# Comments on the Formation of Silanones in the Thermolysis of Hydridosilyl Peroxides

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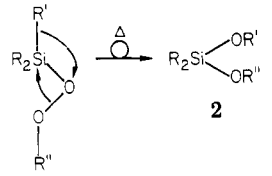
The reported generation of silanones ($R_2Si{=}O$) in the condensed-phase thermolysis of hydridosilyl peroxides ($R_2Si(H)OO$-*t*-Bu) has been reexamined. Alternative mechanisms involving rearrangement of the peroxides followed by various intra- and intermolecular condensations are proposed, and experimental evidence consistent with these alternatives is presented. The reported silanone-trapping reactions with siloxanes, silyl hydride, and α-methylstyrene are interpreted as involving condensation, direct reaction with silyl peroxide, and air oxidation, respectively.

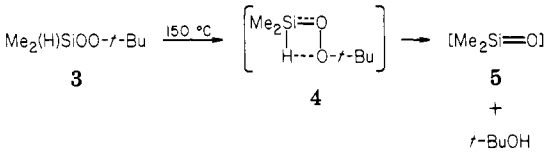
## Introduction

It has long been known[1] that silyl peroxides (**1**) undergo two types of thermal reactions: (1) homolytic cleavage of the O–O bond and (2) rearrangement to dialkoxysilanes such as **2**.



**1** **2**

Recently there have been several reports[2-4] claiming the generation of silanones (compounds with a p–pπ Si=O double bond) in the thermal decomposition of silyl peroxides of the type $R_2(H)SiOOR'$. Considerable evidence has been presented in support of thermal decomposition of these peroxides through a concerted intramolecular transfer of the α-hydrogen from silicon to the nonadjacent peroxide oxygen to concomitantly afford silanone and alcohol. For example, dimethylsilyl *tert*-butyl peroxide (**3**) is reported to decompose in nonane at 150 °C to produce *tert*-butyl alcohol in 81% yield. The transition state was depicted as **4**.



**3** **4** **5** + *t*-BuOH

This work will question the interpretation of the reported results, suggest alternative mechanisms, and present experimental evidence in favor of these different interpretations.

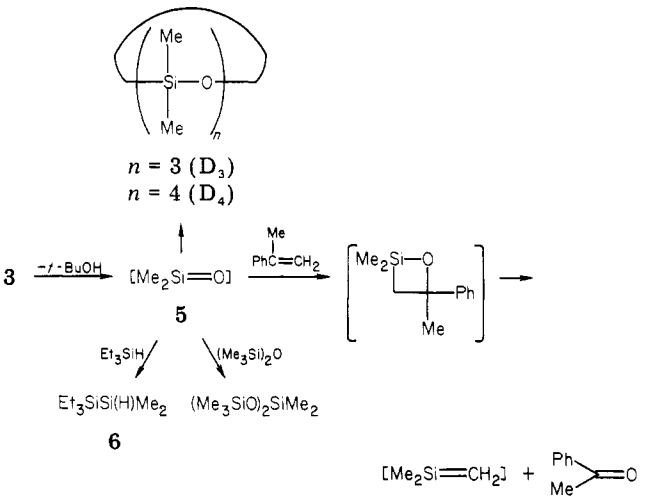
## Results and Discussion

The evidence which has been reported[4] for the decomposition of hydridosilyl peroxides to silanones is as follows.

(A) The rate of peroxide disappearance is cleanly first order, thus ruling out bimolecular reactions of the peroxides.

(B) Negative values of the activation entropies ($\Delta S^{\ddagger}$ = −29 J/(mol deg) for **3**) suggested cyclic transition-state **4**.

Scheme I



(C) Decomposition produced cyclosiloxanes presumably arising from cyclic oligomerization of silanones. For example, thermolysis of **3** afforded hexamethylcyclotrisiloxane ($D_3$, 2%) and octamethylcyclotetrasiloxane ($D_4$, 13%). An increase in initial concentration of silyl peroxide resulted in an increase of cyclosiloxane yields, but no change in decomposition rates.

(D) Cothermolysis of different hydridosilyl peroxides produced mixed cyclosiloxanes. Thus thermal decomposition of **3** and $Et_2(H)SiOO$-*t*-Bu yielded cyclosiloxanes of the general type $(Me_2SiO)_Y(Et_2SiO)_z$.

