acidic aqueous solution is used to synthesize diphosphoryl disulfide.[14]

It is important to form the tetraanion of symmetrical monothiopyrophosphate immediately after dealkylation. As can be seen from Table I, at pH 8.0 and 25 °C, the half-life of the compound is only a few minutes, but, at pH 10.0, it is increased to several hours. The rates of hydrolysis show a strong temperature and pH dependence in analogy to the hydrolysis show a strong temperature and pH dependence in analogy to the hydrolysis of pyrophosphate.[26] The presence of lithium carbonate (approximately 300 mM) slows the hydrolysis considerably. This appears to be the result of a negative salt effect. This was verified by carrying out the hydrolysis of tetralithium symmetrical monothiopyrophosphate in solutions containing less than 50 mM lithium carbonate in the absence and again in the presence of approximately 300 mM lithium sulfate. Such negative salt effects have been previously observed for the hydrolysis of pyrophosphate.[26]

In aqueous solution at high pH, the rearrangement of **1** to unsymmetrical monothiopyrophosphate was not observed. However, the partially hydrolyzed tetralithium salt of **1** containing lithium carbonate forms a small amount of unsymmetrical monothiopyrophosphate, in addition to pyrophosphate, upon thermolysis at 50 °C. Lithium phosphate and lithium thiophosphate containing lithium carbonate do not form these products under identical conditions. This reaction most likely demonstrates the ability of **1** to phosphorylate thiophosphate and phosphate.

It was of interest to determine whether the symmetrical monothiopyrophosphate would be a substrate for inorganic pyrophosphatase. The unsymmetrical isomer has been reported to be hydrolyzed by this enzyme.[22] Detailed kinetic experiments were not possible due to the instability of the compound, but experiments carried out at one concentration of **1** well above the K_m for pyrophosphate[38] showed **1** to be a substrate. A comparison with pyrophosphate under identical conditions showed the rates of enzymatic hydrolysis for the two compounds to be comparable. Pyrophosphate is also a substrate for alkaline phosphatase.[39] However, an attempt to investigate the substrate properties of symmetrical monothiopyrophosphate for alkaline phosphatase was unsucessful. The rates of hydrolysis at pH 9.3 and 10.0 were essentially identical for experiments carried out in the presence and absence of enzyme.

In summary, we have synthesized the tetralithium and dibarium salts of symmetrical monothiopyrophosphate. Although the compounds appear to be stable as solids, they are hydrolyzed considerably more rapidly than pyrophosphate in aqueous solution.

Acknowledgment. This work was supported in part by the National Science Foundation under Grant No. SPI-7914859, assigned to Dr. D. I. Loewus. We wish to thank Mr. Bodo Seeger for help in recording the ^{31}P NMR spectra, Ms. Annette Schelper for her excellent technical assistance, and Ms. Andrea Kirchner for both her excellent technical assistance and several valuable suggestions.

Registry No. *O,O,O*-Trimethyl phosphorothioate, 152-18-1; trimethyl phosphite, 121-45-9; tetralithium symmetrical monothiopyrophosphate, 85202-58-0; dimethoxyoxophosphoranesulfenyl chloride, 13894-35-4; tetramethyl symmetrical monothiopyrophosphate, 71861-22-8; dibarium symmetrical monothiopyrophosphate, 85202-59-1; *O,O,O*-tribenzyl phosphorothioate, 81633-39-8; tribenzyl phosphite, 15205-57-9; tetrabenzyl symmetrical monothiopyrophosphate, 85202-60-4; dibenzyl phosphite, 17176-77-1; tetracyclohexylammonium diphosphoryl disulfide, 85202-61-5; unsymmetrical monothiopyrophosphate, 68488-87-9; dimethyl phosphite, 868-85-9.

