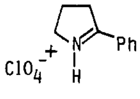
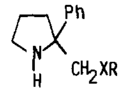
the (trimethylsilyl)methyl ethers **2** and **3** and thioether **4** ($E_{1/2}(+) < +1.9$ V)[2c,9] suggest that these donor–acceptor pairs should participate in efficient electron-transfer processes. Indeed, the ethers **2–4** are quenchers of pyrrolinium salt **1** fluorescence with quenching rate 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]



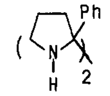
1

R— X— CH_2— SiMe$_3$

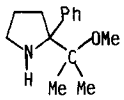
2 (XR = OEt)
3 (XR = O-iPr)
4 (XR = SEt)



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

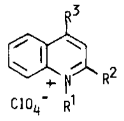


8

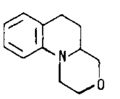


9

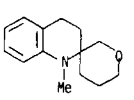
Further investigations with the ([(trimethylsilyl)methoxy]alkyl)quinolinium perchlorates **13–15** demonstrate that sequential electron transfer–desilylation serves as a useful route for diradical generation as part of methods for heterocycle ring construction. The salts employed in this study were prepared 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]



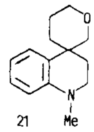
13 (R^1=$(CH_2)_2OCH_2TMS$, R^2=R^3=H)
14 (R^1=Me, R^2=$(CH_2)_3CH_2TMS$, R^3=H)
15 (R^1=Me, R^2=H, R^3=$(CH_2)_3CH_2TMS$)
16 (R^1=Me, R^2=R^3=H)
17 (R^1=R^2=Me, R^3=H)
18 (R^1=R^3=Me, R^2=H)



19



20



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 $RXCH_2CH_2XR$ have not been looked for.

[12] All new compounds have correct elemental compositions as well as mass spectrometric, UV, IR, ^1H 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.

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[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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Table I. Sonochemical Synthesis[a] of Transition-Metal Carbonyl Anions

		obsd yields[b]	
		4.4 atm of CO	1 atm of CO
$W_2(CO)_{10}^{2-}$	from WCl_6	47%	40%
$Mo_2(CO)_{10}^{2-}$	from $MoCl_5$	54%	39%
$Cr_2(CO)_{10}^{2-}$	from $CrCl_3$	7%	3%
$Ta(CO)_6^-$	from $TaCl_5$[c]	6%	
$Nb(CO)_6^-$	from $NbCl_5$	51%	23%
$V(CO)_6^-$	from VCl_3	8%	
$V(CO)_6^-$	from $VCl_3(THF)_3$	35%	23%

[a] Conditions ~20% excess Na, 0.033 M metal halide in THF, 10 °C, 1000-min sonication, ~100 W/cm^2 at 20 KHz. [b] Yields based on metal halide were calculated spectrophotometrically.[12] Control reactions run at the same temperature and pressures but for 1500 min yielded *no* detectable metal carbonyl products, i.e., <0.1% yield. [c] The reaction of $TaCl_5$ was carried out in diglyme. In THF there was no apparent conversion.

The effects of ultrasound in heterogeneous systems come principally from microstreaming[4] and from acoustic cavitation[5] at the surface. The former creates local turbulent flow and thus can induce significant improvements in mass transport between solution and surface. The latter produces the impingement of a supersonic "microjet" of solvent upon the surface, thus creating surface erosion and pitting. These phenomenon are largely responsible for ultrasonic cleaning.[6] In the presence of *reactive* metals such as Zn, Mg, or Li, this pitting action exposes a freshened surface which has proven beneficial in a number of organic syntheses.[7] Other solid reagents have exhibited enhanced reactivity through the use of ultrasound,[8] as have a variety of homogeneous organometallic systems.[9] In order to prove the potential generality of ultrasonic activation of heterogeneous reactions, we have examined the reactivity of early transition metals with carbon monoxide during sonication. These systems were chosen *because of* their very low reactivity, in direct contrast to previous work with reactive metals.

