner, D. D. M.; Arnold, D. R. *Can. J. Chem.* **1985**, *63*, 871.

Coadsorption as a Probe of Mechanism: Cyclic Sulfides and Straight Chain Thiols on Mo(110)

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We recently reported that tetrahydrothiophene and trimethylene sulfide undergo desulfurization on Mo(110) to form gaseous alkanes and alkenes in a temperature-programmed reaction experiment.[1,2] In both cases, straight chain alkane evolution preceded alkene evolution. We proposed that the intermediate leading to straight chain alkanes and alkenes from these two cyclic sulfides is a surface thiolate. The thiolate undergoes competitive C_1-hydrogenation to alkane and C_2-dehydrogenation to alkene, depending on the surface hydrogen concentration. The proposed mechanism of hydrocarbon formation from tetrahydrothiophene on Mo(110) is depicted in Figure 1.

Ethanethiol, 1-propanethiol, and 1-butanethiol also react on Mo(110) to form alkanes and alkenes with alkane production preceding alkene production.[1-3] Comparison to alcohols and thermodynamic considerations suggest that thiols almost certainly react on Mo(110) to form a stable thiolate intermediate which then decomposes to hydrocarbons. Although the temperatures of alkane production from the thiols were approximately 40 K lower than those from the cyclic sulfides, we suggested that the identical temperature *ordering* of the reaction products was strong experimental support for the formation and subsequent decomposition of a thiolate intermediate during the temperature-programmed reaction of trimethylene sulfide and tetrahydrothiophene. Also, adsorption of either of the cyclic sulfides on a hydrogen-presaturated surface resulted in alkane production temperatures virtually identical with those from the thiols. Finally, experiments measuring the extent of surface deuterium incorporation into all hydrocarbon products from the cyclic sulfides and thiols were consistent with the decomposition of cyclic sulfides and thiols by way of the thiolate intermediate. These results are described in detail in previous work.[1-3]

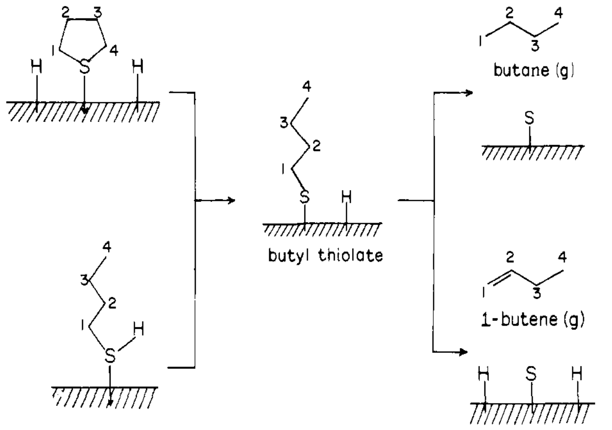

Figure 1. Proposed mechanism of hydrocarbon formation from tetrahydrothiophene on Mo(110).

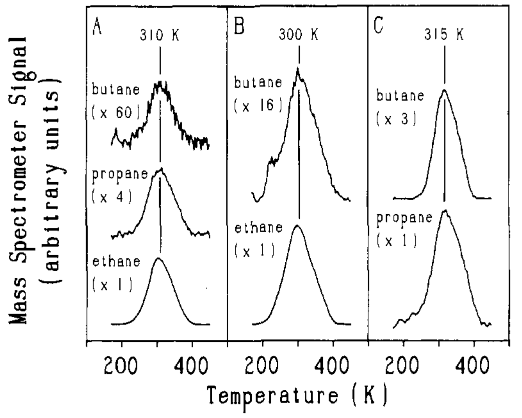

Figure 2. Temperature-programmed reaction spectra of the coadsorbed mixtures. Adsorption was performed at a surface temperature of 150 K. The heating rate during reaction was approximately 15 K/s. The ions detected were chosen so that only one alkane contributed to the signal. The multiplication factors are referenced to the most intense alkane signal from the coadsorbed mixture investigated and are uncorrected for degree of fragmentation and ionization efficiency in the mass spectrometer: (A) ethane (m/e = 30), propane (m/e = 44), and butane (m/e = 58) from multilayers of an ethanethiol/1-propanethiol/1-butanethiol mixture (ratio = 15:3:1) on Mo(110); (B) ethane (m/e = 30) and butane (m/e = 43) from multilayers of an ethanethiol/tetrahydrothiophene mixture (ratio = 6:11); (C) propane (m/e = 44) and butane (m/e = 58) from multilayers of a trimethylene sulfide/1-butanethiol mixture (ratio = 9:1).

We report here that coadsorbed cyclic sulfides $C_nH_{2n}S$ (n = 3, 4) and linear thiols $C_mH_{2m+1}SH$(m = 2, 3, 4) react during a temperature-programmed reaction experiment to form alkanes C_nH_{2n+2} and C_mH_{2m+2} at exactly the same temperature. These experiments lend powerful support to our proposal that cyclic sulfides and straight chain thiols react on Mo(110) by way of a thiolate intermediate.

If multilayers of an ethanethiol/1-propanethiol/1-butanethiol mixture (ratio = 15:3:1)[4] were adsorbed on Mo(110), the expected products were detected in a temperature-programmed reaction

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(1) Roberts, J. T.; Friend, C. M. *J. Am. Chem. Soc.* **1986**, *108*, 7204-7210.

(2) Roberts, J. T.; Friend, C. M. *J. Am. Chem. Soc.* **1987**, in press.

(3) Roberts, J. T.; Friend, C. M., in preparation.

(4) The coadsorbed mixtures described in this work were prepared by mixing the adsorbate molecules in the adsorbate reservoir, so that the molecules were simultaneously adsorbed on the crystal. The ratios are estimated from the mass spectra of the gaseous mixtures. In all cases the relative intensities of the multilayer desorptions were in agreement with the ratios of the gaseous mixtures.

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