than their carbon-centered counterparts,[11] electron delocalization is calculated to have a slightly greater stabilizing effect in H_2B-$SiH_2^{\bullet}$ than in H_2B-$CH_2^{\bullet}$. Presumably, the lower electronegativity of silicon compared to carbon is responsible for making delocalization of the odd electron into the empty BH_2 orbital more important in H_2B-$SiH_2^{\bullet}$ than in H_2B-$CH_2^{\bullet}$.

For substituents that have unshared electron pairs, the greater electronegativity of carbon, compared to silicon, should favor electron donation into the singly occupied orbital on carbon. This effect, coupled with the weaker π bonds formed by silicon and the more highly pyramidalized geometry of silyl radicals, should cause electron donor substituents to be much less stabilizing for silyl-centered radicals than for carbon-centered radicals. This expectation is born out by the results in Table I, which show H_2N, OH, and F substituents all reduce the C–H BDE of X–CH_3 from that in methane. In contrast, all but the least electronegative of these groups, H_2N, actually increase the Si–H BDE of X–SiH_3 to a value above that in SiH_4.[12] The 3.5 kcal/mol greater BDE predicted for F–SiH_3 is slightly more than one third of the 9.8 kcal/mol greater BDE found experimentally for F_3SiH.[2]

Donation of a lone pair of electrons on the substituent is stabilizing for both X–$CH_2^{\bullet}$ and X–$SiH_2^{\bullet}$, as shown for X = NH_2 by the increase in energy in both radicals on rotation by 90° about the bond to the amino group.[13] That electron pair donation is more important for stabilizing carbon-centered radicals is evidenced by the fact that the energy increase of 8.5 kcal/mol on 90° rotation about the C–N bond in H_2N–$CH_2^{\bullet}$ is considerably larger than the increase of 3.3 kcal/mol on 90° rotation about the N–Si bond in H_2N–$SiH_2^{\bullet}$.

Since delocalization of a lone pair on the substituent group, X, in X–$SiH_2^{\bullet}$ is apparently stabilizing, albeit by a significantly smaller amount than in X–$CH_2^{\bullet}$, the calculated increase in the BDE on going from SiH_4 to X–SiH_3 for X = OH and F must have another origin. Inspection of the data in Table I suggests that the BDE in X–SiH_3 generally increases with the electronegativity of X.[12,14] This is revealed more clearly when the very strong electron delocalizing ability of BH_2 is factored out by using the energy for the H_2B–$SiH_2^{\bullet}$ radical with the empty p orbital on boron orthogonal to the singly occupied orbital on silicon.

If, for A = Si, the energetic favorability of the reaction in eq 1 were controlled exclusively by the electronegativity of X, the energy of this reaction would be negative for substituents that are more electronegative than hydrogen. This is, in fact, the case for X = NH_2, when the amino group is twisted 90° about the Si–N bond in order to reduce the stabilizing effect of nitrogen lone pair donation. Since carbon is also slightly more electronegative than hydrogen, it is not surprising that the methyl group in CH_3–SiH_3 too is calculated to cause the Si–H BDE to be larger than that in SiH_4. However, the increase in the BDE is computed to be quite small (0.8 kcal/mol), which is consistent with the experimental fact that alkyl substituents are found to have very little effect on Si–H BDEs.[2,3]

The calculated lowering of the Si–H BDE by a silyl substituent can be largely attributed to the fact that silicon is less electronegative than hydrogen. The computed 2.9 kcal/mol reduction of the Si–H BDE on going from SiH_4 to H_3Si–SiH_3 is slightly less than the 4.0 kcal/mol measured by Walsh and co-workers.[2] Consistent with the experimental results of Griller and co-workers,[3] we calculate the effects of additional silyl substituents to be nearly additive, since the three SiH_3 substituents in $(SiH_3)_3SiH$ are computed to lower the Si–H BDE by 8.2 kcal/mol from that in SiH_4.[15]

In contrast to the case with a silicon-centered radical, both CH_3 and SiH_3 substituents are calculated to stabilize a carbon-centered radical. SiH_3 is predicted to be a slightly more stabilizing substituent than CH_3, in agreement with Walsh's experimental results.[2] However, the computed difference of 1.1 kcal/mol between the stabilizing effects of SiH_3 and CH_3 substituents on a carbon-centered radical is significantly smaller than the calculated difference of 3.7 kcal/mol between the opposite effects of these two substituents on a silicon-centered radical.

