Triplet Quenching by Cyclohexadiene. Seven THF solutions (5 mL) of 1-NpOH (0.030 M) and NND (0.030 M) containing varied concentrations of cyclohexadiene (CHDE, 0–0.009 M) were degassed and irradiated on a merry-go-round in a Rayonet photochemical reactor with 3000-Å lamps (21 W × 16) for 20 min at 31 °C. The actinometer solution of benzophenone (0.050 M)–benzohydrol[44] (0.10 M, $\Phi = 0.74$) in 5 mL of benzene was irradiated under the same conditions, but for 5 min. The concentration of quinone monooxime **2** was determined by HPLC (C_{18} column, MeOH/H_2O = 70/30 by volume) with 1-nitronaphthalene as the internal standard.

Fluorescence Spectra and Fluorescence Intensity Quenching. Fluorescence spectra were either recorded with the standard technique of the right angle configuration of incident and emitting light or by a "front-face" illumination technique.[31-33] If both quencher and quenchee absorb at the wavelength excitation, emission intensities were corrected according to light energy absorbed by two for calculations of $I°/I$.

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Communications to the Editor

Reduction of Silicon–Hydrogen Bond Strengths[1]

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The factors which moderate carbon–hydrogen bond dissociation energies (BDE), eq 1 and 2, are now reasonably well understood. Bond dissociation energies are lowered when conjugated radicals

$$\text{R–H} \rightarrow \text{R}^\bullet + \text{H}^\bullet \tag{1}$$

$$\text{BDE(R–H)} = \Delta H_f(\text{R}^\bullet) + \Delta H_f(\text{H}^\bullet) - \Delta H_f(\text{R–H}) \tag{2}$$

are formed (e.g., R = allyl or benzyl),[2,3] when the radical center has an adjacent heteroatom,[2-6] or when the dissociation relieves steric compression in R–H.[7] The underlying principles of these and other effects have been the subject of extensive debate and discussion.[2,7] However, there is hardly any information on the factors which influence the strengths of silicon–hydrogen bonds.

Almost all of the available thermochemical data on Si–H bond dissociation energies are due to the pioneering work of Walsh and his colleagues.[8] To a large extent, they have shown that the factors which dominate the thermochemistry of the C–H bond are essentially unimportant in the silicon cogeners. For example, BDE(H_3Si–H) = 90.3, BDE(Me_3Si–H) = 90.3, and BDE($PhSiH_2$–H) = 88.2 kcal mol^{-1} whereas the corresponding series of bond strengths in hydrocarbon chemistry[2] would span a range of 26 kcal mol^{-1}! Despite the uniformity of most Si–H bond strengths, there are some interesting anomalies. For example, the presence of three fluorines has a profound strengthening effect,[8] BDE(F_3Si–H) = 100.1 kcal mol^{-1}, whereas the presence of a second silyl group has a moderate weakening effect,[8] BDE(H_3SiSiH_2–H) = 86.3 kcal mol^{-1}. We have pursued this last result and have found that it holds the key to the systematic reduction of Si–H bond strengths.

Silicon–hydrogen bond dissociation energies were measured by a photoacoustic technique which has been described in detail elsewhere.[9,10] Pulses from a nitrogen laser (337 nm; pulse width 10 ns; $h\nu = 84.8$ kcal mol^{-1}) were used to photolyze deoxygenated solutions containing di-*tert*-butyl peroxide (4–16% v/v) and an appropriate silane in isooctane, which were flowed through a standard UV flow cell. The photolysis gave rise to reactions 3 and 4, and the net heat evolved in these processes caused a shock

$$t\text{-BuO–OBu-}t \rightarrow 2t\text{-BuO}^\bullet \tag{3}$$

$$t\text{-BuO}^\bullet + R_3SiH \rightarrow t\text{-BuOH} + R_3Si^\bullet \tag{4}$$

wave in the solution that was detected by a piezoelectric transducer that was clamped to the cell wall. The laser light intensity used in the experiments was sufficiently low that the concentrations of the reagents were essentially unaffected by the photolysis. The signals from the transducer were stored and averaged in an oscilloscope, and their amplitude was found to be proportional to the light absorbed by the peroxide in the solution. The system was calibrated by using *o*-hydroxybenzophenone, which efficiently and rapidly converts light into heat.[9,11]

Table I. Bond Dissociation Energies and Related Kinetic Data for the Si–H Bonds in Silanes

	ΔH_{obsd}, kcal mol^{-1}	k_4, $M^{-1}\,s^{-1}$	k_8, $M^{-1}\,s^{-1}$	BDE(R_3Si–H),[a] kcal mol^{-1}
Et_3SiH	76.3	5.7×10^6 [b]	1.0×10^6 [c]	90.1
$Me_3Si(Me)_2SiH$	84.9	1.7×10^7 [d]	1.5×10^6 [e]	85.3
$(Me_3Si)_3SiH$	95.9	1.1×10^8 [f]	5.9×10^6 [g]	79.0

[a] Relative error ±1 kcal mol^{-1}. Absolute error ±2 kcal mol^{-1}. [b] Reference 21. [c] Reference 22. [d] Reference 23. [e] Reference 24. [f] Reference 20. [g] Reference 25.

