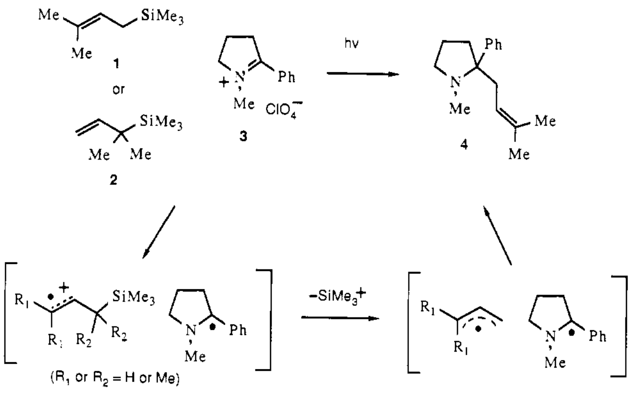
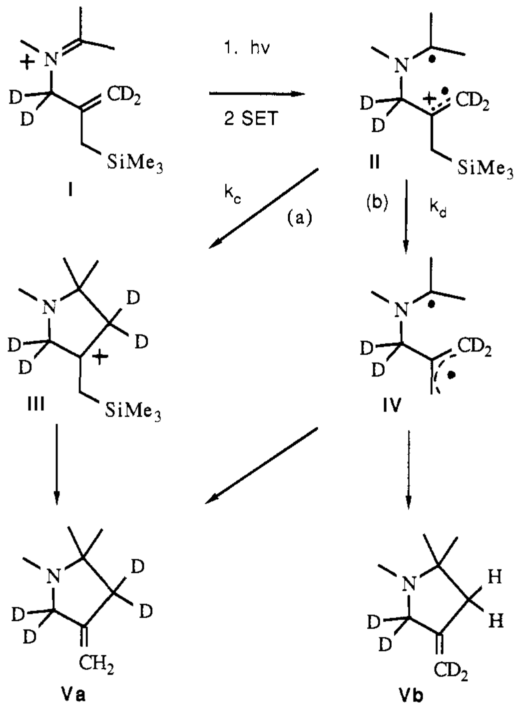
Scheme I



Scheme II



cyclohexenylideneiminium salts **11** and **12** might be a result of the diminished α-amino radical delocalization (stabilization), resulting in larger diradical cation cyclization rates. Furthermore, since cyclization of II^S results in production of more localized cation III^S, it should be facilitated by media which can support charge separation.[12] Thus, the small (**5** and **6**) to modest (**7**) increases in the k_c/k_d ratios in proceeding from MeCN to MeOH might be attributable to this phenomenon.[13]

Alternate explanations for the results presented above do exist. For example, desilylation of a conformationally fixed diradical cation II followed by rapid bond formation prior to rotational equilibration could also lead to product ratios favoring Va.[14] However, in this case it would be difficult to understand the observed substituent, structural, and solvent effects. Thus, while the results presented above are only preliminary, they suggest that allylsilaneiminium salt photocyclization reactions operate by two mechanisms which differ in the timing of C–Si bond cleavage and C–C bond formation.

Table I. Product Isotope Regioisomer Ratios from Irradiations of the Silylallyl Iminium Salts

iminium perchlorates (R = D)	irrdtn condtns	solvent	additives	isotope regioisomer Va:Vb ratios[d]	K_c/k_d[e]
5	direct	MeCN		1.48 ± 0.05	0.24
5	direct	MeOH		1.58 ± 0.05	0.29
5	sensit[b]	MeCN		0.97 ± 0.01	0
6	direct	MeCN		1.68 ± 0.12	0.34
6	direct	MeOH		1.87 ± 0.05	0.44
6	sensit[b]	MeCN		0.99 ± 0.01	0
7	direct	MeCN		2.54 ± 0.23	0.77
7	direct	MeCN	$(n\text{-Bu})_4NClO_4$[c]	2.65 ± 0.07	0.83
7	direct	MeOH		3.20 ± 0.19	1.10
7	direct	MeOH	$(n\text{-Bu})_4NF$[c]	3.06 ± 0.28	1.03
11[a]	direct	MeCN		4.31 ± 0.28	1.66
12[a]	direct	MeCN		7.54 ± 0.69	3.27

[a] See ref 14. [b] Xanthone. [c] Concentrations (0.1 M). [d] Errors obtained from statistical analysis of multiple observations. [e] Rate constant ratios based on mechanistic analysis of the Va:Vb ratios according to Scheme II.