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Absolute Rate Constants for the Addition of Triethylsilyl Radicals to Various Unsaturated Compounds[1]

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Abstract: The absolute rate constants for the reaction of Et$_3$Si· radicals with a large number of unsaturated compounds have been measured by laser flash photolysis techniques. The reactivities of C=C double bonds have a wide range, e.g., the rate constants at ca. 300 K are 1.1×10^9, 2.2×10^8, 1.0×10^7, 3.7×10^6, and 9.4×10^5 M^{-1} s^{-1} for acrylonitrile, styrene, tetrachloroethylene, 1-hexene, and cyclohexene, respectively. The range of reactivities for addition to aromatic and heteroaromatic compounds is rather small, the rate constants at ca. 300 K varying from 4.6×10^5 M^{-1} s^{-1} for benzene to 5.0×10^6 M^{-1} s^{-1} for thiophene and α-methylnaphthalene. Acetylenes are slightly less reactive than structurally analogous 1-olefins. For the other types of multiple bonds examined, reactivities decreased in the order isocyanide > nitrone > nitro > isocyanate > nitrile. Arrhenius parameters were determined for a few olefins including ethylene, for which an EPR spectroscopic competition procedure was required. For styrene, $\log (A/(\mathrm{M}^{-1}\,\mathrm{s}^{-1})) = 9.35 \pm 0.23$ and $E_a = 1.37 \pm 0.29$ kcal/mol; for ethylene, $\log (A/(\mathrm{M}^{-1}\,\mathrm{s}^{-1})) = 8.40 \pm 0.60$ and $E_a = 1.40 \pm 0.80$ kcal/mol.

We have recently shown that the technique of laser flash photolysis can be utilized to measure rate constants for the reactions of trialkylsilyl radicals in solution.[3-5] To date, we have investigated the kinetics for the addition of Et$_3$Si· radicals to carbonyl compounds[4] and the abstraction of halogens from organic halides.[5] In the present paper we extend these studies to several other important classes of organic substrates. Specifically, we have examined the addition of Et$_3$Si· to several multiple bonds as well as to aromatic and heteroaromatic substrates.

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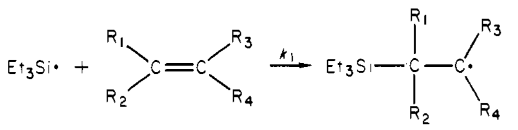
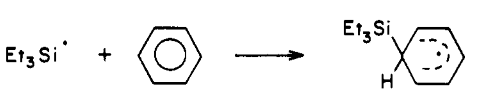
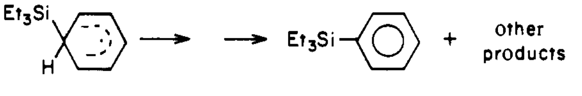
The addition to carbon–carbon double bonds has been exten-


(1)

sively investigated,[6] particularly by EPR spectroscopic examination of the initial adduct radicals.[7,8] However, there are no reliable absolute rate data for the addition of a trialkylsilyl radical to an olefin in solution (see Discussion).

Homolytic aromatic and heteroaromatic substitutions[9] by silicon-centered free radicals are also well-established reactions,[6c,10-21] e.g., eq 2 and 3. In general, previous work has tended


(2)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to center on the composition of the final molecular products[6c,10-12,21] or the EPR spectra of the intermediate cyclohexadienyl-type radicals.[13-21] There have been only four kinetic-type studies on these substitution processes.[10,12,19,21] Relative yields of ortho, meta, and para silyl-substitution products have been determined for the reactions of $Me_3Si\cdot$ radicals at room temperature,[10] of $Me_3Si\dot{S}iMe_2$ radicals at 135 °C[7] with anisole and toluene, of n-$Pr\dot{S}iMe_2$ radicals at 135 °C with toluene,[12] and of $Me_3Si\dot{S}iMe_2$ and n-$Pr\dot{S}iMe_2$ radicals at 135 °C with benzotrifluoride.[12] The reactivities of these three substrates relative to benzene toward the two last named radicals have also been measured.[12] However, since the yields of substitution products rarely exceeded 15%, it is by no means certain that they reflect, even in the competitive studies, the relative reactivities of the different substrates or even of the different positions in the same substrates. The only true kinetic data for processes of this type consist of an estimate[19] that the rate constant for reaction 2, $k_2 = 10^5$ M^{-1} s^{-1} at 298 K, and our own preliminary report[5] that k_2 has a value of 4.6×10^5 M^{-1} s^{-1} at this temperature and that the rate constant for the reaction of $Et_3Si\cdot$ radicals with chlorobenzene is 6.9×10^5 M^{-1} s^{-1}.

