82352-99-6; **9**, 82328-07-2; **10**, 101953-38-2; **11**, 101933-76-0; **12**, 101933-77-1; **13**, 82316-15-2; **14**, 101933-78-2; **15**, 82316-14-1; **16**, 82316-13-0; $H_2C{=}CHHgCl$, 762-55-0; $ClHC{=}CHHgCl$, 1190-78-9; $(CH_3)_3CCH{=}CHHgCl$, 36525-02-7; $PhCH{=}CHHgCl$, 36525-03-8; n-$C_6H_{13}CH{=}CHHgCl$, 36627-23-3; $(CH_3)_3CCH{=}C(CH_3)HgCl$, 38010-69-4; bicyclo[2.2.1]hept-2-ene, 498-66-8; diethyl 2,3-diazabicyclo[2.2.1]-5-ene-2,3-dicarboxylate, 14011-60-0; bicyclo[3.2.1]oct-2-en-6-one, 31444-29-8; bicyclo[2.2.2]oct-2-ene, 931-64-6; bicyclo[2.2.1]hepta-2,5-diene, 121-46-0; 2-(3,3-dimethyl-1-butenyl)-3-methylbicyclo[2.2.1]heptane, 82316-17-4; 2-(3,3-dimethyl-1-butenyl)-3-vinylbicyclo[2.2.1]heptane, 82316-18-5; 2-(3,3-dimethyl-1-butenyl)-3-phenylbicyclo[2.2.1]heptane, 82316-20-9; 2-(3,3-dimethyl-1-butenyl)-3-ethynylbicyclo[2.2.1]heptane, 82316-19-6; 3-cyano-2-(3,3-dimethyl-1-butenyl)bicyclo[2.2.1]heptane, 82316-16-3; lithium chloride, 7447-41-8; palladium chloride, 7647-10-1.

Pentamethyldisilyl Radical: Absolute Rate Constants for Its Formation and for Some Halogen Abstraction and Addition Reactions[1]

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Pentamethyldisilane is a better hydrogen donor than Et_3SiH toward *tert*-butoxyl (k's for the overall reaction are 17 and 5.7×10^6 M^{-1} s^{-1}, respectively, at ca. 27 °C) and toward primary alkyl radicals (k's for Si–H bond cleavage are ca. 10 and 1.0×10^4 M^{-1} s^{-1}, respectively, at 120 °C). Absolute rate constants for various reactions of the $Me_3SiSiMe_2\cdot$ radical have been measured by laser flash photolysis at room temperature. In halogen atom abstractions, for example, the $Me_3SiSiMe_2\cdot$ radical is slightly less reactive than $Et_3Si\cdot$, but it is more reactive than n-$Bu_3Ge\cdot$ and n-$Bu_3Sn\cdot$. Pentamethyldisilane would appear to offer an attractive alternative to n-Bu_3SnH and n-Bu_3GeH in radical chain reactions in which the desired product is formed by a hydrogen transfer not to the organic radical formed initially but to a second radical formed by a slow β-scission or rearrangement of the initial radical.

Tri-n-butyltin hydride has become an extremely popular reagent in organic synthesis by free-radical chain reactions. It is frequently employed in systems in which the initially formed organic radical must first undergo a unimolecular reaction such as a β-scission,[3]

$$n\text{-}Bu_3Sn\cdot + R_1X \rightarrow R_1\dot{X}SnBu_3 \xrightarrow{\beta} R_1\cdot \xrightarrow{n\text{-}Bu_3SnH} R_1H$$

or a rearrangement,[4]

$$n\text{-}Bu_3Sn\cdot + R_2X \rightarrow R_2\cdot \xrightarrow{\varrho} R_3\cdot \xrightarrow{n\text{-}Bu_3SnH} R_3H$$

if the desired product is to be obtained. In certain cases, the scission or rearrangement of the intermediate radical ($R_1\dot{X}SnBu_3$ or $R_2\cdot$) is slow relative to its reduction by tin hydride to form unwanted products ($R_1XHSnBu_3$ or R_2H). Under such conditions, a less active hydrogen donor that can nevertheless fulfill the other requirements of these chain processes can provide a very useful alternative to the usual tin hydride method. We have previously shown that tri-n-butylgermanium hydride has the necessary chemical properties to fulfill these requirements. That is, n-$Bu_3Ge\cdot$ adds to multiple bonds and abstracts halogen atoms with rates similar to those of the n-$Bu_3Sn\cdot$ radical[5] while n-Bu_3GeH is only ca. $^1/_{20}$ as good as n-Bu_3SnH as an H atom donor to primary alkyl radicals.[6] These properties of n-Bu_3GeH/n-$Bu_3Ge\cdot$ have already been demonstrated to be useful in some synthetic procedures.[7]