(E) Silanones were apparently trapped by reagents containing an Si–O σ bond. Thus decomposition of **3** in the presence of hexamethyldisiloxane afforded the formal product of silanone **5** insertion, $(Me_3SiO)_2SiMe_2$ (2%).

(F) Decomposition of the hydridosilyl peroxides in neat triethylsilane led to formation of $Et_3SiOSi(H)R_2$, presumably through insertion of the silanone into the Si–H bond of the solvent. Thus thermolysis of **3** in $Et_3SiH$ afforded the disiloxane insertion product **6** in 98% yield!

(G) Decomposition of hydridosilyl peroxides in α-methylstyrene solution resulted in the formation of acetophenone in 10–12% yield. This was presumed to take place via cycloaddition of silanone to the olefin followed by decomposition of the resulting silaoxetane ring to ketone and a silene.

These reactions are summarized in Scheme I.

Our initial entry into this area was to attempt to use this method to synthesize di-*tert*-butylsilanone. Thus di-*tert*-butylsilyl *tert*-butyl peroxide (**7**) was prepared by treating di-*tert*-butylbromosilane with the complex of DABCO and *tert*-butyl hydroperoxide.[5,6] Thermolysis of **7** in octane at 150 °C resulted primarily in the formation

(1) Brandes, D.; Blaschette, A. *J. Organomet. Chem.* **1974**, *75*, 1.
(2) Tomadze, A. V.; Yablokova, N. V.; Yablokov, V. A. *Zh. Obshch. Khim.* **1979**, *49*, 1171.
(3) Yablokov, V. A.; Tomadze, A. V.; Yablokova, N. V.; Razuvaev, G. A. "Proceedings of the 9th International Conference on Organometallic Chemistry", Dijon, France, Abstract, 1979; p A2.
(4) Tomadze, A. V.; Yablokova, N. V.; Yablokov, V. A.; Razuvaev, G. A. *J. Organomet. Chem.* **1981**, *212*, 43.
(5) Oswald, A. A. U.S. Patent 3 236 850, 1966.
(6) Fan, Y. L.; Shaw, R. G. *J. Chem. Soc.*, **1973**, *38*, 2410.

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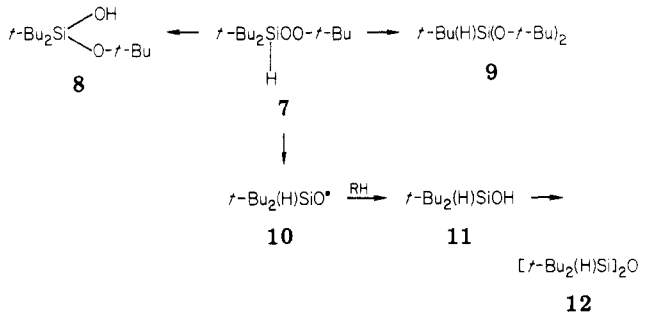
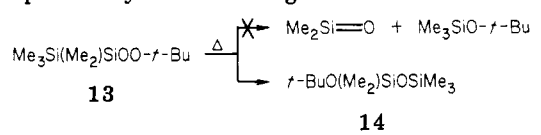
Table I. Thermolysis of 7 in Octane at 150 °C

| | time, h | 8 | 9 | 11 | 12 | total yield, % |
|---|---|---|---|---|---|---|
| without $Et_3N$ | 3 | 30.8 | 41.7 | 2.5 | 5.3 | 80.3 |
| 0.1 equiv of $Et_3N$ | 1 | 28.4 | 40.7 | 11.8 | 4.3 | 85.2 |

of silyl ethers **8** and **9**. These are of course the products expected from the ususal thermal rearrangement of silyl peroxides. Thus migration of hydrogen from silicon to oxygen with migration of *tert*-butoxy to silicon affords **8**, while *tert*-butyl migration yields **9**. In addition some homolytic cleavage to form siloxy radical **10** occurred as evidenced by the observation of small amounts of silanol **11** and disiloxane **12** in the product mixture. There was *no* evidence for the formation of di-*tert*-butylsilanone. Triethylamine was found to catalyze this reaction. Thermolysis of **7** with 0.1 equiv of $Et_3N$ present increased the rate ca. fourfold but changed the yields of the products only slightly (Table I).