Table I. Rate Constants at ca. 300 K for Addition of Triethylsilyl Radicals to Molecules Having Carbon–Carbon Double Bonds[a]

substrate	k_1,[b] M^{-1} s^{-1}
$H_2C{=}CHC{\equiv}N$	$(1.1 \pm 0.2) \times 10^9$
$H_2C{=}C(CH_3)C(O)OCH_3$	$(4.6 \pm 0.8) \times 10^8$
$H_2C{=}CHC_6H_5$	$(2.2 \pm 0.2) \times 10^8$
$H_2C{=}CCl_2$	$(2.7 \pm 0.3) \times 10^8$
trans-$CH_3CH{=}CHC(O)OCH_3$	$(4.3 \pm 0.4) \times 10^7$
$H_2C{=}CH_2$	$(2.2 \pm 0.4) \times 10^7$ [c]
cis-$ClCH{=}CHCl$	$(2.1 \pm 0.4) \times 10^7$
norbornadiene	$(1.5 \pm 0.1) \times 10^7$
$Cl_2C{=}CCl_2$	$(1.0 \pm 0.2) \times 10^7$
trans-$ClCH{=}CHCl$	$(8.9 \pm 0.2) \times 10^6$
$H_2C{=}C(CH_2)_5$	$(7.4 \pm 1.3) \times 10^6$
$H_2C{=}CH(CH_2)_3CH_3$	$(4.8 \pm 0.5) \times 10^6$
$H_2C{=}CHC(CH_3)_3$	$(3.7 \pm 0.3) \times 10^6$
$HC{=}CH(CH_2)_3$	$(2.2 \pm 0.3) \times 10^6$
$HC{=}CHO(CH_2)_3$	$(1.2 \pm 0.1) \times 10^6$
trans-$CH_3CH_2CH{=}CHCH_2CH_3$	$(9.6 \pm 1.5) \times 10^5$
$HC{=}CH(CH_2)_4$	$(9.4 \pm 1.1) \times 10^5$

[a] Unless otherwise noted the data were obtained by laser flash photolysis with benzil as the probe in di-*tert*-butyl peroxide–triethylsilane as solvent. Errors correspond to 95% confidence limits. [b] Value calculated at 300 K from Arrhenius parameters when available. Otherwise, value measured at 300 ± 3 K. [c] By an EPR competition method.

Table II. Rate Constants for the Reactions of Triethylsilyl Radicals with Some Aromatic and Heteroaromatic Compounds at ca. 300 K[a]

substrate	k, M^{-1} s^{-1}	substrate	k, M^{-1} s^{-1}
benzene	$(4.6 \pm 1.0) \times 10^5$	phenylacetylene	$(1.0 \pm 0.1) \times 10^8$
chlorobenzene	$(6.9 \pm 0.2) \times 10^5$	styrene	$(2.2 \pm 0.2) \times 10^8$
toluene	$(1.2 \pm 0.2) \times 10^6$	pyridine	$(1.3 \pm 0.3) \times 10^6$
anisole	$(1.7 \pm 0.1) \times 10^6$	pyrrole	$(6.0 \pm 0.3) \times 10^5$
benzonitrile	$(3.2 \pm 0.2) \times 10^6$	furan	$(1.4 \pm 0.1) \times 10^6$
1-methylnaphthalene	$(5.0 \pm 0.5) \times 10^6$	thiophene	$(5.0 \pm 0.2) \times 10^6$

[a] Same as footnote *a*, Table I.

There is little or no information available regarding the addition of silicon-centered radicals to other types of multiple bonds.

Experimental Section

The experimental procedures were identical with those employed to study the addition of $Et_3Si\cdot$ radicals to carbonyl groups.[4] The triethylsilyl radicals were generated by laser flash photolysis of di-*tert*-butyl peroxide in the presence of triethylsilane. Rate constants for the addition reactions of $Et_3Si\cdot$ were determined in peroxide-silane (1:1 v/v) as solvent with benzil as the probe,[4] the growth of the triethylsilyl–benzil adduct being monitored at 378 nm. All error limits are reported as 2 standard deviations and include only random errors.