Trialkylsilyl radicals are more reactive in additions to multiple bonds[8,9] and in halogen atom abstractions[10] than n-$Bu_3Sn\cdot$ and n-$Bu_3Ge\cdot$, but they are rather poor H atom donors toward alkyl radicals and tend therefore not to support chain reactions except at elevated temperatures.[11,12] However, disilanes have been shown by com-

Table I. Rate Constants for the Reaction of *tert*-Butoxyl Radicals with Some Silanes[a]

silane	k, M^{-1} s^{-1}	ref
$Me_3SiSiMe_2H$	1.7×10^7	this work
$Me_3SiSiMe_2D$	9.9×10^6	this work
$PhSiH_3$	7.5×10^6	14
$PhSiMe_2H$	6.6×10^6	14
Et_3SiH	5.7×10^6	14

[a] Temperatures: 294 ± 1 K for $Me_5Si_2H(D)$ and ca. 300 for the other three silanes.

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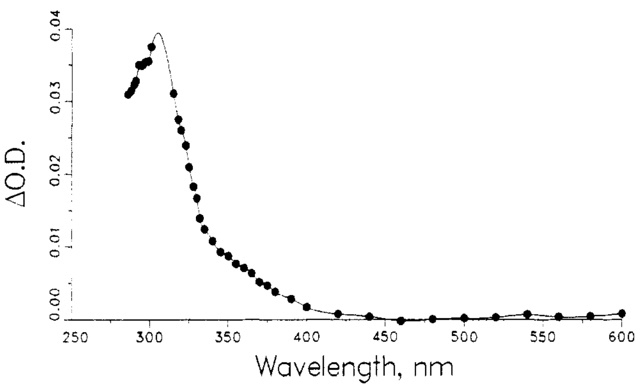


Figure 1. Absorption spectrum of $Me_5Si_2\cdot$ radical obtained by 308-nm photolysis of ~0.4 M di-*tert*-butyl peroxide and ~1.4 M Me_5Si_2H in isooctane. (Solid line is only an artist's "fit" to the experimental points.)

petitive studies to be significantly better hydrogen donors than silanes toward the $CCl_3\cdot$ radical.[12] In this note we report on the results of a kinetics investigation of the generation of the $Me_3SiSiMe_2\cdot$ radical from Me_5Si_2H and on some of its reactions. Our results suggest that in a synthesis which involves a necessary, but very slow, β-scission or rearrangement the use of a disilane will probably give better yields of the desired product than will tri-*n*-butylgermane.

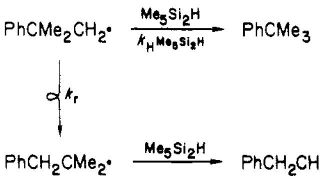
Results

Formation and Characterization of the $Me_3SiSiMe_2\cdot$ Radicals. Laser flash photolysis[5,8-10,13,14] of di-*tert*-butyl peroxide in isooctane containing pentamethyldisilane using 308-nm light pulses from an excimer laser yielded the transient absorption spectrum shown in Figure 1. We ascribe this spectrum to the $Me_3SiSiMe_2\cdot$ radical (eq 1) and

$$Me_3CO\cdot + Me_3SiSiMe_2H \rightarrow Me_3COH + Me_3SiSiMe_2\cdot \quad (1)$$

note that its absorption occurs at significantly longer wavelengths than does that of the $Et_3Si\cdot$ radical ($\lambda_{max} <$ 280 nm).[13] Indeed, the spectrum of this disilyl radical (λ_{max} ~310 nm) is more similar to that of $Ph_3Si\cdot$ ($\lambda_{max} = 331$ nm)[13] than to that of $Et_3Si\cdot$. By monitoring the growth of this absorption (at 320 or 325 nm) the rate constants for reaction 1 and for the analogous reaction with $Me_3SiSiMe_2D$ were determined. These results are compared with rate constants for H abstraction from some other silanes by the $Me_3CO\cdot$ radical[14] in Table I. Although the range of reactivities is not large it is clear that the disilane is a better H donor to *tert*-butoxyl than are the monosilanes.

