ground-state effect and does not reflect the relative stabilities of the intermediate fluorinated trimethylenemethane diradicals. In fact, it appears that as the number of fluorine substituents on an allyl radical increases, its delocalization energy decreases.[12,13]

If one makes the reasonable assumption that the cyclopropane ring strains of **1** and **4** should be approximately the same, then their rates of fragmentation should be about the same, and an equilibrium constant for $\mathbf{3} \rightleftharpoons \mathbf{4}$ ($K = 7850$) and a $\Delta G° \approx -7.5$ kcal/mol can be estimated. This compares with the $\Delta G° = -1.7$ kcal/mol for $\mathbf{1} \rightleftharpoons \mathbf{2}$. The experimental $\Delta G^{\ddagger}$ values for **3** and **1** are 30.3 and 37.7 kcal/mol, respectively. These numbers reflect a tremendous "extra" destabilization by the second CF_2 group of **3**. This perhaps should not be totally surprising since cyclopropanes are generally considered to have significant "olefinic" character, and it is well-known that adding a second pair of fluorines to vinylidene fluoride to create tetrafluoroethylene also gives rise to further substantial, nonadditive destabilization of the olefinic system.[14-16] (Vinylidene fluoride and tetrafluoroethylene are estimated to be more strained than ethylene by 4 and 16 kcal/mol, respectively.) Indeed, the disparate equilibria for the two systems perhaps can be best understood by viewing **3** as a tetrafluoroethylene-type species that, consequently, is significantly more destabilized than **1**, **2**, or **4**.

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Detection of Trialkylstannyl Radicals Using Laser Flash Photolysis

Sir:

The reactions of organotin compounds in photochemical and free-radical processes have received considerable attention.[1] Trialkylstannanes are widely used as reducing agents, reflecting the high reactivity of the tin-hydrogen bond toward free radicals and excited states.[2] Stannyl radicals are very reactive in halogen abstraction reactions[3] and have found wide application in ESR spectroscopy where they are frequently used to generate radicals from organic halides.[4] Trialkyltin radicals can be generated by a variety of methods, including hydrogen abstraction from the stannane,[2] attack of alkoxy radicals on hexalkylditin compounds,[4-6] and direct photolysis of the organotin substrates.[7] Despite the studies and applications mentioned above, few absolute rate constants involving the formation or reactions of tin radicals are known;[6] in addition, their ESR detection, while possible, remains difficult.[6-8] This communication reports preliminary results of a study of the formation and decay of tri-*n*-butylstannyl radicals by using laser flash photolysis.

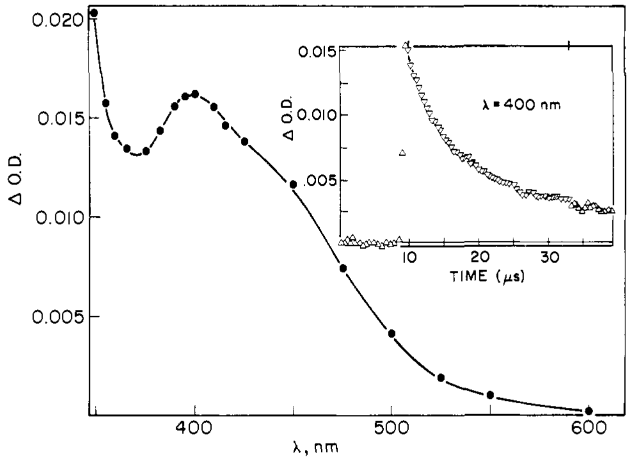

Figure 1. Transient spectrum obtained upon excitation of a 0.08 M solution of Bu_3SnH in di-*tert*-butyl peroxide. (Insert) Decay trace and second-order fit. The markers at the top indicate the region of the trace used to calculate the kinetics.