Since the rate constants for reaction 4 are known (Table I) it was a simple matter to adjust the silane concentrations (0.2–1.0 M) so that reaction 4 was complete in a time which was short compared to the ca. 2-μs response of the system.[9] At the same time this response was long compared to the lifetimes for bimolecular decay of the silyl radicals. The observed heat deposition, ΔH_{obsd}, therefore reflected the contribution from the laser pulse (84.8 kcal mol^{-1}) and that from ΔH_r, the combined heats of reactions 3 and 4. The relationship between the experimental result and the heats of formation of the reactants and products is defined in eq 5 and 6, where Φ is the quantum yield for peroxide

$$-\Delta H_{obsd} = 84.8 - \Delta H_R \Phi \text{ kcal mol}^{-1} \tag{5}$$

$$\Delta H_R = 2\Delta H_f(t\text{-BuOH}) + 2\Delta H_f(R_3Si^\bullet) - \Delta H_f(t\text{-BuOOBu-}t) - 2\Delta H_f(R_3SiH) \tag{6}$$

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photolysis.[12] Combination of these results with the literature values for the heats of formation of t-BuOH,[13] t-BuOOBu-t,[14] and $H^{\bullet}$[13] led to the bond dissociation energies in the silanes (eq 1 and 7).

$$\mathrm{BDE}(R_3Si\text{–}H) = \Delta H_R/2 + 86.1 \text{ kcal mol}^{-1} \qquad (7)$$

To prove that the system correctly conformed to the kinetic constraints described above, we demonstrated the ΔH_{obsd} was independent of the laser light intensity which was attenuated by the use of neutral density filters. In addition, we obtained data in a range where ΔH_{obsd} was independent of the silane concentration.

In this study, small corrections had to be applied because attack at the Si–H bonds of the silanes by *tert*-butoxyl was the dominant but not unique mode of reaction. In fact, there was generally a small amount of attack at the methyl or methylene groups of the silanes, eq 8. The corrections were calculated by using the ratio

$$t\text{-BuO}^{\bullet} + R_3SiH \rightarrow t\text{-BuOH} + R(\text{–}H)R_2SiH \qquad (8)$$

of rate constants k_4/k_8 and the appropriate C–H bond strengths.[15,16] In all cases the corrections were small, ≤ 1 kcal mol^{-1}, so that any imprecision in these data was of little consequence. The results are summarized in Table I. The relative errors of ± 1 kcal mol^{-1} on the bond dissociation energies reflect random errors in the photoacoustic experiment. The absolute error of ± 2 kcal mol^{-1} takes into account experimental errors in the heats of formation of *tert*-butyl alcohol[13] and di-*tert*-butyl peroxide[14] that were used in the calculations, eq 6 and 7. The value obtained for BDE(Et_3Si–H) of 90.1 kcal mol^{-1} was in excellent agreement with that of 90.3 kcal mol^{-1} reported for trimethylsilane and lends weight to the accuracy of the photoacoustic approach.

The silicon–hydrogen bond in tris(trimethylsilyl)silane is so weak that the compound serves as an excellent free radical reducing agent that rivals tributyltin hydride (BDE(Sn–H) = 74 $\pm$ 2 kcal mol^{-1})[9] in its efficiency, eq 9 and 10. For example, alkyl bromides can be reduced quantitatively by the use of this reagent in monoglyme as solvent.[17]

$$(Me_3Si)_3Si\text{–}H + R^{\bullet} \rightarrow (Me_3Si)_3Si^{\bullet} + RH \qquad (9)$$

$$(Me_3Si)_3Si^{\bullet} + R\text{–}X \rightarrow (Me_3Si)Si\text{–}X + R^{\bullet} \qquad (10)$$

Taken as a whole, the results demonstrate that silicon–hydrogen bonds can be dramatically weakened by successive substitution of silyl groups at the Si–H function, although the origin of the effect is unclear. It is possible that steric compression in $(Me_3Si)_3SiH$ is relieved on radical formation thus making the Si–H bond quite weak.[17] In addition, the radical may be stabilized by interactions between the unpaired electron and the silicon d-orbitals.[19] However, simple electronic effects do not account for the phenomenon since Si–H bond dissociation energies do not correlate with the group electronegativities of the ligands.

Registry No. Et_3SiH, 617-86-7; $Me_3Si(Me)_2SiH$, 812-15-7; $(Me_3Si)_3SiH$, 1873-77-4.

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A Novel Nickel–Chromium Catalyst System for Cyclization via Intramolecular Carbametalation

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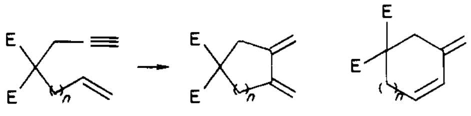
Intramolecular carbametalations promise to be an exciting approach for ring construction under very mild conditions.[1] In seeking catalytic rather than stoichiometric metal reactions, we have been exploring the palladium(2+)-catalyzed cyclization of enynes.[2] To expand the utility of this palladium-based methodology, we sought alternative catalysts. In this communication, we report the development of a nickel–chromium system[3] which requires attachment to a polymer for adequate catalytic activity.[4]

The enyne **1** was taken as a test substrate. Treatment with a variety of Ni(2+) salts led only to recovered starting material in stark contrast to the Pd system. With the notion that a catalytic system based upon a Ni(1+) – Ni(3+) cycle might be more active,[5] we treated $(Ph_3P)_2NiCl_2$ (**2**) with 1 equiv of sodium naphthalenide in THF and then added enyne **1**. After 15 min at room temperature, a 2.5:1 mixture of five- and six-membered ring products, **3** and **4**, respectively, was formed in 38% yield in a stoichiometric nickel reaction. Replacing sodium naphthalenide with chromous chloride, also a one-electron reducing agent, and keeping everything else the same gave similar results.



1, n = 1
5, n = 2

3, n = 1
6, n = 2

4, n = 1
7, n = 2

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