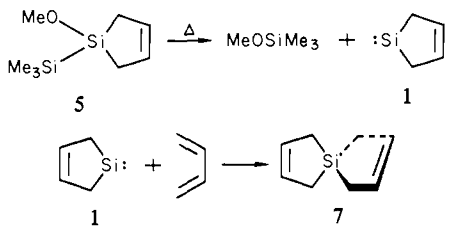


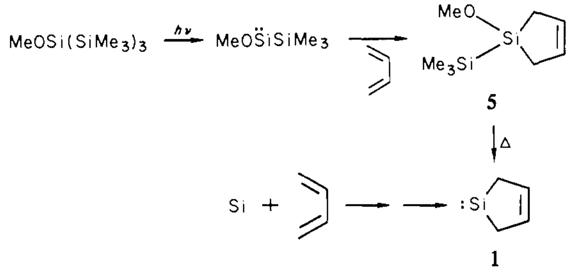
of its vapor chromatographic retention times with those of an authentic sample[12] on three columns of widely varying retention characteristics.[14]

The spirosilanonadiene **7** has also been found as the only volatile product detected from the cocondensation of silicon vapor with butadiene in a Timms "freeze-fry" metal evaporation apparatus[15] modified to reach the ca. 1600 °C required for vaporization of silicon.[16] While the yield was again low (ca. 1%), this is the first stable product obtained from cocondensation of silicon vapor with a hydrocarbon.

Although its yield from the hot atom experiments is small, the detection of **7**, an unambigously identified product that is formed in >50% yield (based on the immediate silylene precursor) from 1-silacyclopent-3-en-1-ylidene (**1**) and butadiene supports the view that this cyclic silylene is an intermediate in the recoil reactions. We have also found two other as yet unidentified products in higher yield (ca. 5%) whose chromatographic behavior suggests that they are $^{31}SiC_8$ compounds. While these may turn out to be rearrangement products of the spiro silanonadiene **7**, there is the more interesting possibility that they are cycloadducts of rearrangement products of the cyclic silylene **1**. The gas-phase rearrangements of **1** are presently under investigation.

The formation of spirosilanonadiene **7** from cocondensation of silicon vapor and butadiene also implies the intermediacy of silacyclopentenylidene (**1**), since silicon vapor is known to be principally monatomic.[16] Even the low product yield obtained raises the question whether "direct synthesis"[17] of organosilanes is possible via monoolefins.

Finally it is worth noting that, in a two-step process, all the



appendages to the central silicon atom of methoxytris(trimethylsilyl)silane have been removed, and the same end product obtained as arose in much lower yields from recoiling silicon atoms and silicon vapor. Thus both the methoxytris(trimethylsilyl)silane and the methoxy(trimethylsilyl)silylene may be viewed as synthetic equivalents of a silicon atom.

Acknowledgment. We are grateful to the United States Department of Energy for support of this research. This is technical report C00-1713-98. We thank John Hood and the Washington University Cyclotron for fast neutron irradiations and the Washington University Cyclotron Machine Shop for fabrication of the metal evaporation apparatus.

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[14] Retention times at 80 mL/min of He flow, $^1/_4$-in. columns, 10% W/W stationary phase on 40–50 mesh Anakrom ABS: 35 min on 20-ft SF96 silicone oil, 125 °C; 14.5 min on 20-ft carbowax 20M, 130 °C; 19 min on 15-ft tricresyl phosphate, 110 °C.

[15] P. L. Timms, *Adv. Inorg. Chem. Radiochem.*, **14**, 121 (1972).

[16] Ca. 150 mg of silicon was evaporated within a period of 15 min from a beryllia crucible supported within a tungsten spiral through which a current of 76 A at 9.5 V was passed. Silicon vapor at 1660 K is reported to consist of 94% Si_1, 3% Si_2, 1.5% Si_3, 1% Si_4, and $^1/_2$% $Si_{>4}$. R. E. Honig, *J. Chem Phys.*, **22**, 1610 (1954).