Rate of Reaction of $Me_3SiSiMe_2H(D)$ with a Primary Alkyl Radical. To measure this rate we chose the neophyl rearrangement as our "clock".[15] The original, EPR measured Arrhenius parameters for this rearrangement[16] have been revised by Franz et al.[17] as a result of a careful study of the n-Bu_3SnH/neophyl chloride reaction. The Arrhenius parameters given by Franz et al.[17] for the rearrangement (viz., $\log A/s^{-1} = 11.5$, $E = 11.82$ kcal/mol) are based on the assumption that the neophyl radical will react with n-Bu_3SnH at the same rate as that measured for primary alkyl radicals.[18] However, recent studies[19] have shown that the Arrhenius parameters for reaction of the neopentyl radical with n-Bu_3SnH are slightly different from those for an n-alkyl radical. Fortunately, the "corrected" Arrhenius parameters for the neophyl rearrangement (viz., $\log A/s^{-1} = 10.98$, $E = 10.83$ kcal/mol) yield essentially the same rate constant for the rearrangemet at 120 °C, the temperature of our current experiment (viz., 9.0×10^4 s^{-1} vs. 9.4×10^4 s^{-1} calculated from Franz et al.'s equation.)



The relationship,

$$\frac{k_H^{Me_5Si_2H}}{k_r} = \frac{1}{[Me_5Si_2H]} \cdot \frac{[PhCMe_3]}{[PhCH_2CHMe_2]} \quad (2)$$

is valid provided that the disilane is the only source of hydrogen and that its concentration does not change significantly during an experiment.

To check on the validity of eq 2 a number of experiments were carried out in which 0.04 M di-*tert*-butyl peroxide, 0.2 M neophyl bromide, and Me_5Si_2D at concentrations from 0.5 to 2.0 M were heated for periods of 5 to 60 min in *n*-octane as solvent (*n*-nonane as internal standard) at 120 °C in sealed, degassed glass tubes. A chain reaction ensued (chain lengths, ν = ca. 30–110), the yield of the two butylbenzenes was >90% based on neophyl bromide consumed. However, both of these butylbenzenes contained significant fractions of undeuterated material even with 2.0 M Me_5Si_2D (ca. 30% for *tert*-butylbenzene and ca. 20% for isobutylbenzene). Since the reaction is a chain process we assume that the solvent acts as a hydrogen donor/chain transfer agent:

$$PhCMe_2CH_2\cdot + C_8H_{18} \rightarrow PhCMe_3 + C_8H_{17}\cdot$$

$$C_8H_{17}\cdot + Me_5Si_2D \rightarrow C_8H_{17}D + Me_5Si_2\cdot$$

$$Me_5Si_2\cdot + PhCMe_2CH_2Br \rightarrow Me_5Si_2Br + PhCMe_2CH_2\cdot$$

In neat Me_5Si_2D (4.6 M, no internal standard) under similar conditions the monodeuterated fraction of the *tert*-butylbenzene was >90%, which indicates that the neophyl radical is reacting as would be expected. The ratio[20] [*tert*-butylbenzene]/[isobutylbenzene] was 1.81 and hence $k_D^{Me_5Si_2D}/k_r = 0.39$ M^{-1}. Under exactly the same conditions with neat Me_5Si_2H (ν = 120–600) the product ratio was 5.34 which yields $k_H^{Me_5Si_2H}/k_r = 1.16$ M^{-1} and hence $k_H^{Me_5Si_2H}/k_D^{Me_5Si_2D} = 3.0$. This kinetic isotope effect is in the range reported[21] for abstraction by alkyl radicals from Si_2H_6 vs. Si_2D_6 in the gas phase. Furthermore, taking $k_r = 9.0 \times 10^4$ s^{-1} (vide supra) yields $k_H^{Me_5Si_2H} = 1.0 \times 10^5$ M^{-1} s^{-1} at 120 °C.

