

Dual Diradical and Cation Diradical Cyclization Mechanisms for Silylalkenyl Iminium Salt. Electron-Transfer-Induced Photocyclization Reactions

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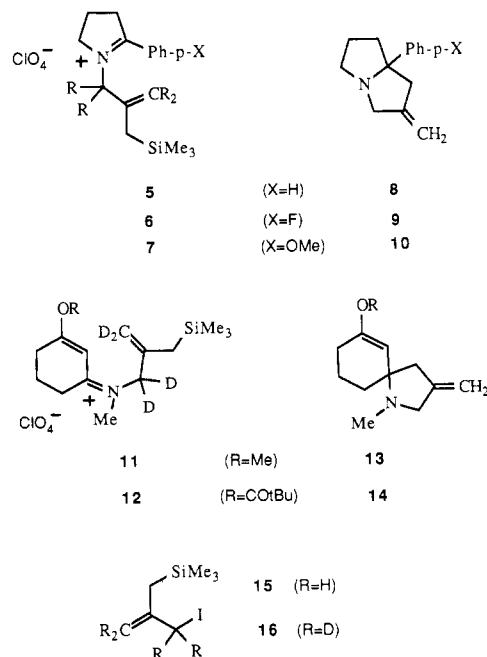
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Previously, we have described the electron-transfer induced, photoaddition reactions of allylsilane iminium salt systems¹ exemplified by the additions of the allylsilanes **1** and **2** to 2-phenyl-1-pyrrolinium perchlorate (**3**) to produce the 2-prenylpyrrolidine **4**. The regioselectivities of these processes led us to propose mechanisms in which desilylation of intermediate cation radical pairs is followed by radical coupling (Scheme I). Another route in which coupling occurs in the radical cation pair prior to desilylation was ruled out on the basis of the regioselectivity observed in the **1** + **3** reaction.

These observations led to the design of several synthetically useful² photocyclization reactions of silylallyl iminium salt systems (e.g., **I** in Scheme II). By analogy to the intermolecular systems, we suggested that the mechanisms for these intramolecular processes involve cyclization of diradical intermediates **IV** generated by desilylation of diradical cations **II** (path b, Scheme II). However, the possibility exists for facile carbon-carbon bond formation in diradical cations **II** (path a). Thus, two mechanisms differing in the timing of bond making and breaking appear possible for allylsilane iminium salt photocyclizations. In order to address this issue, a series of regiospecifically deuterated iminium salts with the isotope labeling pattern shown in **I** (Scheme II) were prepared. We anticipated that differentiation between the two pathways could be made based upon the isotope distribution in the methylenepyrrolidines **V** produced. Cyclization by path a should form the **Va** isotopomer exclusively while path b would produce a near³ equal mixture of isotopomers **Va** and **Vb**. The results summarized below suggest that both mechanisms are operable in the electron-transfer induced photoprocesses and that the contribution from each is dependent upon the iminium salt structure, substituents and excited-state multiplicity, and the reaction medium.

The *N*-(silylallyl)-1-pyrrolinium perchlorates (**5-7**, **R** = **H**) were prepared by AgClO₄ (MeCN) assisted allylations of the corresponding 1-pyrrolines⁴ with trimethylsilylmethyl iodide **15**.^{5,6} Photocyclizations of these substances, induced by direct irradiation in MeCN or MeOH, generated the corresponding pyrrolizidines **8-10** in 46-65% yields.⁷ Photocyclizations of **5** and **6** can be triplet sensitized. Irradiation of xanthone solutions (MeCN) of these salts led to production of **8** and **9** (ca. 47%), respectively.⁸ Also, *E,Z* mixtures of the cyclohexenylidene iminium salts **11** and **12** (**R** = **H**), as shown previously,^{2a} produced the spirocyclic amines **13** and **14** upon direct irradiation (MeCN).⁸



In order to delineate the mechanism for these cyclization processes, the tetradeuterio analogues **5-7**, **11**, and **12** (**R** = **D**) were prepared starting with the deuterated iodide **16** by alkylation procedures described above or earlier.^{2a} Irradiation (direct or xanthone sensitized for **5** and **6**) of these iminium-*d*₄ salts in MeCN or MeOH led to generation of regioisomeric mixtures (type **Va** and **Vb**, Scheme II) of the corresponding methylenepyrrolidine products.^{9c} The **Va** and **Vb** isomer ratios (Table I) were determined by ¹H NMR integration methods. To probe for possible ionic strength and silophile effects on the regioisomer ratios, direct irradiations of **7** were conducted on 0.1 M solutions of (*n*-Bu)₄NClO₄(MeCN) and (*n*-Bu)₄NF(MeOH) (Table I).

The results found appear consistent with the operation of the two mechanisms shown in Scheme II for the photocyclization processes. By this interpretation, the predominance of type **Va** over **Vb** isotopomers from the direct irradiations reflects the relative rates of cyclization (*k_c*) and desilylation (*k_d*) of the intermediate, singlet radical cations **II**^S. A number of observations are consistent with this view. The results of the triplet-sensitized reactions of **5** and **6** suggest that the predominance of the **Va** isomers in the direct reactions is not due to an inverse isotope effect on cyclization of diradicals related to **IV**. Thus, the near unit **Va**:**Vb** ratios obtained in these cases are in accord with routes in which a triplet cation diradicals **II**^T undergo exclusive desilylation to produce diradicals **IV**^T. Intersystem crossing transforms **IV**^T to **IV**^S which then cyclizes with near equal rates at both allyl radical termini.¹⁰ Cyclization of **II**^T is prohibited by the high-energy pathway which would be required to generate the triplet, β-silyl cation **III**^T.