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Lewis Acid Enhancement of Photochemical Trans → Cis Isomerization of α,β-Unsaturated Esters[1]

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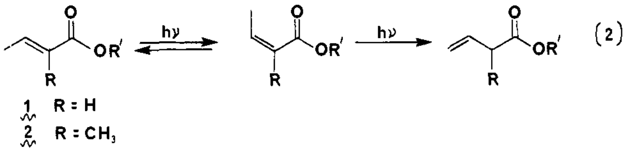
The photochemical cis–trans isomerization of alkenes has played a central role in the development of theoretical and mechanistic photochemistry.[2,3] Synthetic applications of this reaction[4] have been limited by its reversible nature, which, in the absence of other reactions, leads to a photostationary state mixture of isomers (eq 1). Photostationary states enriched in the thermodynamically

$$\frac{[\text{cis}]}{[\text{trans}]} = \frac{(\Phi_{t\to c})(\epsilon_t)}{(\Phi_{c\to t})(\epsilon_c)} \qquad (1)$$

less stable cis isomer can be obtained via direct irradiation if the trans isomer is more strongly absorbing than the cis isomer ($\epsilon_t > \epsilon_c$), as is the case for the stilbenes,[3] or via triplet sensitization if the triplet energy of the trans isomer is lower than that of the cis isomer, as is the case for β-ionol.[5] Unfortunately, neither direct nor triplet-sensitized irradiation provides a general method for the efficient conversion of trans to cis isomers. The use of various additives (protic acids,[6] copper salts,[7] metal carbonyls,[8] π acceptors,[9a] free radical precursors[9b]) and restricted environments[10] have also failed to yield cis-rich isomer mixtures. Cis–trans photoisomerization may be further complicated by competing reactions, such as the deconjugation of *cis*-crotonate (**1**) and angelate (**2**) esters (eq 2).[11] We wish to report that the irradiation of several α,β-unsaturated esters in the presence of Lewis acids leads to photostationary states enriched in the cis isomer, without substantial deconjugation in the case of esters **1** and **2**. The mechanistic basis for this novel and preparatively useful application of Lewis acids to organic photochemistry is an increase in both ϵ_t/ϵ_c and $\Phi_{t\to c}/\Phi_{c\to t}$ upon Lewis acid complexation of the α,β-unsaturated esters.



Irradiation of the trans α,β-unsaturated esters **1**–**7** in the absence of Lewis acids results in 5–49% optimum conversion to the cis isomers (conditions specified in Table I). A true photostationary state is obtained for esters **3**–**7** but not for esters **1** and **2** due to photochemical deconjugation as shown for ester **2** in Figure 1a. Irradiation of these esters in the presence of selected Lewis acids results in a substantial increase in the optimum conversion to the cis isomers and suppression of deconjugation,

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[1] Dedicated to George S. Hammond on the occasion of his 60th birthday.

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0002-7863/81/1503-7345$01.25/0

Table I. Optimum Conversion of Trans to Cis Isomers

	Lewis acid			
alkene	none	$BF_3\cdot OEt_2$[b]	$EtAlCl_2$[c]	$AlCl_3$[d]
methyl crotonate[a] (1)	42			76
ethyl tiglate[a] (2)	49	48	86	83
methyl cinnamate[b] (3)	46	88	88	87
ethyl cinnamate[b] (4)	42	81	85	87
tert-butyl cinnamate[b] (5)	42		85	86
methyl α-methylcinnamate[b] (6)	42		86	
methyl β-furylacrylate[c] (7)	5	94	92	

[a] Methylene chloride solutions 0.01 M in ester and Lewis acid irradiated in a Rayonet RPR-100 reactor with 254-nm lamps. [b] Benzene solutions 0.01 M in ester and 0.01 M in $BF_3\cdot OEt$ or $EtAlCl_2$ or 0.004 M in $AlCl_3$ irradiated with a Hanovia 450-W medium-pressure mercury lamp in a Pyrex cooling well. [c] Methylene chloride solutions irradiated in a Rayonet reactor with 350-nm lamps.