Rate of Reaction of $Et_3SiH(D)$ with a Primary Alkyl Radical. For comparative purposes we also em-

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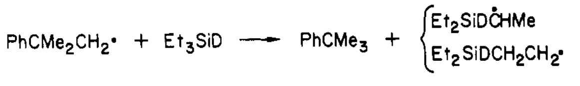
Table II. Absolute Rate Constants for Some Reactions of $Me_3SiSiMe_2\bullet$, $Et_3Si\bullet$, n-$Bu_3Ge\bullet$, and n-$Bu_3Sn\bullet$ Radicals at Room Temperature[a]

substrate	$Me_3SiSiMe_2\cdot$ k, $M^{-1}\ s^{-1}$	$Et_3Si\cdot$ k, $M^{-1}\ s^{-1}$	n-$Bu_3Ge\cdot$ k, $M^{-1}\ s^{-1}$	n-$Bu_3Sn\cdot$ k, $M^{-1}\ s^{-1}$
tert-butyl bromide	$(2.6 \pm 0.2) \times 10^8$	1.1×10^{9} [b]	8.6×10^{7} [f]	1.7×10^{8} [f]
n-butyl bromide	$(1.6 \pm 0.15) \times 10^8$	5.4×10^{8} [b,c]	4.6×10^{7} [f,h]	2.6×10^{7} [f,h]
tert-butyl chloride	$(4.2 \pm 0.2) \times 10^5$	2.5×10^{6} [b]	$<5 \times 10^{4}$ [f]	2.7×10^{4} [f]
tetrachloroethylene	$(4.0 \pm 0.15) \times 10^6$	1.0×10^{7} [d,e]		
1,3-*trans*-pentadiene	$(7.6 \pm 0.5) \times 10^7$	1.4×10^{8} [f]	4.6×10^{7} [f]	6.8×10^{7} [f]
1-hexene	$(3.9 \pm 0.3) \times 10^6$	4.8×10^{6} [d]		
benzil	$(4.4 \pm 0.3) \times 10^8$	3.3×10^{8} [g]	9.6×0^{7} [f]	1.3×10^{8} [f]
propionaldehyde	$(2.0 \pm 0.2) \times 10^7$	1.2×10^{7} [g]	$<1 \times 10^{5}$ [f]	

[a] Temperatures: 294 ± 2 K for $Me_3SiSiMe_2\cdot$ and 295–302 K for the other three radicals. Error limits for $Me_3SiSiMe_2\cdot$ data represent 95% confidence limits. [b] Reference 10. [c] 1-Bromopentane. [d] Reference 9. [e] Note that this reaction is primarily a chlorine atom abstraction, see: Horowitz, A. *J. Am. Chem. Soc.* **1985**, *107*, 318–321. [f] Reference 5. [g] Reference 8. [h] 1-Bromopropane.

ployed the neophyl "clock" to measure the rate of H(D) abstraction from triethylsilane. In neat Et_3SiD (5.45 M) at 120 °C under conditions similar to those described above $PhCMe_2CH_2D$ and $PhCMe_3$ were formed in approximately equal amounts in a chain reaction ($\nu = 15–50$). It is clear that hydrogen abstraction from the ethyl groups,



$$PhCMe_2CH_2\cdot + Et_3SiD \longrightarrow PhCMe_3 + \begin{cases} Et_2SiD\dot{C}HMe \\ Et_2SiDCH_2CH_2\cdot \end{cases}$$

is competitive with deuterium abstraction,

$$PhCMe_2CH_2\cdot + Et_3SiD \xrightarrow{k_D^{Et_3SiD}} PhCMe_2CH_2D + Et_3Si\cdot$$

The carbon-centered radicals produced from the Et_3SiD must continue the chain, presumably by abstracting D from the Et_3SiD. To calculate the reactivity of the silyl deuterium we take the measured ratio $[PhCMe_2CH_2D]/[\text{isobutylbenzene}] = 0.21$, from which $k_D^{Et_3SiD}/k_r = 0.039\ M^{-1}$ and $k_D^{Et_3SiD} = 3.5 \times 10^3\ M^{-1}\ s^{-1}$ at 120 °C. With the reasonable assumption[21] that the deuterium kinetic isotope effect will be ca. 3 for this reaction, we can estimate that $k_H^{Et_3SiH} \approx 1 \times 10^4\ M^{-1}\ s^{-1}$ at this temperature.