Transition-metal carbonyl complexes continue to play a major role in organometallic chemistry because of their diverse chemistry and their importance as stoichiometric and catalytic synthetic reagents.[10] Nonetheless, their preparation from the bulk metal remains difficult, and high pressures of CO and high temperatures traditionally have been required to achieve adequate yields.[10b,11] While some recent developments have reduced the pressure and temperature requirements,[3a,b] these syntheses involve case by case recipes which have not proved to be interchangeable with other transition metals. The preparation of "activated", transition-metal dispersions, as investigated by Rieke,[3c–e] might appear to be one general method for carbonyl or carbonyl anion syntheses. These activated metals nevertheless require "bomb" conditions (100–300 atm of CO, 100–300 °C) to synthesize transition-metal carbonyls. We have found that the use of ultrasonic irradiation facilitates the reduction of a variety of transition-metal salts to an active form that will react *with low pressures* of CO to form the simple carbonyl anions.

In a typical reaction 1 mmol of transition-metal halide was dissolved in 30 ml of THF (tetrahydrofuran) and an excess of sodium sand was added. The mixture was flushed with CO and then maintained under CO during sonication. The system was thermostated so that the maximum temperature reached during ultrasonic irradiation was 10 °C; sonications were carried out for 1000 min.[12a] This procedure works for a wide range of soluble metal halides. Most noteworthy, however, are the results shown in Table I for the synthesis of early transition-metal carbonyl anions, which are notoriously difficult to prepare. Solubility of the metal halide is important: low yields are observed for the sparingly soluble VCl_3 or $TaCl_5$ in THF compared to the soluble systems of $VCl_3(THF)_3$ in THF or $TaCl_5$ in diglyme. In all cases the yields are at least comparable to other methods requiring elevated temperatures and pressures of CO.

Reductions under ultrasonic irradiation of the halide salts of Mn, Fe, and Ni were also carried out. The species $Mn(CO)_5^-$, $Fe(CO)_4^{2-}$, $Fe_2(CO)_8^{2-}$, and $Ni_6(CO)_{12}^{2-}$ were observed as products of their respective systems through infrared spectroscopy.[13] The manganese and iron reactions are quite efficient, while the nickel cluster is formed in small yield. Owing to the increased sensitivity of the manganese and iron compounds, the quantification of these reactions is difficult.

The use of ultrasound has dramatically reduced the temperature and pressure requirements for these reactions. For example, our preparation of $V(CO)_6^-$ requires pressures of 4.4 atm and 10 °C as opposed to the usual conditions[10b,11] of 200 atm and 160 °C. It might also be noted that our reported yields, comparable to those using the standard method, were obtained without the use of the $Fe(CO)_5$ catalyst called for in the earlier preparation. Even at 1 atm of CO, yields of the carbonyl anions remain significant using sonochemical conditions (see Table I). An interesting comparison to the recent work by Calderazzo and Ellis shows that, while using different approaches for the preparation of $Nb(CO)_6^-$ and $Ta(CO)_6^-$, neither method works for the synthesis of $V(CO)_6^-$. In our worst case, the formation of $Ta(CO)_6^-$, the yields based on $TaCl_5$ are poor but comparable to those from the other available

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methods; this limitation probably reflects the low solubility of $TaCl_5$.

The possible mechanisms of this ultrasonic activation include (1) the creation of extremely reactive, high dispersions of transition metal on NaCl matrix, (2) improved mass transport between bulk solution and the reactive surfaces, and (3) direct trapping with CO of reactive metallic species formed during the reduction of the metal halide. We can eliminate the first and second mechanism: complete reduction of metal halide by Na with ultrasonic irradiation *under Ar*, followed by exposure to 4.4 atm of CO in the absence or presence of ultrasound, yielded no metal carbonyl. In the case of WCl_6, Fourier transform infrared spectra taken during sonication under CO show the initial formation of tungsten carbonyl halides followed by their conversion to $W(CO)_6$ and finally its further reduction to $W_2(CO)_{10}^{2-}$. Thus the reduction process appears to be sequential, wherein reactive metal species are formed upon partial reduction at the sodium surface and trapped by CO.

These reaction conditions have been run at small scale and may prove uniquely useful, for example, in the production of ^{13}CO labeled carbonyl complexes where the low CO pressures are mandatory. Scale-up of ultrasonic irradiation is, however, extant technology used industrially, e.g., for the production of emulsions.[14] Thus the use of ultrasound in chemical synthesis may well develop an important niche in the chemical community.