Measurement of the rate constants for the addition of $Et_3Si\cdot$ to ethylene were made by the competitive steady-state EPR method[22] since the laser equipment is ill adapted to the quantitative study of a reactant

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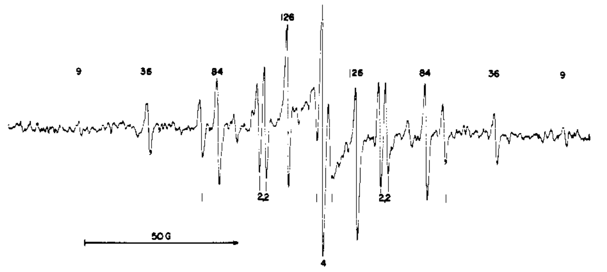

Figure 1. EPR spectrum obtained by UV photolysis of 1.10 M *tert*-butyl chloride and 0.12 M ethylene in di-*tert*-butyl peroxide, triethylsilane, and cyclopropane (1:1:8 v/v) as solvent at 253 K. The peaks with numbers above them come from the *tert*-butyl radical and those with the numbers below them from the $Et_3SiCH_2\dot{C}H_2$ radical. The numbers on the peaks refer to their intensity relative to the weakest line in each radical's spectrum. The spectrum was run with full light intensity at a modulation amplitude of 0.63 G and a microwave power of 3.5 mW.

that is gaseous at room temperature. Competitive experiments were carried out between ethylene and *tert*-butyl chloride, the laser having been previously used to measure the Arrhenius parameters for chlorine atom abstraction by $Et_3Si\cdot$ radicals from the latter compound[5] (eq 4).

$$Et_3Si\cdot + (CH_3)_3CCl \xrightarrow{k_4} Et_3SiCl + (CH_3)_3C\cdot \qquad (4)$$

An equimolar mixture of ethylene and *tert*-butyl chloride (0.5 M in each) was dissolved in di-*tert*-butyl peroxide, triethylsilane, and cyclopropane (1:1:8 v/v) as solvent and was sealed under vacuum and photolyzed with the UV light from a 1000-W xenon-mercury lamp in the cavity of a Varian E-104 EPR spectrometer. Only the spectrum of the adduct radical $Et_3SiCH_2\dot{C}H_2$ could be observed at all temperatures. However, both $Et_3SiCH_2\dot{C}H_2$ and the *tert*-butyl radical could be observed simultaneously in the same solvent mixture at temperatures in the range 154-270 K when the ethylene concentration was reduced to 0.12 M and the *tert*-butyl chloride concentration was increased to 1.10 M (see Figure 1). For such relatively small, sterically unhindered, carbon-centered radicals it is now well established that the bimolecular self-reactions occur at the diffusion-controlled limit,[23] i.e., the rate constants for such processes are essentially equal. The following equation should therefore be obeyed:

$$\frac{k_1^{C_2H_4}}{k_4} = \frac{[Et_3SiCH_2\dot{C}H_2][(CH_3)_3CCl]}{[(CH_3)_3C\cdot][C_2H_4]}$$

Relative concentrations of the two radicals at different temperatures and at different light intensities (i.e., different total radical concentrations) together with the derived values of the rate constant ratio for addition vs. abstraction are given in the supplementary material. These data yield the relationship

$$\log (k_1^{C_2H_4}/k_4) = -0.34 + 1.76/\theta$$

where $\theta = 2.3RT$ kcal/mol and the least-squares linear regression had a correlation coefficient of 0.974. The temperature dependence of the triethylsilyl radical-*tert*-butyl chloride reaction can be represented by[5]

$$\log (k_4/(M^{-1}\ s^{-1})) = (8.7 \pm 0.5) - (3.2 \pm 0.7)/\theta$$

Therefore, the Arrhenius equation for the addition of $Et_3Si\cdot$ to ethylene is

$$\log (k_1^{C_2H_4}/(M^{-1}\ s^{-1})) = (8.4 \pm 0.6) - (1.4 \pm 0.8)/\theta$$

Results

Rate constants for the reactions of $Et_3Si\cdot$ with various kinds of substrates at ca. 300 K (specific temperatures are given in the supplementary tables) are given in Tables I-III. Arrhenius parameters for the reaction with a few olefins are given in Table IV. Full kinetic data are available as supplementary material.