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Supplementary Material Available: UHF optimized 6-31G* geometries and energies for the radicals listed in Table I with bond lengths in Å, angles in deg, and energies in hartrees (5 pages). Ordering information is given on any current masthead page.

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(11) The effect of silyl radical pyramidalization on the π bond strengths of molecules containing doubly bonded silicon has been discussed: Hrovat, D. A.; Sun, H.; Borden, W. T. *Theochem.*, in press. Sun, H.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1987**, *109*, 5275. Although the SiH_2 group is planar at the optimized geometry of H_2B–$SiH_2^{\bullet}$, the SiH_2 group is pyramidalized at the 90° twisted geometry. At the latter geometry a planar SiH_2 group is computed to be 5.4 kcal/mol higher in energy. This may be taken as the cost of silyl radical pyramidalization on the electron delocalization energy in H_2B–$SiH_2^{\bullet}$, since the delocalization energy for a planar silyl radical would be larger by this amount.

(12) Very electronegative substituents, for instance, NH_3^+ and three fluorines, are found to increase C–H BDEs too.[1] A simple explanation of this effect is that an electronegative substituent, X, increases the amount of s character in the A–H bonds of X–AH_3, which results in an increase in the A–H BDE [Bent, H. A. *Chem. Rev.* **1961**, *61*, 275].

(13) When both groups in H_2N–$AH_2^{\bullet}$ are pyramidalized, the energy maximum on rotation about the N–A bond occurs near but not at this geometry.

(14) Substituent electronegativities have been calculated to have the same type of effect on the energies required to dissociate two Si–H bonds to form triplet silylenes: Luke, B. T.; Pople, J. A.; Krogh-Jespersen, M.-B.; Apeloig, Y.; Karni, M.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 270.

(15) Since for X = SiH_3 and A = Si the energy calculated for the reaction in eq 1 is essentially the same at both the SCF/UHF and MP4SDTQ levels of theory, the calculations on the stabilizing effect of three SiH_3 substituents were performed at the former level of theory.

Study of Energy Transfer from Upper Triplet States in Solution with Two-Laser Two-Photon Excitation[1]

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Recent work from our laboratory has shown that upper triplet states, generated by photoexcitation of the first excited triplet, are readily quenched by aromatic substrates, in particular benzene.[2,3] Thus, excitation of triplet benzophenone in benzene in its visible absorption band (λ_{max} 525 nm)[4] results in the repopulation of ground-state benzophenone. Among the various mechanisms which could explain this result (energy transfer, electron transfer, or ring addition), we have favored energy transfer, although no definitive proof supporting this preference was available from our earlier results.[2] This quenching process appears to be general for a wide variety of aromatics and ketones, and while our reported results deal only with benzophenone[2] and 1,2-di-1-naphthylethane[3] in benzene, preliminary work in our laboratory has provided numerous examples showing similar behavior.[5]

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(1) Issued as NRCC 28639.

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(5) In particular, the compounds referred to in this report all exhibit quenching behavior in benzene, i.e., 2-acetylphenanthrene, 2-acetylnaphthalene, dibenzosuberenone, and *p*-terphenyl. It is now recognized that this quenching process is also *partially* responsible for the observed bleaching of the triplet states of benzil[6] and 1,3-di-1-naphthyl-2-propanone[7] in benzene. Upper state quenching occurs concurrently with the reluctant Type I cleavage on which we reported earlier.[6,7]

