amorphous polymer electrolytes.[4,12,13]

The conductivity of a polymer electrolyte, as given by a configuration entropy model, follows eq 2, where the A term is

$$\sigma = AT^{-1/2} \exp(-B/(T - T_0)) \qquad (2)$$

proportional to the number of charge carriers, and the T_0 term, in the exponential, is closely related to the glass transition of the sample.[4,13] The conductivity of $(AgSO_3CF_3)_x$·MEEP complexes increased with increasing salt concentration as expected ($0 < x < 0.17$), however, further increases in salt concentration resulted in diminished conductivities (Figure 2). The progressive immobilization of polymer chains resulting in restricted segmental motion of the polymer and increased rigidity would account for the rising T_g values and decreasing conductivities observed.[12-14]

Complexes of poly(ethylene oxide), and $LiSO_3CF_3$ or $LiClO_4$ (0.125:1), are useful battery electrolytes above 100 °C.[15-17] Between room temperature and 100 °C, the conductivity of $(LiSO_3CF_3)_{0.25}$·MEEP is 1-3 orders of magnitude larger than that of the poly(ethylene oxide) systems. Thus in contrast with the poly ether-based electrolytes the new polyphosphazene electrolyte is a good candidate for a room-temperature thin-film battery. Concentration dependence of the ion mobility and T_g for the new phosphazene electrolytes substantiate current models for the influence of charge carrier concentration and fluididity on the ion transport in solvent-free polymer-salt complexes.

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A Novel Method for Heteroatom-Substituted Free Radical Generation by Photochemical Electron-Transfer-Induced Desilylation of $RXCH_2Me_3Si$ Systems

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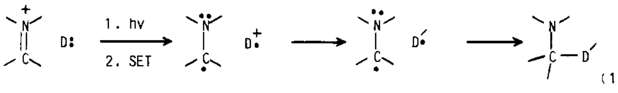
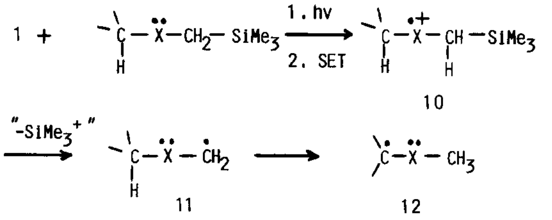
Our recent investigations in the area of electron-transfer photochemistry have led to the development of preparatively useful photoaddition and -cyclization reactions initiated by electron transfer from donors to iminium salt systems.[2] In general, the key, product-nature-determining step in the mechanistic pathways followed in these processes involves conversion of initially formed, cation radical pair or diradical intermediates to neutral, radical precursors of products (eq 1).

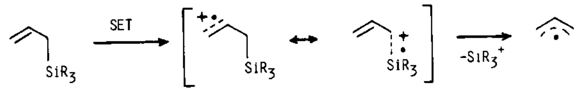


(1)

Scheme I



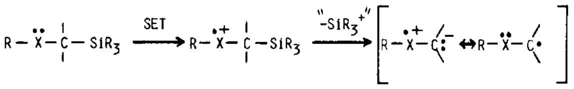
The charge-neutralizing, secondary transformations of the cation radical species include addition of nucleophiles and loss of electrofugal groups from sites adjacent to the positively charged centers.[3] The actual routes selected appear to be governed by the nature of the cation radical species, the types of electrofugal groups present in the systems, and the solvent. More recent efforts have focused on excited-state reactions of this type activated by cation radical desilylation. Examples in which allylsilane-derived cation radicals are converted to allyl radical counterparts by loss of trialkylsilyl fragments have been described (eq 2).[4]



(2)

Owing to the large rate of cation radical desilylation relative to nucleophilic addition or α-deprotonation,[5] pathways involving sequential electron transfer–desilylation serve as useful methods for site-selective radical generation.