Table III. Rate Constants for the Reactions of Triethylsilyl Radicals with Some Unsaturated Compounds at ca. 300 K[a]

substrate	k, $M^{-1}\ s^{-1}$
$HC{\equiv}CC(CH_3)_3$	$(2.3 \pm 0.2) \times 10^6$
$H_2C{=}CHC(CH_3)_3$	$(3.7 \pm 0.3) \times 10^6$
$HC{\equiv}CC_6H_5$	$(1.0 \pm 0.1) \times 10^8$
$H_2C{=}CHC_6H_5$	$(2.2 \pm 0.2) \times 10^8$
$N{\equiv}CC(CH_3)_3$	$\leqslant 3 \times 10^5$ [b]
$N{\equiv}CC_6H_5$	$(3.2 \pm 0.2) \times 10^6$
$C{=}N(CH_2)_3CH_3$	$(1.6 \pm 0.2) \times 10^8$
$H_2C{=}CH(CH_2)_3CH_3$	$(4.8 \pm 0.5) \times 10^6$
$O{=}C{=}NC(CH_3)_3$	$(5.5 \pm 1.0) \times 10^6$
$C_6H_5CH{=}N({\rightarrow}O)C(CH_3)_3$	$(7.1 \pm 2.8) \times 10^7$
O_2NCH_3	$(4.3 \pm 0.3) \times 10^7$

[a] Same as footnote *a*, Table I. [b] Too slow to measure.

Table IV. Arrhenius Parameters for the Addition of Triethylsilyl Radicals to Certain Olefins

olefin	temp range, K	log (A/ ($M^{-1}\ s^{-1}$))	E, kcal/mol
$H_2C{=}CH(CH_2)_3CH_3$	261-332	9.00 ± 0.57	3.18 ± 0.76
$H_2C{=}CHC_6H_5$	236-324	9.35 ± 0.23	1.37 ± 0.29
$H_2C{=}CCl_2$	233-327	9.35 ± 0.36	1.25 ± 0.46
$H_2C{=}CH_2$	154-270	8.40 ± 0.60	1.40 ± 0.80

Discussion

Examination of the data in Tables I-III reveals that the addition of $Et_3Si\cdot$ to multiple bonds is frequently a remarkably facile process. Thus, even acyclic 1,2-diakyl olefins react with rate constants of ca. 10^6 $M^{-1}\ s^{-1}$ at 300 K. For cyclic olefins the rate appears to be enhanced by ring strain. Monoalkyl and 1,1-dialkyl olefins are somewhat more reactive than 1,2-dialkyl olefins, and olefins in which the double bond is activated by conjugation with a neighboring π-electron system are substantially more reactive.

As we have noted in other reactions involving the triethylsilyl radical, the rate is greatly enhanced when electron-withdrawing atoms such as chlorine or groups such as $C(O)OCH_3$ are located at the new radical center.[4,5] This is also true of the $Et_3Si\cdot$ radical additions to olefins. For example, all the chlorinated olefins are more reactive than their alkylated counterparts. Even the sterically crowded tetrachloroethylene reacts readily, and 1,1-dichloroethylene is highly reactive. The $Et_3Si\cdot$ radical would be expected to add to the CH_2 end of the double bond of the latter olefin both on kinetic grounds and by analogy with the known[7g] direction of its addition to $CH_2{=}CF_2$. This regiospecificity was confirmed by EPR spectroscopy, the only radical that could be detected on photolysis of di-*tert*-butyl peroxide, Et_3SiH, and $CH_2{=}CCl_2$ in cyclopropane was the $Et_3SiCH_2\dot{C}Cl_2$ adduct (at 171 K, $a^{35Cl}(2Cl) = 4.2$ G, $a^H(2H) = 13.5$ G; at 267 K, $a^{35Cl}(2Cl) = 3.5$ G, $a^H(2H) = 11.5$ G).

The Arrhenius parameters listed in Table IV are remarkable only in that the preexponential factors for 1-hexene, styrene, and $CH_2{=}CCl_2$ are slightly larger than would generally be considered to be "normal" for free-radical additions to double bonds, viz,[24] $10^{8.5\pm0.5}$ $M^{-1}\ s^{-1}$. This implies that the transition states for these three reactions, which are strongly exothermic,[25] are fairly "loose".[24] The preexponential factor for the addition of $Et_3Si\cdot$ radicals to ethylene is more "normal",[28] which suggests a somewhat

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(25) The addition of $Me_3Si\cdot$ radicals to 1-octene was originally estimated to be exothermic by 15 kcal/mol,[6b,26] this estimate being based on bond strengths of 79 kcal/mol for $D[Me_3Si-CH_3]$ and 87 kcal/mol for $D[CH_3-CH_3]$. More recent work[27] indicates that these two bond strengths should be 89 and 88 kcal/mol, respectively. The addition of a trialkylsilyl radical to a simple 1-olefin will therefore by exothermic by ca. 26 kcal/mol.