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(11) (a) The rate of diradical cation cyclization should be increased by increases in the α-amino radical SOMO energy owing to its effect on lowering the SOMO (radical)–HOMO (radical cation) energy gap (ref 11b). The σ_p^+ values for H, F, and OMe (0, –0.07, and –0.78, respectively) should be a measure of the electron-donating ability of these substituents (ref 11c). (b) Giese, B. *Angew. Chem., Int. Ed.* Engl. **1983**, *22*, 753. (c) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958**, *80*, 4979.

(12) Cyclization causes movement of positive charge away from the perchlorate counter ion. Thus, rates should increase in solvents of higher Z or E_T value (83.6 and 55.5 for MeOH and 71.3 and 46.0 for MeCN, respectively).

(13) It is unlikely that the medium effects are due to changes in k_d, since MeOH should be a better silophile than MeCN. Also, the lack of a fluoride ion effect upon Va:Vb ratios is consistent with observations made earlier on cation radical desilylations (ref 1b). The lack of an ionic strength effect by addition of $(n\text{-Bu})_4NClO_4$ is surprising.

(14) We have attempted to gain information about this mechanistic alternative. The *E* and *Z* isomers of both **11** and **12** can be partially separated by silica gel chromatography and assigned configuration by NOE methods. We expected that the *E* and *Z* isomers of each would have different conformations in the silicon containing methally side chain. Thus, if conformations in diradical intermediates cause unequal coupling rates, different Va:Vb ratios would be expected from the *E* and *Z* isomers. However, these efforts have been confounded because **11** and **12** undergo *E*–*Z* photoisomerization with efficiencies comparable to those of photocyclization.

The Generation of Methylene from CH_2I_2 on Al Surfaces

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The formation and desorption of methylene from Al surfaces covered with CH_2I_2 ($\theta \leq 1$) was directly observed at ca. 170 K in an ultrahigh vacuum system ($\sim 10^{-10}$ Torr).

It is well known that methylene (CH_2:) is an important intermediate for various reactions, i.e., abstraction, addition, and insertion. The Simmons–Smith reaction for the formation of cyclopropane ring by means of the CH_2I_2/Zn reagent is a useful process, and methylene formation has been considered a fundamental reaction step. Furthermore, in heterogeneous catalysis, adsorbed CH_2 is regarded as one of the key species in many surface reactions.[1-3] Therefore, it is an interesting subject to study with surface analytical techniques.

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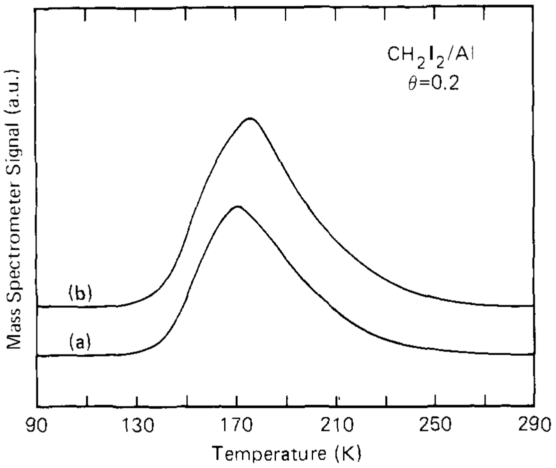

Figure 1. Thermal desorption spectra of CH_2 (a) and C_2H_4 (b) for CH_2I_2 adsorbed on Al at 90 K: $\theta = 0.2$ and heating rate about 30 K/s.

We have investigated the adsorption and decomposition behavior of CH_2I_2 on a clean Al surface at low temperatures. A polycrystalline Al disk (12-mm diameter) was cleaned by Ar^+ bombardment and annealed at 700 K. The sample was cooled down to about 90 K by LN_2 before being exposed to CH_2I_2. The surface cleanliness as well as the CH_2I_2 coverage (θ) was determined by X-ray photoemission spectroscopy (XPS). Here $\theta = 1$ means one monolayer of coverage of about 4×10^{14} molecules/cm^2. After the dosage of CH_2I_2, the sample was warmed up by a rf induction heating method.[4] The desorbed species were detected by a quadrupole mass spectrometer.