This proposal has been successfully tested recently in explorations targeted at the development of regioselective methods for heteroatom-substituted radical generation. We envisaged that cation radicals arising from (trialkylsilyl)methyl ether, sulfide, or amine precursors would undergo rapid, nucleophile-assisted loss of the trialkylsilyl fragment to selectively generate α-alkoxy-, α-alkylthio-, or amino-substituted carbon radicals (eq 3).



(3)

The facility of this process would be a result of the good overlap existing between the filled $\sigma_{C\text{-}Si}$ MO and half vacant heteroatom sp^3 AO, and the propensity for nucleophilic attack on silicon of β-silyl cations.[6] Moreover, this method for heteroatom-substituted radical formation would be superior to the more common photochemically induced, sequential electron-transfer–deprotonation route observed for a number of amine[7] and ether[2c] systems since the site of radical generation can be controlled by preselected placement of the trialkylsilyl grouping at the proper α-position. The results of our preliminary investigations concentrating on the photochemistry of 2-phenyl-1-pyrrolinium and quinolinium salt systems demonstrate that this pathway serves as a mild, regioselective method for radical generation.

Calculations[8] based upon the known singlet-excited-state reduction potential of 2-phenyl-1-pyrrolinium perchlorate (**1**) ($E_{1/2}^{S1}(-) = +2.9$ V)[2d] and the estimated oxidation potentials of

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(1) Current address: Department of Chemistry, College of National Sciences, Busan National University, Busan, Korea 607.

(2) (a) Stavinoha, J. L.; Mariano, P. S. *J. Am. Chem. Soc.* **1981**, *103*, 3136. (b) Stavinoha, J. L.; Mariano, P. S.; Leone-Bay, A.; Swanson, R.; Bracken, C. *J. Am. Chem. Soc.* **1981**, *103*, 3148. (c) Mariano, P. S.; Stavinoha, J. L.; Bay, E. *Tetrahedron* **1981**, *37*, 3385. (d) Mariano, P. S. *Acc. Chem. Res.* **1983**, *16*, 130. (e) Mariano, P. S. *Tetrahedron* **1983**, *39*, 3845.

(3) Information about the chemistry of radical cation species can be derived by inspection of mass spectrometric fragmentation and electrochemical processes.

(4) (a) Ohga, K.; Yoon, U. C.; Mariano, P. S. *J. Org. Chem.* **1984**, *49*, 213. (b) Ullrich, J. W.; Chiu, F. T.; Harding, T.; Mariano, P. S. *J. Org. Chem.* **1984**, *49*, 220. (c) Chiu, F. T.; Ullrich, J. W.; Mariano, P. S. *ibid.* **1984**, *49*, 228. (d) Chen, S. F.; Ullrich, J. W.; Mariano, P. S. *J. Am. Chem. Soc.* **1983**, *105*, 6160.

(5) (a) Recent results[5b] indicate that the desilylation rate is >7-fold larger than the rate of deprotonation from analogous benzyl cation radicals. (b) Quillen, S. L.; Lan, A.; Mariano, P. S., unpublished results.

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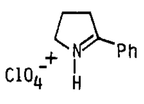
(8) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