Reactivity of the $Me_3SiSiMe_2\cdot$ Radical. Absolute rate constants for some reactions of the disilyl radical were measured at ambient temperatures. The radical was generated from the disilane (~1.4 M) in an essentially "instantaneous" manner by using *tert*-butoxyl radicals formed from di-*tert*-butyl peroxide (~0.4 M) by the pulse from an excimer laser (308 nm, ~4 ns, up to 80 mJ per pulse). The rate of decay of the radical in the presence of various concentrations of substrate was monitored at 325 nm, and absolute rate constants were calculated from these decay traces in the usual way.[5] The rate constant for reaction with benzil was determined by monitoring the growth of the disilyl radical/benzil adduct at 378 nm; benzil was also used as a "probe" to measure the rate constant for reaction of $Me_3SiSiMe_2\cdot$ with propionaldehyde.[8-10] In these two experiments the *tert*-butoxyl radicals were generated from the peroxide (~2.8 M) by photolysis with the pulse from a nitrogen laser (337.1 nm, ~8 ns up to 10 mJ per pulse). The results are presented in Table II together with previously determined absolute rate constants for reaction of the $Et_3Si\cdot$, n-$Bu_3Ge\cdot$, and n-$Bu_3Sn\cdot$ radicals with the same substrates.

Discussion

In retrospect, the similarity in the absorption spectra of the $Me_3SiSiMe_2\cdot$ and $Ph_3Si\cdot$ radicals is not too surprising. For these two species the configuration at their radical centers (degree of nonplanarity) and/or the extent of the delocalization of the unpaired electron have been shown to be rather similar by ESR spectroscopy. That is, the $^{29}Si_\alpha$ hyperfine splittings (hfs) for $Me_3SiSiMe_2\cdot$ and trimesitylsilyl[22] radicals in solution are 137[27,28] and 135 G,[24] respectively, indicating that both these radicals are much more nearly planar than trialkylsilyl radicals, e.g., for $Me_3Si\cdot$ the $^{29}Si_\alpha$ hfs is ca. 181 G.[27-30] It is well-known that when a silicon atom replaces carbon in a position adjacent to a radical center it "flattens" the radical.[31,32] Similarly, such substitution activates the radical's precursor.[33]

Table III. Rate Constants for Some Hydrogen Abstraction Reactions at 120 °C

reaction[a]	k, $M^{-1}\ s^{-1}$	ref
$PhCMe_2CH_3\cdot + Et_3SiH \rightarrow Et_3Si\cdot$	1.0×10^4	this work
$PhCMe_2CH_2\cdot + Me_5Si_2H \rightarrow Me_5Si_2\cdot$	1.0×10^5	this work
$CH_2{=}CH(CH_2)_4\cdot + n\text{-}Bu_3GeH \rightarrow n\text{-}Bu_3Ge\cdot$	6.7×10^5	6
$Me_3CCH_2\cdot + n\text{-}Bu_3SnH \rightarrow n\text{-}Bu_3Sn\cdot$	1.0×10^7	19
$RCH_2CH_2\cdot + n\text{-}Bu_3SnH \rightarrow n\text{-}Bu_3Sn\cdot$ [b]	1.1×10^7	18

[a] The hydrocarbon product is not shown. [b] Combined data for R = H and C_2H_5.

In Table III are listed rate constants at 120 °C for hydrogen atom abstraction by primary alkyl radicals from trialkyl hydrides of tin, germanium, and silicon and from $Me_3SiSiMe_2H$. The values for the tin and germanium hydrides were calculated from the given Arrhenius parameters for the reaction in question. The order of reactivity is n-Bu_3SnH > n-Bu_3GeH > Me_5Si_2H > Et_3SiH, as expected, with hydrogen donating ability covering a 10^3 range. The estimated rate constant of $1 \times 10^4\ M^{-1}\ s^{-1}$ for abstraction of the silane hydrogen from Et_3SiH at 120 °C is in satisfactory agreement with global rate constants of