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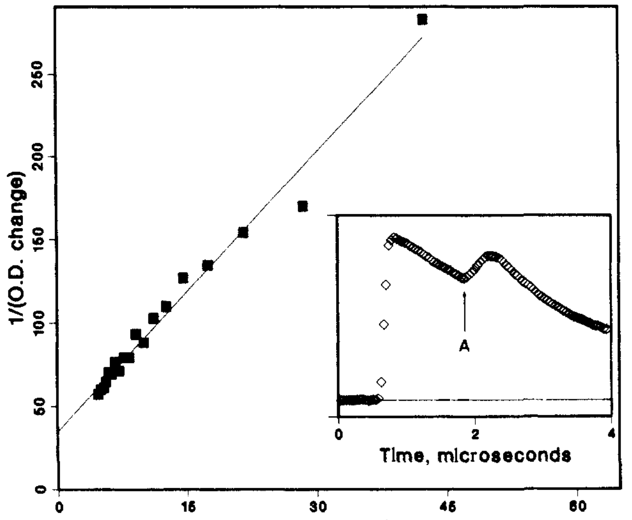

Figure 1. Double reciprocal plot of the o.d. change (A_{370}) and the quencher concentration for the 2-acetylphenanthrene–biphenyl system in acetonitrile. Inset: transient absorption decay monitored at 370 nm under two-laser excitation conditions (dye laser fires at "A") for [2-acetylphenanthrene] = 7 × 10^{-5} M and [biphenyl] = 0.208 M.

The suggestion that upper triplet states in solution at ambient temperatures could be sufficiently long lived to undergo triplet energy transfer processes is not new. In the late 1960's Liu et al.[8-11] showed that excited anthracenes could sensitize photochemical and photophysical processes usually associated with triplet reactivity (e.g., the norbornadiene-to-quadricyclane rearrangement).[11] Saltiel et al.[12] have also demonstrated the involvement of upper states in the anthracene-sensitized isomerization of stilbene and 2,4-hexadiene. These processes were attributed to energy transfer from T_2. As in our early reports, no direct, conclusive proof for acceptor triplet generation could be obtained.

Our experiments allow now the direct observation of triplet–triplet energy transfer involving upper excited states. Further, our data allow the determination of Stern–Volmer constants for upper triplet state quenching, and by incorporating some assumptions we have been able to estimate the lifetimes of the upper states involved. We use biphenyl as an upper triplet state quencher. We have selected molecules with lowest triplet state energies <65 kcal/mol, i.e., energies well below a lower limit for the triplet energy of biphenyl. These molecules also possess adequate ground-state extinction coefficients at 308 nm, where ground-state biphenyl is essentially transparent. Thus, 308 nm excimer laser excitation of 2-acetylphenanthrene (which meets the above requirements), in acetonitrile yields its readily detectable triplet (λ_{max} 490 nm).[13] The decay of 2-acetylphenanthrene triplet, which is independent of biphenyl concentration, is controlled by a mixture of first- and second-order processes[14] with typical half-lives of several microseconds at room temperature. Dye laser excitation of the triplet (λ_{dye} 460 nm) leads to different consequences in the presence or absence of biphenyl; in its absence triplet excitation has essentially no detectable photophysical or photochemical consequences (i.e., no bleaching or new absorptions were observed). In the presence of biphenyl we observe the formation and decay of the biphenyl triplet state (monitored at 370 nm, see insert in Figure 1)[15] following the dye laser pulse, as well as concurrent bleaching and recovery of the 2-acetylphenanthrene triplet (not shown). Spectral analysis shows conclusively that the change in absorption at 370 nm is due to the biphenyl triplet;[4] we attribute its formation to triplet–triplet energy transfer from an upper triplet state (T_2?) of the substrate, 2-acetylphenanthrene. Thus, under our conditions biphenyl behaves exclusively as an upper triplet state quencher; in fact, biphenyl triplets are relatively short lived as a result of energy transfer back to the substrate, 2-acetylphenanthrene, which also leads to the recovery of the substrate triplet absorption; i.e., for the lowest triplet state of the substrate, biphenyl is actually a sensitizer not a quencher. Scheme I illustrates the mechanism proposed