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"tighter" transition state for this reaction.

We are aware of only two previous attempts to measure the absolute rate constant for the addition of a silicon-centered radical to a C=C double bond. The first, by Strausz and co-workers,[30] which yielded a rate constant of 4×10^6 M^{-1} s^{-1} for the addition of the $SiD_3\dot{S}iD_2$ radical to ethylene in the gas phase at room temperature, is not necessarily comparable with our own data for the $Et_2Si\cdot$ radical.

The second, by Choo and Gaspar,[31] involved a kinetic EPR spectroscopic study of the addition of the $Me_3Si\cdot$ radical to ethylene. A rate constant of $(1.7 \pm 1.0) \times 10^5$ M^{-1} s^{-1} at 293 K was obtained for this reaction. Neither this rate constant nor the reported Arrhenius parameters, viz,[31] $E = 2.5 \pm 0.2$ kcal/mol and $A = 10^{7.0 \pm 0.2}$ M^{-1} s^{-1}, are consistent with our data, which is not entirely surprising. A careful examination of this[31] and an earlier paper[32] reveals that the initial $Me_3Si\cdot$ radical concentration (ca. 10^{-6} M) was not affected by the addition of ca. 10^{-2} M ethylene. Moreover, the addition of this quantity of ethylene did not change the time required for decay of the $Me_3Si\cdot$ EPR signal, e.g., at 293 K with 10^{-6} M $Me_3Si\cdot$ initially, the half-life was 0.33 ms without[32] and 0.40 ms with the ethylene.[31] The reaction in question is, in fact, too fast for a kinetic EPR experiment of the Choo and Gaspar type unless the ethylene concentration was considerably less than 10^{-2} M, in which case of flow system would be required in order to prevent depletion of the ethylene.

The addition of triethylsilyl radicals to aromatic and heteroaromatic compounds is a rather facile process. For compounds that do not contain a conjugated C–C double or triple bond, the rate constants range from 4.6×10^5 M^{-1} s^{-1} (benzene) to 5.0×10^6 M^{-1} s^{-1} (thiophene and α-methylnaphthalene). This range of reactivities is very small in comparison with the range observed for addition to carbonyl-containing compounds (viz,[4] 2.2×10^9 M^{-1} s^{-1} for duroquinone to $\leq 10^2$ M^{-1} s^{-1} for methyl acetate) or abstraction of halogen atoms (viz,[5] 1.4×10^{10} M^{-1} s^{-1} for 2-iodopropane to 3.1×10^5 M^{-1} s^{-1} for 1-chloropentane). For these simple aromatic and heteroaromatic compounds the triethylsilyl radical adds to the ring, as has been shown by EPR spectroscopy in many instances.[14,15,18-20] For chlorobenzene we deduce that addition is much more important than the abstraction of a chlorine atom because chlorobenzene is twice as reactive as 1-chloropentane, whereas bromobenzene ($k = 1.1 \times 10^8$ M^{-1} s^{-1})[5] is only one-fifth as reactive as 1-bromohexane ($k = 5.4 \times 10^8$ M^{-1} s^{-1}).[5] For benzonitrile Alberti and Pedulli[18] have already shown by EPR spectroscopy that triphenylsilyl radicals add mainly to the 4-position of the aromatic ring, rather than to the N or C of the cyano group (to form an imidoyl[33] or ketiminyl[34] radical, respectively). Triethylsilyl radicals can be presumed to react in a similar manner.

It is interesting to note that all the ring-substituted benzenes are more reactive than benzene itself. If all reaction occurs by addition to the ring, this indicates that both electron-withdrawing groups and electron-donating groups must accelerate the addition reaction. Polar effects of the kind that could lead to a Hammett type of log rate vs. substituent constant correlation are therefore relatively unimportant. Reactivity is determined mainly by the degree of stabilization of the cyclohexadienyl-type radical that is produced. This will be enhanced both by substituents such as methyl (via hyperconjugation) and by substituents such as chlorine and methoxy (via conjugative electron delocalization).