The variations in **Va**:**Vb** ratios with substituents, structures, and solvents are consistent with a duality in mechanism. For example, the increase seen in the **Va**:**Vb** ratio with changes in the *p*-substituent from **H** or **F** to **OMe** parallel the expected effects of α-pyrrolidinyl radical nucleophilicity (increase in SOMO energy with EDG substitution) on the rates of singlet diradical cation cyclization.¹¹ The much larger *k_c*/*k_d* ratios observed for the

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(2) (a) Ullrich, J. W.; Chiu, F. T.; Tiner-Harding, T.; Mariano, P. S. *J. Org. Chem.* **1984**, *49*, 220. (b) Chiu, F. T.; Ullrich, J. W.; Mariano, P. S. *J. Org. Chem.* **1984**, *49*, 228. (c) Ahmed-Schofield, R.; Mariano, P. S. *J. Org. Chem.* **1985**, *50*, 5667.

(3) An inverse isotope effect would perhaps lead to greater amounts of **Va** (ref 10).

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(6) All new compounds reported had spectroscopic and analytical data which match those expected.

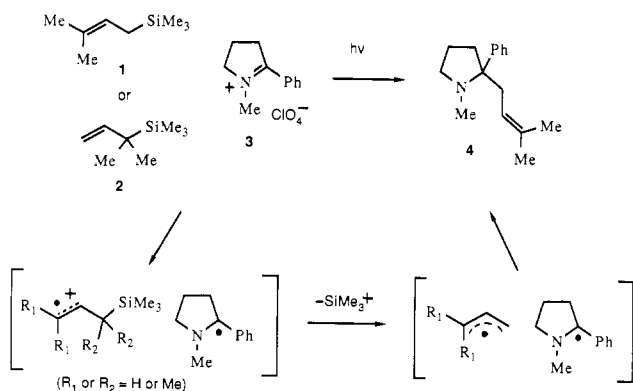
(7) Filtered-light (Corex, λ > 250 nm, for **5** and **6** and Flint, λ > 310 nm, for **7**) was used.

(8) (a) The iminium salts **7**, **11**, and **12** do not undergo triplet-sensitized photocyclization with xanthone. *E,Z* Isomerization about the C=N bond occurs with **11** and **12** (ref 8b for precedent). The salt **7** is recovered unchanged, suggesting either that energy transfer does not occur or that the triplet of **7** is inert. (b) Childs, R. F.; Dickie, B. *J. Chem. Soc., Chem. Commun.* **1981**, 1268.

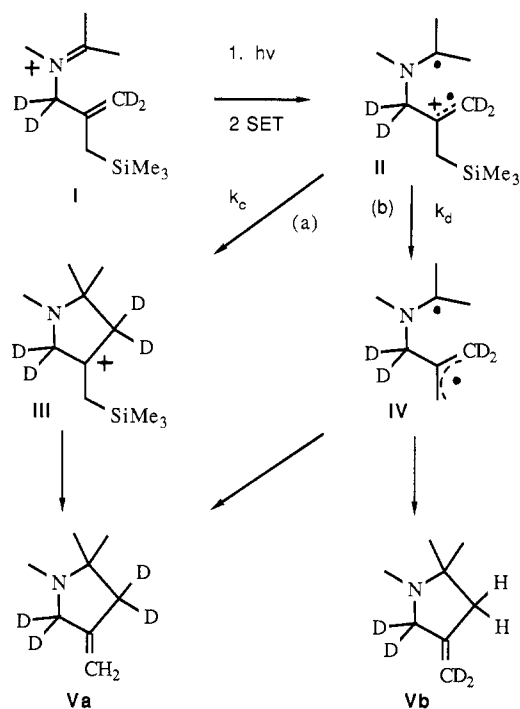
(9) (a) This substance was prepared by LiAlD₄ reduction of the diethyl trimethylsilylmethylmalonate by known procedures (ref 9b) followed by mesylate formation and iodide substitution (ref 5). (b) Knapp, S.; O'Connor, U.; Mobilio, D. *Tetrahedron Lett.* **1980**, *21*, 4557. (c) Starting pyrrolinium salt **6-d**₄ recovered from low conversion photolysates was shown to retain completely the original deuterium distribution, thus indicating that isotope scrambling is not occurring under the reaction conditions.

(10) (a) It is difficult to predict the magnitude of the isotope effect for this diradical coupling process. Crawford (ref 10b) has reported results which suggest that no isotope effect exists for 1,1-dideuterioallyl radical coupling processes. (b) Al-Sader, B. H.; Crawford, R. J. *Can. J. Chem.* **1970**, *48*, 2745.

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

(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 $(n\text{-Bu})_4\text{NClO}_4$ is surprising.

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

iminium perchlorates (R = D)	irradiation conditions	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	$(n\text{-Bu})_4\text{NClO}_4$ ^c	2.65 ± 0.07	0.83
7	direct	MeOH		3.20 ± 0.19	1.10
7	direct	MeOH	$(n\text{-Bu})_4\text{NF}$ ^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.

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.

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(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 methallyl 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 $\text{CH}_2\text{I}_2/\text{Zn}$ 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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