Scheme I

$$\mathrm{S} \xrightarrow{h\nu_1} {}^1\mathrm{S}^* \xrightarrow{\mathrm{ISC}} {}^3\mathrm{S}^*$$

$${}^3\mathrm{S}^* \xrightarrow{\overset{\bullet}{k_d}} \mathrm{decay}$$

$${}^3\mathrm{S}^* \xrightarrow{h\nu_2} {}^3\mathrm{S}^{**}$$

$${}^3\mathrm{S}^{**} \xrightarrow{\overset{\bullet\bullet}{k_d}} {}^3\mathrm{S}^*$$

$${}^3\mathrm{S}^{**} + \mathrm{PhPh} \xrightarrow{\overset{\bullet\bullet}{k_{\mathrm{ET}}}} \mathrm{S} + {}^3\mathrm{PhPh}^*$$

$${}^3\mathrm{PhPh}^* + \mathrm{S} \xrightarrow{\overset{\mathrm{B}}{k_{\mathrm{ET}}}} {}^3\mathrm{S}^* + \mathrm{PhPh}$$

$${}^3\mathrm{PhPh}^* \xrightarrow{\overset{\mathrm{B}}{k_d}} \mathrm{PhPh}$$

where S is the substrate, $h\nu_1$ and $h\nu_2$ refer to the 308 nm and dye laser pulses, and the superscripts indicate excitation and multiplicity. Thus, the lifetime of triplet biphenyl (^{3}PhPh*) is a function of the substrate concentration, which has to be kept quite low ($\leq 10^{-4}$ M) to ensure that the lifetime of ^{3}PhPh* is longer than the duration of the dye laser pulse (~250 ns). The yield of triplet biphenyl, required for the Stern–Volmer studies (vide infra), is most accurately measured when the triplet lifetime meets this criterium.

The mechanism of Scheme I lends itself to quantitative analysis. Thus, at constant dye laser dose and ^{3}S* concentration, the yield of ^{3}PhPh* (as measured by the dye-induced change in absorbance at 370 nm)[16] will be a function of the biphenyl concentration, such that

$$\frac{1}{A_{370}} = \alpha + \frac{\alpha}{\overset{\bullet\bullet}{k}_{\mathrm{ET}}\tau^{**}[\mathrm{PhPh}]} \qquad (1)$$

where τ^{**} is the lifetime of ^{3}S**, the α parameter relates various experimental conditions, and A_{370} is the transient absorption due to a biphenyl triplet induced by dye laser excitation. We note that no absorption at 370 nm is generated if the dye laser pulse is not preceded by 308-nm excitation. The results of these measurements are shown in Figure 1 and lead to $\overset{\bullet\bullet}{k}_{\mathrm{ET}}\tau^{**} = (6.2 \pm 1.5)\ \mathrm{M}^{-1}$ (errors as $\pm 2\sigma$) in acetonitrile at room temperature.

In order to estimate $\overset{\bullet\bullet}{k}_{\mathrm{ET}}$ we have measured the rate constant for xanthone triplet quenching by biphenyl in acetonitrile ($k_q = 1.03 \times 10^{10}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$). The triplet energy of xanthone lies above that of biphenyl but probably below that of the upper triplet state

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(13) A description of the laser flash photolysis system used can be found in the following: Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747. In addition, a description of the two-laser technique which is used to produce excited reaction intermediates is given in the following: Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396.

(14) The second-order contribution to the decay kinetics is a result of triplet–triplet annihilation. This process is common at the high triplet concentrations produced by laser excitation.

(15) This is close to the maximum of the T–T absorption spectrum of biphenyl.[4]

(16) Biphenyl triplet yield was determined by measuring the dye laser induced absorbance change at 370 nm, corrected for the expected bleach of the 2-acetylphenanthene triplet which also shows some absorption at this wavelength.

of 2-acetylphenanthrene. Thus, k_q for xanthone is probably a lower limit for k_{ET}^{**}. The value of k_q is close to that for diffusion control in acetonitrile which in itself represents the upper limit for k_{ET}^{**}. Thus, as a first approximation we estimate $k_{\mathrm{ET}}^{**} \sim 10^{10}$ $\mathrm{M}^{-1}\ \mathrm{s}^{-1}$, which leads to $\tau^{**} \sim 620$ ps for 2-acetylphenanthrene in acetonitrile. A number of other substrates are currently being examined by using the same approach. For 2-acetonaphthone we obtained $k_{\mathrm{ET}}^{**}\tau^{**} = 1.8$ M^{-1}, and for dibenzosuberenone preliminary experiments suggest a very short lifetime for τ^{**}, probably ≤ 100 ps;[17] experiments of this type are difficult because the intercept in plots generated according to eq 1 is small. *p*-Terphenyl also yields triplet biphenyl upon two-laser sensitization, but other absorptions (perhaps resulting from charge transfer) are also produced.