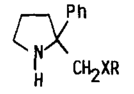
the (trimethylsilyl)methyl ethers **2** and **3** and thioether **4** ($E_{1/2}(+)$ < +1.9 V)[2c,9] suggest that these donor–acceptor pairs should participate in efficient electron-transfer processes. Indeed, the ethers **2–4** are quenchers of pyrrolinium salt **1** fluorescence with quenching rate constants approaching the diffusion-controlled limit (ca. (1–3) × 10^9 M^{-1} s^{-1} in MeCN at 25 °C). As expected, sequential electron transfer–desilylation in these systems is competitive with the quenching mode involving reversible electron transfer and results in generation of photoaddition products. Thus, irradiation[10] of MeCN solutions of **1** (0.04 M) in the presence of ethers **2–4** (0.11 M) followed by base workup and purification by chromatographic methods leads to isolation of the photoadducts **5–7** (20–35%) along with the bipyrrolidine **8** (9–39%).[11] Assignment of product structures is aided by comparisons of characteristic spectroscopic data[12] for these substances with those of closely related materials.[2c] Careful analysis of the product mixtures in each case failed to reveal the presence of regioisomeric adducts, which could have arisen through isomerization of the initially formed primary radicals **11** to thermodynamically more stable secondary or tertiary counterparts **12**[13] or of silicon-containing photoadducts arising by deprotonation of the cation radical intermediates **10** (Scheme I). Finally, the superiority of the regiocontrol offered by the desilylation route for electron-transfer-promoted radical production is exemplified by the comparative results of reactions of the salt **1** with the silylmethyl-substituted ether **3** and methyl isopropyl ether. In the latter case, photoaddition (MeCN) occurs to generate an ca. 2:1 ratio of the adducts **6** and **9** arising by nonselective radical cation deprotonation and resulting in insertion of the pyrrolidinyl unit into the respective primary and tertiary α-CH bonds.[14]



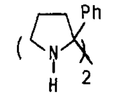
1

R—X—CH$_2$—SiMe$_3$

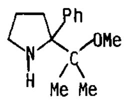
2 (XR = OEt)
3 (XR = O-iPr)
4 (XR = SEt)



5 (XR = OEt)
6 (XR = O-iPr)
7 (XR = SEt)

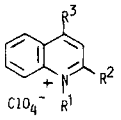


8

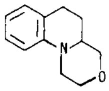


9

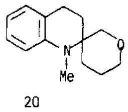
Further investigations with the ([(trimethylsilyl)methoxy]alkyl)quinolinium perchlorates **13–15** demonstrate that sequential electron transfer–desilylation serves as a useful route for diradical generation as part of methods for heterocycle ring construction. The salts employed in this study were prepared by either N- or C-alkylation of the corresponding quinolines with the appropriate [(trimethylsilyl)methoxy]alkyl iodide or mesylate followed by N-methylation (for **14** and **15**) and perchlorate ion exchange. The greatly diminished fluorescence quantum yields for **13–15** vs. the methyl analogues **16–18**[15] suggests that intramolecular electron transfer occurs efficiently in the singlet excited states of the silicon-containing salts. Irradiation of MeCN solutions of **13–15**[10a] followed immediately by hydrogenation (PtO$_2$), base workup, and silica gel chromatography leads to isolation of the respective cyclized products **19–21** in yields ranging from 41% to 61%.[12] The reduction step is required in the workup procedure in order to convert the initially formed dihydroquinolines into the more stable, isolated tetrahydroquinoline ring containing products.[16]



13 (R^1=(CH$_2$)$_2$OCH$_2$TMS, R^2=R^3=H)
14 (R^1=Me, R^2=(CH$_2$)$_3$CH$_2$TMS, R^3=H)
15 (R^1=Me, R^2=H, R^3=(CH$_2$)$_3$CH$_2$TMS)
16 (R^1=Me, R^2=R^3=H)
17 (R^1=R^2=Me, R^3=H)
18 (R^1=R^3=Me, R^2=H)



19



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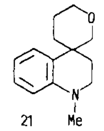

21

The results presented above show that routes mediated by photoinduced, sequential electron transfer–desilylation serve as unique methods for regiocontrolled production of heteroatom-substituted carbon radicals. Continuing efforts are designed to explore the generality of the process and, in particular, to determine if electron-transfer-sensitized reactions of (trialkylsilyl)methyl ether and amine systems are useful for radical generation in a variety of synthetic applications.[17]

Acknowledgment. Support for these studies by NSF (CHE-08240) and NIH (GM-27251) is acknowledged. The Korean Science and Engineering Foundation provided partial funding for a portion of the studies conducted by U.C.Y. The expert technical assistance offered by Susan M. Hanley is appreciated.