The experiments were carried out by monitoring the transient absorptions produced when the samples were excited with the pulses (337.1 nm, ~8 ns, ~10 mJ) from a nitrogen laser. For example, when a 0.08 M solution of Bu_3SnH in di-*tert*-butyl peroxide is irradiated, it leads to the formation of a transient species which exhibits the spectrum of Figure 1 and decays with second-order kinetics as illustrated in the insert in the same figure. Under these conditions, the laser pulses are absorbed almost exclusively (over 95%) by the peroxide which undergoes a fast and efficient decomposition to yield *tert*-butoxy radicals.[11] We propose that the transient spectrum shown in Figure 1 is due to the free radical $Bu_3Sn\cdot$ generated in reaction 2 which decays by recombination according to reaction 3.

$$t\text{-BuOO-}t\text{-Bu} \xrightarrow{h\nu} 2\text{-}t\text{-BuO}\cdot \qquad (1)$$

$$t\text{-BuO}\cdot + Bu_3SnH \rightarrow Bu_3Sn\cdot + t\text{-BuOH} \qquad (2)$$

$$2Bu_3Sn\cdot \rightarrow Bu_6Sn_2 \qquad (3)$$

While it is rather surprising that $Bu_3Sn\cdot$ would absorb in this region, our assignment is also supported by the detection of the same species in the photolysis of azobis(isobutyronitrile) (AIBN) in the presence of Bu_3SnH. In this case, the spectrum was considerably weaker, reflecting the lower reactivity of carbon radical centers (compared with *tert*-butoxy) and, perhaps, a lower quantum yield of AIBN photodecomposition.

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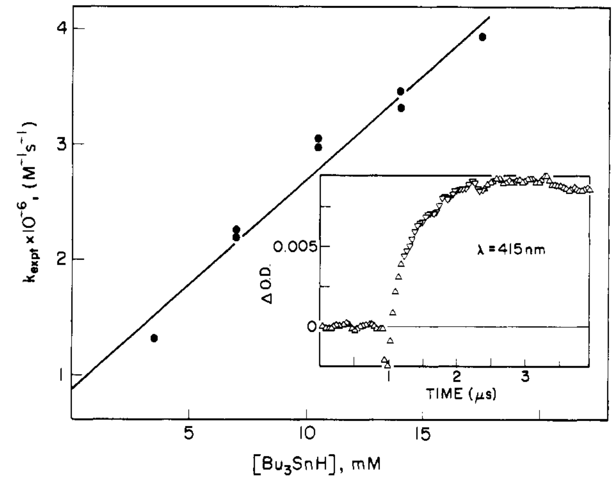

Figure 2. Experimental pseudo-first-order rate constant for the formation of $Bu_3Sn\cdot$ as a function of substrate concentration. (Insert) Trace obtained for [Bu_3SnH] = 0.007 M. The negative signal observed at the beginning of the buildup is due to luminescence, presumably originating from trace impurities.

Consistent with the mechanism of reactions 1–3, we observe that the transient signals are produced in a pseudo-first-order process following excitation (see insert in Figure 2). A plot of the pseudo-first-order rate constant (k_{exptl}), derived from the buildup of the signal, as a function of [Bu_3SnH] yields k_2 from the slope while the intercept is determined by the lifetime of *tert*-butoxy in this solvent (Figure 2).[12] From this plot, we obtained $k_2 = 1.9 \times 10^8$ M^{-1} s^{-1} at 22 °C with di-*tert*-butyl peroxide as solvent. An analysis of the second-order decay traces mentioned before yields $2k_3/\epsilon l = 1.1 \times 10^7$ s^{-1} which, taking $2k_3 \sim 1.4 \times 10^9$ M^{-1} s^{-1},[3] and taking into consideration the optical path (l), leads to an estimate of the extinction coefficient as $\epsilon_{400} \sim 450$ M^{-1} cm^{-1}.