Figure 1 shows the thermal desorption spectra (TDS) of CH_2^+ (14 amu) and $C_2H_4^+$ (28 amu) at $\theta = 0.2$. The signals increased with the surface coverage. A trace of 42 amu species, probably due to C_3H_6, was also detected at ca. 170 K. In contrast, no desorption signals of I^+, CH_2I^+, and $CH_2I_2^+$ or species that can be attributed to C_2H_6 or CH_4 were observed at $\theta \leq 1$. When the coverage was increased to $\theta = 1.5$, CH_2I^+ desorption was detected at 210 K. This may be due to a different CH_2I_2 dissociation channel at a coverage slightly higher than a monolayer. At $\theta \geq 4$, the desorption of $CH_2I_2^+$ parent molecules was clearly observed at 260 K. The results suggest that at $\theta \leq 1$, CH_2I_2 dissociates on the Al surface with the increase of substrate temperature from 90 to 170 K. Apparently, CH_2 radicals are formed around 150–170 K and subsequently desorb as CH_2 and C_2H_4 species. The integrated intensity ratio of $CH_2^+/C_2H_4^+$ signals was 0.8 at $\theta = 0.2$, whereas the ratio of $CH_2^+/C_2H_4^+$ for pure C_2H_4 cracking in our mass spectrometer was 0.08. Thus, the major part of observed CH_2^+ signal should be attributed to methylene desorbed from the surface and not from the cracking of C_2H_4 in the mass spectrometer. A small but clear difference in the peak positions of TDS between CH_2^+ and $C_2H_4^+$ (Figure 1) also supports this conclusion. To our knowledge, this is the first direct observation of methylene desorption from a solid surface.

The XPS spectra of I($3d_{5/2}$) and C(1s) were taken before and after the thermal desorption. The result at $\theta = 1$ is shown in Figure 2. For I($3d_{5/2}$), the peak position shifted from 621.3 to 619.6 eV when the sample was heated from 90 to 300 K. The former corresponds to the iodine of associatively adsorbed CH_2I_2 and the latter to I^- species.[5] A small part of adsorbed CH_2I_2 may dissociate even at 90 K, because the peak is skew slightly toward the lower binding energy. The signal intensity after the thermal desorption was almost the same as before the treatment. This means that I^- remains on the surface after the molecular decomposition. When the sample was heated to 700 K, I($3d_{5/2}$) signal disappeared, probably due to the desorption of AlI_3 (boiling point = 645 K). For C(1s), the peak shifted from 286.2 eV, corresponding to the carbon in CH_2I_2, to ca. 283.5 eV after the thermal desorption up to 300 K. The intensity decreased to ca. 40% of the original value (see Figure 2). Thus, about 60% of adsorbed CH_2I_2 desorbed as methylene and ethylene by heating to room temperature. Judging from the C(1s) binding energy, the remaining carbon seems to exist as an adsorbed surface carbon[2] or as a carbide.

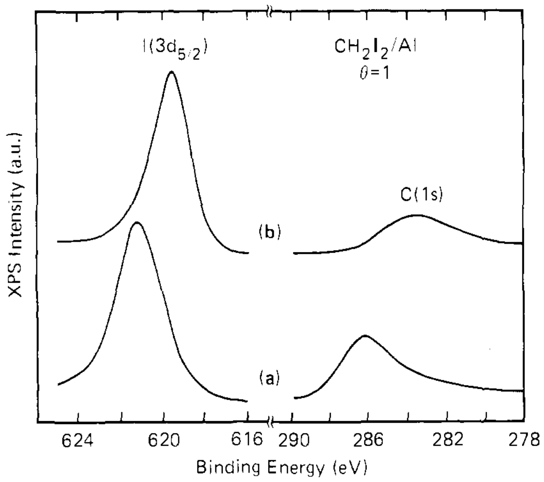

Figure 2. I($3d_{5/2}$) and C(1s) XPS spectra of a monolayer of CH_2I_2 adsorbed on Al at 90 K (a) and after heating to 300 K (b).

Intramolecular Radical Additions to the Azo Group. Fast and Indiscriminate 5-Exo and 6-Endo Cyclizations

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The utility of free radical cyclizations for the synthesis of ring systems has been demonstrated with many recent examples.[1] Most of the studies involved a carbon-centered radical, an olefinic or acetylenic multiple bond, and a product with one or more newly formed carbocyclic rings. Although radicals having a heteroatom at the radical site or between the radical site and the unsaturated group also cyclize, there are few examples of radical cyclizations that afford a heterocyclic ring by closure onto the heteroatom of

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[4] For details, see: Chuang, T. J.; Seki, H.; Hussla, I. *Surf. Sci.* **1985**, *158*, 525–552, and references therein.

[5] See: *Handbook of X-ray Photoelectron Spectroscopy*; Muilenberg, G. E., Ed.; Perkin-Elmer Corp.: Eden Prairie, MN, 1979; pp 124–125.

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