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[9] The ether and thioether systems were prepared by alkylation of the corresponding alcohol or thiol anions with (trimethylsilyl)methyl iodide.

[10] (a) Irradiations were conducted in a preparative apparatus with a Corex (for **1**) or Flint (for **13–15**) glass filter on ca. 300–600-mg scale. (b) The conditions used for reaction of **1** with ethers **2–4** favored singlet-state electron transfer.

[11] (a) This substance has been previously synthesized.[11b] It should be noted that the yields reported for the photoadduts and bipyrrolidine are for materials isolated by preparative GLC. Under these conditions both the photoadducts and bipyrrolidine undergo slight decomposition to generate 2-phenyl-1-pyrroline, the only other substance isolated in varying quantities from these processes. (b) Hornback, J. M.; Proehl, G. S.; Starner, I. J. *J. Org. Chem.* **1975**, *40*, 1077. Coupling products RXCH$_2$CH$_2$XR have not been looked for.

[12] All new compounds have correct elemental compositions as well as mass spectrometric, UV, IR, ^{1}H NMR, and ^{13}C NMR data in full agreement with the assigned structures.

[13] (a) Recently, Peters[13b] has observed isomerization of a primary α-amino radical to a more stable, conjugated counterpart. (b) Manring, L. E.; Peters, K. S. *J. Am. Chem. Soc.* **1983**, *105*, 5108.

[14] (a) The selectivity here for deprotonation at the primary over the tertiary position is similar to that observed for amine radical cations.[14b] (b) Lewis, F. D.; Ho, T. I. *J. Am. Chem. Soc.* **1980**, *102*, 1751.

[15] The fluorescence quantum yields in MeCN at 25 °C: **13**, 0.004; **14**, 0.027; **15**, 0.021; **16**, 0.85; **17**, 0.36; **18**, 0.60.

[16] Yoon, U. C.; Quillen, S. L.; Mariano, P. S.; Swanson, R.; Stavinoha, J. L.; Bay, E. *J. Am. Chem. Soc.* **1983**, *105*, 1204.

[17] (a) Radical-mediated cyclization reactions are becoming of increasing importance as synthetic methods.[17b] (b) See, for example: Stork, G.; Baine, N. H. *J. Am. Chem. Soc.* **1982**, *104*, 2321. Hart, D. J.; Tsai, Y. M. *J. Am. Chem. Soc.* **1982**, *104*, 1430.

Sonochemical Activation of Transition Metals

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The activation of transition metals remains an important goal and continues to engender major efforts in heterogeneous catalysis,[1] metal-vapor chemistry,[2] and synthetic organometallic efforts.[3] We wish to report that the use of high-intensity ultrasound dramatically enhances the reactivity of transition-metal dispersions. Ultrasound ameliorates the condition necessary for the preparation of early-transition-metal carbonyl anions, and we believe that the technique has general ramifications.

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[1] Poncelet, G., Grange, P., Jacobs, P. A., Eds. "Preparation of Catalysts"; Elsevier: New York, 1983; Vol. III.

[2] Blackborow, J. R.; Young, D. "Metal Vapour Synthesis in Organometallic Chemistry"; Springer-Verlag: New York, 1979.

[3] (a) Calderazzo, F.; Englert, U.; Pampaloni, G.; Pelizzi, G.; Zamboni, R. *Inorg. Chem.* **1983**, *22*, 1865–1890. (b) Dewey, C. G.; Ellis, J. E.; Fjare, K. L.; Pfahl, K. M.; Warnock, G. F. P. *Organometallics* **1983**, *2*, 388–391. (c) Rieke, R. D.; Ofele, K.; Fischer, E. O. *J. Organomet. Chem.* **1974**, *76*, C19–C21. (d) Rieke, R. C. *Acc. Chem. Res.* **1977**, *10*, 301–306. (e) Rochfort, G. L.; Rieke, R. D. *Inorg. Chem.* **1984**, *23*, 787–789.