The rate constant for the reaction of *tert*-butoxy radicals with Bu_3SnH can also be obtained by using the method employed in earlier studies,[11,14] using diphenylmethanol as a probe. In this method, one monitors the kinetics of the formation of diphenylhydroxymethyl radicals as a function of the concentration of added reagent. The method is quite accurate because the intense signal from $Ph_2\dot{C}OH$ makes detection quite easy. This approach led to $k_2 = 2.2 \times 10^8$ M^{-1} s^{-1} at 22 °C in a 1:2 (v/v) mixture of benzene/di-*tert*-butyl peroxide as solvent. While the excellent agreement of the rate constant obtained by this method with the value obtained by direct detection (Figure 2) is not in itself definitive proof for the assignment given above, it certainly supports our conclusion that the species detected is the $Bu_3Sn\cdot$ radical. Similar experiments with Bu_3SnD (using diphenylmethanol as a probe) led to a kinetic isotope effect $k_H/k_D = 1.23 \pm 0.15$. The low value obtained is not unusual for fast exothermic reactions,[15] though in this particular case the involvement of charge transfer in the transition configuration could conceivably contribute to the low value observed.

The similarities in the behavior of alkoxy radicals and n-π* ketone triplets have been widely documented in the literature;[16] in order to compare the behavior of these two species in the case of tin–hydrogen bonds, we examined the reaction of benzophenone triplets with Bu_3SnH. A kinetic study led to a rate constant for triplet quenching by the tin hydride of 2.9×10^8 M^{-1} s^{-1}, quite similar to the value observed in the case of *tert*-butoxy radicals. The transient spectrum immediately after triplet decay is consistent with a 1:1 mixture of $Ph_2\dot{C}OH$ and $Bu_3Sn\cdot$. A slower process, which is believed to reflect the addition of $Bu_3Sn\cdot$ to benzophenone, has also been detected and is currently under study. The rate constant measured for benzophenone is ca. three times smaller than the values reported for acetone[2b] and acetophenone;[19] at this point, it is not clear whether the difference simply reflects the sum of the errors of the various measurements (this seems unlikely) or whether it is the result of the higher triplet energy in the case of acetone and acetophenone.[2b,19]

The radical $Bu_3Sn\cdot$ is efficiently scavenged by oxygen.[17] From a study of the radical lifetimes in the presence of different oxygen concentrations, we obtained $k_{O_2} = 1.8 \times 10^9$ M^{-1} s^{-1} in benzene at 22 °C.[18] Finally, we have carried out a few preliminary experiments with hexabutylditin in the hope of monitoring reaction 4. Our results indicate that reaction 4 involves another intermediate in addition to the stannyl radical; our spectroscopic evidence requires that this intermediate be produced by reaction of *tert*-butoxy with the ditin compound. Two explanations are possible; in one, the intermediate (that has a spectrum different from $Bu_3Sn\cdot$) would correspond to a pentacoordinate tin radical produced by radical addition at one of the tin centers. Such a radical would be similar to phosphoranyl and boranyl radicals detected in other S_H2 processes.[20] The other possibility is an electron-transfer process leading to the ditin radical cation which could then cleave to yield $Bu_3Sn\cdot$.

$$t\text{-BuO}\cdot + \text{Bu}_6\text{Sn}_2 \rightarrow t\text{-BuOSnBu}_3 + \text{Bu}_3\text{Sn}\cdot \qquad (4)$$

The mechanism of reaction in the case of the ditin compounds and the possibility of using laser photolysis to examine the reactions of tin radicals with halogen donors are currently under study.

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Model Approach to Retinal Pigments. Remarkable Red Shift Due to Proximal Ammonium Ion

Sir:

The retinal pigments have attracted strong attention from chemists, especially because of the significant effect of such an apoprotein as opsin upon the physicochemical behavior of the chromophore, Schiff base of retinal. Absorption maxima of the bacteriorhodopsin or rhodopsins, for example, are spread over a wide range (432–575 nm) of wavelengths, depending on the nature of the proteins, suggesting that the tight binding of the chromophore to the protein affords electrostatic destabilization of the ground state and/or stabilization of the excited state of the chromophore[1] and special medium effects due to the high polarizability of the protein residue(s)[2] or conformational twisting

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