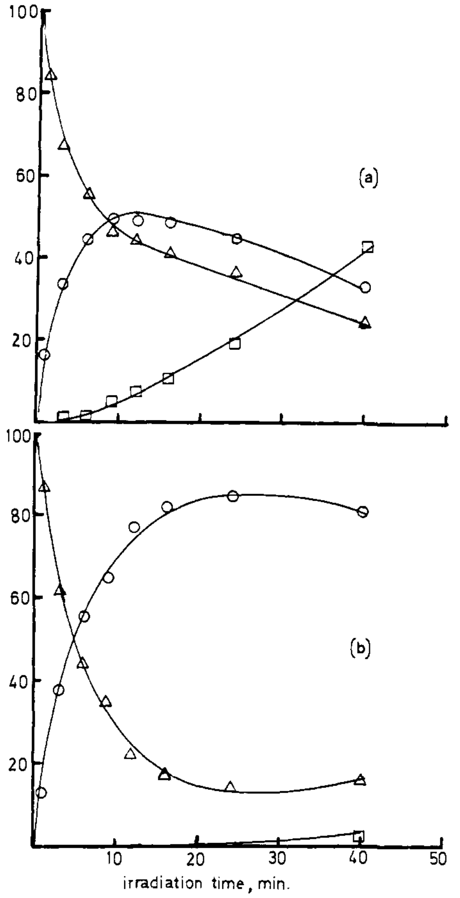

Figure 1. Conversion of ethyl tiglate (△) to ethyl angelate (○) and ethyl 2-methylbut-3-enoate (□) in the absence (a) and presence (b) of $EtAlCl_2$.

as shown for ester **2** in Figure 1b. The data reported in Table I are obtained by using standard commerical light sources. Even higher conversions to the cis isomer may be possible in some cases by using monochromatic light sources. In a typical preparative reaction, irradiation of 1.0 g of *trans*-**3** and 0.35 g of $AlCl_3$ in 0.5 L of benzene under nitrogen with a 450-W Hanovia medium-pressure mercury lamp in a Pyrex lamp well followed by flash column chromatography on silica gel (1% ethyl acetate–hexane) afforded 0.75 g of pure *cis*-**3**.

The ultraviolet absorption spectra of *trans*-**2** and *cis*-**2** with and without excess $EtAlCl_2$ are shown in Figure 2. A new long-wavelength maximum is observed for *trans*-**2** and a weaker shoulder for *cis*-**2** upon complexation. Reported in Table II are the observed 254-nm absorption data for this system and the 313-nm absorption data for the **3**–$BF_3\cdot OEt_2$ system along with the isomerization quantum yields determined by using monochromatic light. Values for the Lewis acid enhanced photostationary states calculated using eq 1 and the data in Table II for esters **2** (91% cis) and **3** (86% cis) are in good agreement with the experimental values (Table I).[12] No room temperature luminescence is observed for esters **1**–**7** either with or without added Lewis acid.

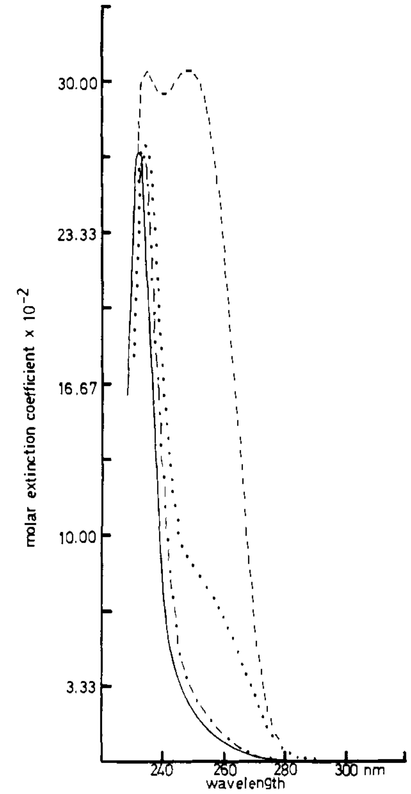

Figure 2. Absorption spectra of 6 × 10^{-4} M ethyl tiglate (—), with 1.2 × 10^{-3} M $EtAlCl_2$ (- - -) and ethyl angelate (-·-) with $EtAlCl_2$ (···).