Comparison of the rate constants for $Et_3Si\cdot$ radical additions from Table II with recently acquired[35] kinetic data for the reactions of phenyl radicals with aromatics shows that these two radicals exhibit remarkably similar behavior. For example, the rate constants at room temperature for the reaction of phenyl radicals with benzene, chlorobenzene, toluene, and styrene are 4.5×10^5, 1.2×10^6, 1.7×10^6, and 1.1×10^8 $M,^{-1}$ s^{-1}, respectively.[35]

For aromatics with a conjugated C–C double or triple bond the rate constant is enhanced by 2 orders of magnitude relative to simple aromatics. It is clear that addition occurs at the terminus of the double or triple bond to form a resonance-stabilized benzylic radical, e.g.

$$Et_3Si\cdot + H_2C{=}CHC_6H_5 \rightarrow Et_3SiCH_2\dot{C}HC_6H_5$$

The acetylenes are only slightly less reactive toward $Et_3Si\cdot$ than the olefins (compare entry 1 with 2–4 in Table III) while nitriles are considerably less reactive (see entry 5). In this connection, it is worth noting that trialkylsilyl radicals have been shown by EPR spectroscopy to add to *tert*-butylacetylene[7h,7i,36] and to pivalonitrile[37] to form persistent radicals of various types. Although these persistent radicals gave very strong EPR signals, it is clear that the initial step in their formation is not particularly fast.

The addition of $Et_3Si\cdot$ radicals to the isocyanide group is substantially faster than their addition to a nitrile, a terminal olefin, or an isocyanate. It has been shown by EPR spectroscopy[33h] that the triethylsilyl/*n*-butyl isocyanide reaction yields the imidoyl radical, $Et_3SiN{=}\dot{C}(CH_2)_3CH_3$. Attempts to identify by EPR the radical formed in the triethylsilyl/*tert*-butyl isocyanate reaction gave spectra that could not be unequivocally assigned to a particular adduct.

Silicon-centered free radicals, like radicals of many other classes, can be spin-trapped by certain nitrones[38] such as phenyl-*tert*-butyl nitrone (PBN).[38a,c] As might be expected, the rate constants for addition of the $Et_3Si\cdot$ radical to the C=N double bond of PBN are considerably greater than the rate constants for the addition of primary alkyl radicals (viz,[39] 1.3×10^5 M^{-1} s^{-1}) and secondary alkyl radicals (viz,[40] 6.8×10^4 M^{-1} s^{-1}). Certain aromatic nitroso spin traps such as 2,4,6-tri-*tert*-butylnitrosobenzene,[41] which are also known to form adducts with trialkylsilyl radicals,[42] were not examined because of their rather facile photolysis at the wavelength of the nitrogen laser (337 nm).[45]

Both aromatic and aliphatic nitro compounds trap trialkylsilyl[46,47] and related group 4 centered radicals.[47,48] Persistent

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(28) The following preexponential factors have been reported for radical additions to ethylene in the gas phase:[29] $10^{8.5}$ ($CH_3\cdot$); $10^{8.3}$ ($\dot{C}_2H_5$); $10^{7.8}$ ($(CH_3)_2\dot{C}H$); $10^{7.5}$ ($(CH_3)_3C\cdot$); $10^{8.0}$ ($\dot{C}F_3$) $10^{8.0}$ ($CF_2Br\cdot$); $10^{7.6}$ ($CH_2F\cdot$); $10^{7.8}$ ($\dot{C}Cl_3$).

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trialkylsiloxy nitroxide radicals have been obtained with nitromethane, nitroethane, and α-nitrotoluene.[47] Nitrobenzene absorbed too strongly at the excitation wavelength for the rate constant for its reaction with $Et_3Si\cdot$ radicals to be measured. However, our kinetic results with nitromethane show that the addition of $Et_3Si\cdot$ radicals to nitro groups is rapid. Nitro compounds should therefore make very effective spin traps for trialkylsilyl radicals.