Acknowledgment. This research was supported by grants from the National Science Foundation (CHE8319929) and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. $W_2(CO)_{10}^{2-}$, 45264-18-4; $Mo_2(CO)_{10}^{2-}$, 45264-14-0; $Cr_2(CO)_{10}^{2-}$, 45264-01-5; $Ta(CO)_6^-$, 45047-35-6; $Nb(CO)_6^-$, 45046-84-2; $V(CO)_6^-$, 20644-87-5; $Mn(CO)_5^-$, 14971-26-7; $Fe(CO)_4^{2-}$, 22321-35-3; $Fe_2(CO)_8^{2-}$, 58281-28-0; $Ni_6(CO)_{12}^{2-}$, 52261-68-4; WCl_6, 13283-01-7; $MoCl_5$, 10241-05-1; $CrCl_3$, 10025-73-7; $TaCl_5$, 7721-01-9; $NbCl_5$, 10026-12-7; VCl_3, 7718-98-1; $VCl_3(THF)_3$, 19559-06-9; CO, 630-08-0; Na, 7440-23-5.

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Distance Dependence of Electron-Transfer Reactions: Rate Maxima and Rapid Rates at Large Reactant Separations

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Early in the history of electron-transfer studies it was pointed out that bimolecular electron transfer can occur over a range of reactant separations.[1] However, the values of certain parameters needed for rate calculations have only recently been determined. Specifically, an increasing amount of experimental data on the distance dependence of the electronic coupling element[2,3] and on the nuclear configuration changes accompanying electron transfer have become available.[4] Important advances in the formulation of the electron-transfer problem have also been made.[5-9] Recently we have undertaken detailed calculations of the distance dependence of the rates of electron-transfer reactions in solution. We find that the dependences of the electronic coupling element and of the solvent reorganization energy on distance have important implications for intramolecular electron transfers and for the forward and back reaction rates and cage-escape yields in light-induced electron-transfer processes.

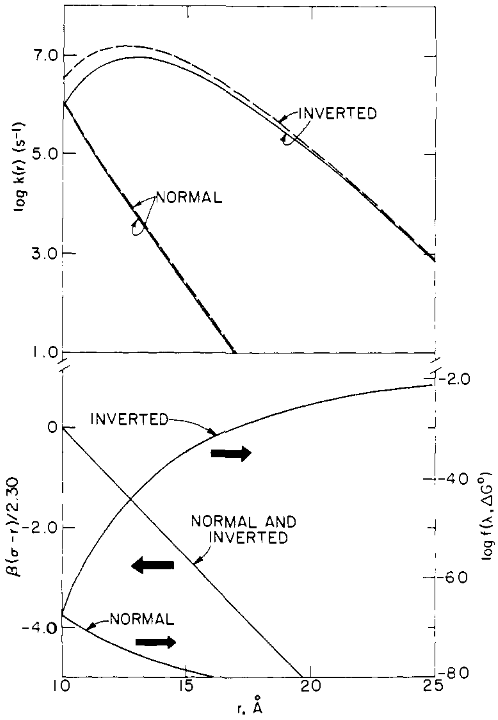

Figure 1. Distance dependence of the first-order rate constant $k(r)$ in the normal and inverted regions, calculated from eq 2-4 using $\beta = 1.2$ Å^{-1}, $H_{AB}° = 200$ cal, $\lambda_{in} = 1.92$ kcal mol^{-1} and $\sigma = 10$ Å. Upper figure: normal region, $\Delta G° = +0.25$ eV; inverted region, $\Delta G° = -2.00$ eV; solid line, classical calculation; dashed line, quantum-mechanical calculation[6] with $\nu_{in} = 450$ cm^{-1}. Lower figure: the distance dependence of the components of $k(r)$; $f(\lambda,\Delta G°) = (1/\lambda^{1/2}) \exp[-(\lambda + \Delta G°)^2/(4\lambda RT)]$.

Since bimolecular electron transfer can occur over a range of separation distances, each with a unique first-order rate constant $k(r)$, the net second-order rate constant for the reaction is given by[1,5]

$$k_{obsd} = \frac{4\pi N}{1000} \int_0^\infty g(r)k(r)r^2 \, dr \quad M^{-1} s^{-1} \tag{1}$$

where r is the distance between the two redox sites, and $g(r)$ is the pair distribution function. For spherical reactants r is the center-to-center distance and it is generally assumed that $g(r) =$

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