Table II. Extinction Coefficients and Isomerization Quantum Yields

ester	e^a	$e_{comp}{}^b$	Φ^a	$\Phi_{comp}{}^b$
ethyl tiglate[c] (2)	200	2830	0.48	0.70
ethyl angelate[c]	225	808	0.19	0.25
trans-methyl cinnamate[d] (3)	408	1980	0.30	0.70
cis-methyl cinnamate[d] (3)	674	800	0.28	0.30

[a] Data for uncomplexed esters. [b] Data for Lewis acid complex. [c] Methylene chloride solutions, 254-nm excitation. [d] Benzene solutions, 313-nm excitation.

Lewis acid complexation of esters is known to involve the carbonyl oxygen.[13,14] Since deconjugation of esters **1** and **2** requires γ-hydrogen abstraction by the carbonyl oxygen of the cis isomer,[11] it is not surprising that Lewis acid complexation inhibits this reaction (Figure 1). The absence of any apparent steric effect on the results for esters **3**–**5** is also consistent with carbonyl oxygen complexation. We find $SnCl_4$ to be a somewhat less effective photoisomerization catalyst than $AlCl_3$, $ZnCl_2$ to be ineffective, and $TiCl_4$ to yield complex product mixtures. $BF_3\cdot OEt_2$ is an effective catalyst for ester **3**, but not for **2**. The more intense long-wavelength absorption of the trans vs. cis complexes (Figure 2, Table II) may reflect the different electronic structures of the planar trans vs. nonplanar cis isomer.[15]

From a mechanistic standpoint, the most striking result of the present investigation is the large increase in $\Phi_{t\rightarrow c}$ upon Lewis acid

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(12) The calculated photostationary state for **2** in the absence of Lewis acid (68% cis) is higher than the experimental value due to the occurrence of deconjugation.

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complexation (Table II). Isomerization via a common twisted intermediate (singlet or triplet) requires that $\Phi_{t\to c} + \Phi_{c\to t} = 1.0$,[3] as is the case in the presence, but not in the absence, of Lewis acids. Thus complexation serves to eliminate some energy wasting process. A singlet state mechanism has been proposed for the isomerization of ester **3** and cinnamic acid.[16] A small barrier to rotation might allow nonradiative decay to compete with bond rotation for singlet *trans*-**3** but not for *cis*-**3**. In support of this proposal we find that $\Phi_{t\to c}$ increases with increasing temperature, but $\Phi_{c\to t}$ does not. A decrease in the barrier to rotation upon Lewis acid complexation would thus be expected to increase $\Phi_{t\to c}$ but not $\Phi_{c\to t}$ as is experimentally observed. Other mechanisms for the effect of Lewis acids on isomerization quantum yields might also be envisioned (e.g., enhanced intersystem crossing, inversion of n,π* and π,π* state energies, sudden polarization, etc.).

As a preparative procedure, Lewis acid enhanced photoisomerization constitutes a substantial improvement in yield and convenience over previously published photochemical and nonphotochemical methods for the preparation of cis α,β-unsaturated esters.[17] In view of the importance of *cis*-crotonic and angelic acids as intermediates in organic synthesis,[18] we anticipate that this procedure will find widespread application. Preliminary results with α,β-unsaturated ketones and nitriles and with dienoic esters indicate that the scope of Lewis acid enhanced photoisomerization extends well beyond the examples here reported.[19]

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(19) Support of this work by the National Science Foundation (CHE-8026020) is gratefully acknowledged.

On the Formation of Aminyl vs. Aminoalkyl Radicals in the Photooxidation of Diethylamine†

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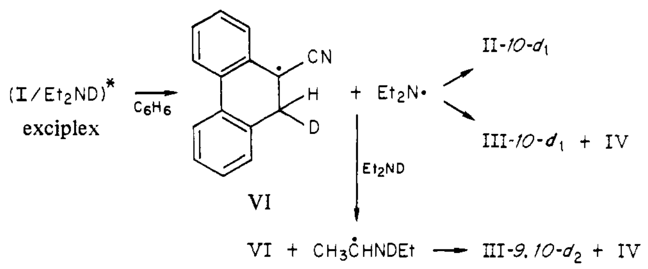
The abstraction of hydrogen atoms from amines in photochemical, free-radical, electrochemical, chemical, and enzymatic reactions continues to fascinate chemists.[2] One of the unsolved mysteries in this field is the reported ability of dialkylamines to form either dialkylaminyl or α-aminoalkyl radicals (eq 1).[3-9] In