Registry No. $Et_3Si\cdot$, 24669-77-0; $H_2C{=}CHC{\equiv}N$, 107-13-1; $H_2C{=}C(CH_3)C(O)OCH_3$, 80-62-6; $H_2C{=}CHC_6H_5$, 100-42-5; $H_2C{=}CCl_2$, 75-35-4; *trans*-$CH_3CH{=}CHC(O)OCH_3$, 623-43-8; $H_2C{=}CH_2$, 74-85-1; *cis*-$ClCH{=}CHCl$, 156-59-2; $Cl_2C{=}CCl_2$, 127-18-4; *trans*-$ClCH{=}CHCl$, 156-60-5; $H_2C{=}\overline{C(CH_2)_4C}H_2$, 1192-37-6; $H_2C{=}CH(CH_2)_3CH_3$, 592-41-6; $H_2C{=}CHC(CH_3)_3$, 558-37-2; $H\overline{C{=}CH(CH_2)_2C}H_2$, 142-29-0; $H\overline{C{=}CHO(CH_2)_2C}H_2$, 110-87-2; *trans*-$CH_3CH_2CH{=}CHCH_2CH_3$, 13269-52-8; $H\overline{C{=}CH(CH_2)_3C}H_2$, 110-83-8; $HC{\equiv}CC(CH_3)_3$, 917-92-0; $H_2C{=}C$, 536-74-3; $N{\equiv}CC(CH_3)_3$, 630-18-2; $N{\equiv}C{-}C_6H_5$, 100-47-0; $C{\equiv}N(CH_2)_3CH_3$, 2769-64-4; $O{=}C{=}NC(CH_3)_3$, 1609-86-5; $C_6H_5CH{=}N(O)C(CH_3)_3$, 3376-24-7; O_2NCH_3, 75-52-5; triethylsilane, 617-86-7; benzene, 71-43-2; chlorobenzene, 108-90-7; toluene, 108-88-3; anisole, 100-66-3; 1-methylnaphthalene, 90-12-0; phenylacetylene, 536-74-3; pyridine, 110-86-1; pyrrole, 109-97-7; furan, 110-00-9; thiophene, 110-02-1; norbornadiene, 121-46-0.

Supplementary Material Available: Tables V–XXXVII, giving detailed kinetic data (25 pages). Ordering information is given on any current masthead page.

Models for Compounds I of Peroxidases: Axial Ligand Effects

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Abstract: A combination of model studies, theoretical calculations, and "in vivo" experiments has recently shown that ferryl porphyrin π cations provide viable models for the two-electron oxidation intermediates (compounds I) observed in the catalytic cycles of peroxidases and catalases. Extended Hückel calculations predict significant spin delocalization on the axial ligand, if an electron is abstracted from the a_{2u} orbital of the ferryl porphyrin. Similar profiles are computed for zinc porphyrins. Redox, optical, and ESR data are presented that probe the effect of bound pyridine on zinc cation radicals. The ESR results support the trend predicted by the calculations and provide evidence of spin density delocalization on the axial pyridine in a_{2u} radicals. Such axial delocalization in vivo may provide a conduit for electron exchange between the oxidized transients and neighboring protein residues. A mechanism is therefore proposed for the formation of compound ES of cytochrome *c* peroxidase in which reaction with peroxide leads to a transient ferryl-a_{2u} radical followed by electron transfer from an easily oxidized residue via the proximal histidine. Studies of a_{1u} zinc radicals indicate that complexation by nitrogenous ligands does not alter the ground-state occupancy and offer a reasonable explanation for the recent observation that compound I of horseradish peroxidase reconstituted with zinc protoporphyrin exhibits an optical spectrum similar to that of catalase.

Peroxidases and catalases are hemoprotein enzymes which decompose hydrogen peroxide in animals and plants[2,3] (catalase has recently been invoked[4] in photosystem II of green plants and may thus be involved in photosynthetic oxygen evolution). Three spectrally distinct transients, which lie two oxidation levels above the resting enzymes, have been observed on treatment of the ferrihemes with peroxide: the two green species typified by compounds I of horseradish peroxidase[5] (HRP) and bovine liver catalase[6] (CAT) or chloroperoxidase[7] (CPO), and the red compound ES of cytochrome *c* peroxidase[8] (CCP). Compounds I have been assigned to ferryl porphyrin π-cation radicals in which one oxidizing equivalent is stored in the form of a tetravalent iron stabilized by oxygen [$O{=}Fe^{IV}$] and the second equivalent resides in a porphyrin cation.[9-16] On the other hand, compound ES is described as a ferryl species with the second electron abstracted from a nearby protein residue.[8,17] On the basis of model studies

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