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(22) Triphenylsilyl is too reactive (in addition to aromatic rings, in particular, and hence to the $Ph_3Si\cdot$ precursor) to have been detected in solution. A single-crystal study[23] of $Ph_3Si\cdot$ in Ph_3SiH gave 79.6 G as the isotropic $^{29}Si_\alpha$ hfs. We presume crystal forces have flattened the radical center quite considerably relative to its solution configuration. The reactivity problem of the triarylsilyl radicals' precursor can be overcome by steric hindrance of the aromatic rings as has been found for trimesitylsilyl[24,25] and tris(3,5-di-*tert*-butylphenyl)silyl.[26]

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1.4×10^4 and 0.45×10^4 M^{-1} s^{-1} that can be calculated for the overall hydrogen abstraction reaction of $CCl_3\cdot$ with Et_3SiH and Me_3SiH in solution at this temperature.[34] It is also in agreement with a value of $\sim 1.0 \times 10^4$ M^{-1} s^{-1} that can be calculated for abstraction of silane hydrogen from Me_3SiH by the methyl radical in the gas phase[21b] at 120 °C.

If we make the reasonable assumption that the Arrhenius preexponential factors for hydrogen abstraction have "normal" values[35] of $10^{8.5}$ M^{-1} s^{-1}, then we can calculate that at 25 °C $k_H^{Me_5Si_2H} \approx 8 \times 10^3$ M^{-1} s^{-1} and $k_H^{Et_3SiH} \approx 4 \times 10^2$ M^{-1} s^{-1}. These values may be compared with rate constants of $\sim 3 \times 10^6$ M^{-1} s^{-1} and $\sim 1 \times 10^5$ M^{-1} s^{-1} for hydrogen abstraction from *n*-Bu_3SnH[18,19] and *n*-Bu_3GeH,[6] respectively, by primary alkyl radicals at this temperature.

The pentamethyldisilyl radical is highly reactive in halogen abstractions and in additions to C═C and C═O double bonds (see Table II). It is less reactive than triethylsilyl in abstractions and in additions to C═C double bonds as expected, but it appears to be slightly more reactive in additions to C═O double bonds.

Concluding Remarks. Pentamethyldisilane would appear to offer an alternative to tin hydride (and germanium hydride) in radical chain reactions in which the desired product must be formed by a *slow* hydrogen transfer.[36] The pentamethyldisilyl radical is more reactive in halogen abstractions and additions than the tri-*n*-butyltin or tri-*n*-butylgermyl radicals and it is only slightly less reactive than $Et_3Si\cdot$ (see Table II). As a hydrogen donor to primary alkyl radicals the disilane has ca. 8–16% of the reactivity of *n*-Bu_3GeH and ca. 0.3–1% of the reactivity of *n*-Bu_3SnH in the temperature range 25–120 °C.

Experimental Section

Pentamethyldisilane was prepared by reaction of pentamethyldisilyl chloride with lithium aluminum hydride[37] (or deuteride). The chloride was obtained by treating hexamethyldisilane with concentrated H_2SO_4 and NH_4Cl according to the procedure of Kumada et al.[38] Et_3SiD was prepared from Et_3SiCl by reaction with $LiAlD_4$. Neophyl bromide was prepared from neophyl chloride (Columbia Organic Chemicals) by the procedure of Fainberg and Winstein.[39] All other compounds were commercial materials that were, in general, purified before use by standard methods. The laser flash photolysis equipment has been described in previous papers from this laboratory.[5,40,41] The relative (and absolute) yields of *tert*-butylbenzene and isobutylbenzene were determined by VPC on a Varian 6000 gas chromatograph on a DB1-30W column and the extent of deuterium incorporation in these compounds by GC/MS on a Hewlett-Packard 5995 instrument.

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Registry No. $Me_3SiSiMe_2\cdot$, 23290-58-6; $Me_3C\cdot$, 3141-58-0; $Me_3SiSiMe_2H$, 812-15-7; $Me_3SiSiMe_2D$, 101932-87-0; Me_3CBr, 507-19-7; *n*-BuBr, 109-65-9; Me_3CCl, 507-20-0; $PhCMe_2CH_2\cdot$, 25087-41-6; Et_3SiH, 617-86-7; 1,3-*trans*-pentadiene, 2004-70-8; 1-hexene, 592-41-6; benzil, 134-81-6; propionaldehyde, 123-38-6; tetrachloroethylene, 127-18-4.

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