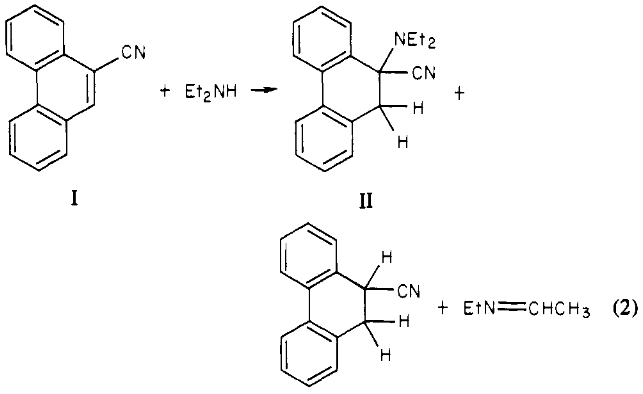
$$R_2CHNHR' \xrightarrow{-H\cdot} R_2CH\dot{N}R' \text{ or } R_2\dot{C}NHR' \qquad (1)$$

fact two recent reports from the same research institution present different conclusions as to which radical is formed upon reaction of *tert*-butoxy radicals with dialkylamines.[6,7] According to the most current thermochemical data, the α-C-H homolytic bond dissociation energy should be lower than the N-H energy for α-substituted dialkylamines (diethyl, diisopropyl, etc.) and similar to the N-H energy for dimethylamine.[10,11] We recently reported that the photochemical reaction of singlet stilbene with some tertiary amines occurs via a free-radical mechanism in nonpolar solvents and via an electron-transfer, proton-transfer mechanism in polar solvents.[12] We now report that the photochemical reaction of singlet 9-phenanthrenecarbonitrile (I) with diethylamine in nonpolar solvent yields the diethylaminyl radical exclusively, whereas reaction in polar solvent yields both diethylaminyl and 1-(ethylamino)ethyl radicals. Furthermore the conversion of aminyl to aminoalkyl radical is more rapid in polar than in nonpolar solvent. These results serve to further elucidate the mechanisms of photochemical and nonphotochemical reactions of dialkylamines.

Scheme I



Irradiation of I (0.01 M) and diethylamine (0.1 M) in nitrogen-purged benzene solution with a Pyrex-filtered medium-pressure mercury lamp results in essentially quantitative conversion to 9-(9-diethylamino-9,10-dihydro)phenanthrenecarbonitrile (II) and lesser amounts of 9-(9,10-dihydro)phenanthrenecarbonitrile (III) and *N*-ethylideneethylamine (IV) (eq 2). Chromatography (silica gel or GC) of the reaction mixture results in quantitative loss of HCN from adduct II to yield *N*,*N*-diethyl-9-phenanthrylamine (V). Irradiation of I and diethylamine in acetonitrile solution yields only III and IV. Stern-Volmer fluorescence quenching constants ($k_q\tau$) and quantum yields for formation of products II ($\Phi_{II} = \Phi_V$) and III are given in Table I. With use of literature values for the singlet lifetime of I (τ),[13] fluorescence quenching rate constants near the diffusion-controlled limit are calculated for both benzene and acetonitrile solution. In solvents of intermediate polarity (ethyl acetate-acetonitrile mixtures) Φ_{II} decreases continuously with increasing solvent polarity, while Φ_{III} displays a minimum value in ethyl acetate ($\epsilon = 6.0$) and increases in more polar solvents, attaining a value in acetonitrile comparable to that in benzene.



I II III

Crucial mechanistic evidence is provided by the results of irradiation of I with the deuterated amines Et$_2$ND and (CH$_3$C-

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† Dedicated to George S. Hammond on the occassion of his 60th birthday.

[1] Address correspondence to this author.

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