In summary, our results demonstrate the occurrence of upper triplet state energy transfer processes in solution at room temperature and lead to estimates of these upper state lifetimes. The lifetimes can be sufficiently long for intermolecular processes to occur not only with just neat solvents but also with added scavengers/quenchers. Further work is currently in progress which is expected to yield $k_{\mathrm{ET}}^{**}\tau^{**}$ values which we hope to correlate with photophysical and chemical processes occurring from these upper states as well as with expectations based on Kasha's rule.

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[17] The determination of lifetimes as short as 100 ps requires the addition of biphenyl concentrations up to ~1–2 M. Under these conditions the actual value of k_{ET}^{**} may contain contributions due to both dynamic quenching controlled by diffusion and static quenching. While Andre and co-workers[18,19] have developed a quenching theory which takes into account both static and dynamic processes, we feel that such a refinement is not justified at the current preliminary stage of our work.

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A Simple Synthesis of Dienones via Isomerization of Alkynones Effected by Palladium Catalysts

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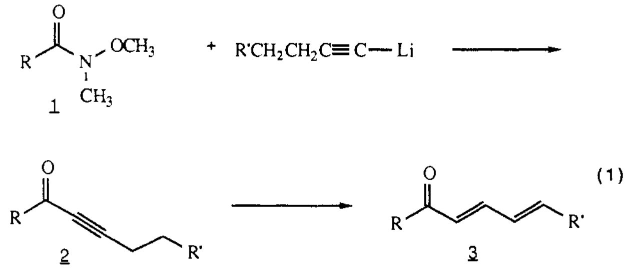
The isomerization of alkynes to conjugated dienes can represent a useful synthetic approach to these valuable building blocks due to the ready accessibility and elaboration of alkynes. While the acetylenic migration along an alkyl chain in the presence of base has proven of great value,[1] conjugated dienes are not detected.[2-4] On the other hand, allenes form readily by base rearrangement of alkynes.[3,5] The failure to obtain the thermodynamically preferred conjugated dienes[3] from acetylenes appears to be a kinetic problem.[6-8] Indeed, in the special case of 4-butynoic acid, the isomerization to 2,4-butadienoic acid succeeds since the allene that arises from base treatment, 3,4-butadienoic acid, requires prototropic shift of a proton from an allylic methylene group that is further activated by a carboxylate group.[7,9] Transition-metal catalysts offer a mild approach for hydrogen migrations that are not necessarily dependent upon acidity. In view of the well-known ability of transition metals to effect olefin isomerizations[10,11] and the vast literature on the reactions of alkynes under the influence of transition-metal catalysts,[12] the absence of a synthetically useful isomerization of alkynes to the thermodynamically more stable isomeric conjugated dienes is quite surprising. We wish to report a facile synthesis of the 2,4-alkadien-1-ones by a palladium-catalyzed isomerization of 2-alkyn-1-ones.

Equation 1 represents the overall sequence. By using the Weinreb–Nahm procedure,[13] we generated the alkynones **2** in 61–97% yield by treating the hydroxylamine derivatives **1** with the lithiated terminal acetylene in THF–hexane, initially at −78 °C with subsequent warming to room temperature. The chemoselectivity noted in entry 3 suggests that the hydroxylamine unit specifically activates the carbonyl group toward addition since an amide is normally less reactive than an ester toward nucleophilic addition.



Heating the alkynone **2** with 5 mol% of palladium acetate in the presence of a phosphine in toluene at 100 °C leads to the rearranged dienone in excellent yields as summarized in Table I. The parameters for the isomerization were examined in the case of alkynones **1** and **2**. That the reactions were metal catalyzed was demonstrated by a control experiment in the case of alkynone **2** where, in the absence of the catalyst, only slow decomposition was observed. Addition of DIBAL-H to a reaction identical with entry 5 led only to recovered starting material (84% recovery).

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