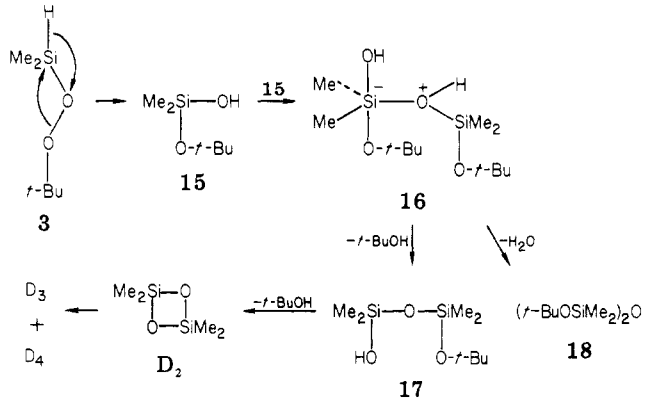



Next, attempts were made to synthesize disilanyl peroxide **13** from chloropentamethyldisilane and DABCO·$2HO_2$-*t*-Bu. However, only the product of thermal rearrangement, **14**, could be isolated (73%) as had been earlier reported by Kawazumi and Marai.[7] Following the reaction by NMR did allow observation of **13**, but it was always accompanied by an increasing amount of disiloxane **14**.

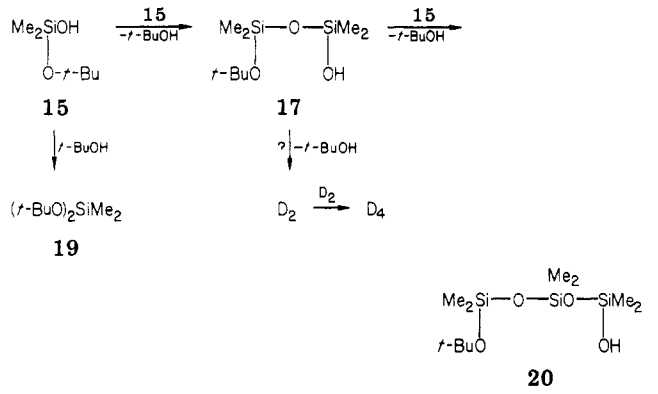



Since neither of our hydridosilyl peroxides (**7** and **13**) gave any evidence of silanone formation upon thermolysis, it was not obvious why the reported systems such as **3** should behave differently. It has been known for some time that if there is a good migrating group on silicon, thermally induced intramolecular rearrangement of silyl peroxides will compete with homolytic cleavage.[1] Since the results of thermolysis of **7** reveal hydrogen to be even better than *tert*-butyl in such migrations, it would be expected that a major pathway in the thermolysis of **3** would be intramolecular rearrangement to form dimethyl-*tert*-butoxysilanol (**15**). It is also possible that **15** could serve as the precursor to the observed cyclosiloxane products, $D_3$ and $D_4$ (Scheme II). Silanols are known to readily condense with elimination of water to form disiloxanes. Alkoxysilanols present the possibility of condensation occurring with alcohol expulsion to form disiloxanes. Indeed, the reaction of silanols with alkoxysilanes to afford alcohols and disiloxanes is long established.[8] Since such

Scheme II




Scheme III

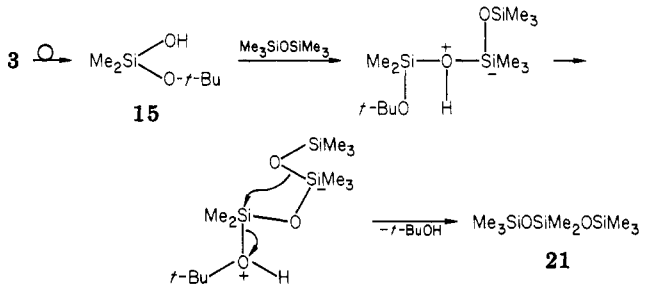



condensations are thought to occur by way of an intermediate pentacoordinate silicon,[9] the release of steric strain should favor loss of *tert*-butyl alcohol from intermediate **16** to form silanol **17** rather than loss of water to form disiloxane **18**. Silanol **17** could then undergo intramolecular condensation with loss of *tert*-butyl alcohol to form the often postulated (but never observed) cyclodisiloxane, $D_2$. Dimerization of $D_2$ would lead to the observed $D_4$, while condensation of $D_2$ and **15** could lead to $D_3$ and *tert*-butyl alcohol. Thus the route displayed in Scheme II is totally consistent with the results of the Russian workers in that all products are accounted for, unimolecular kinetics are consistent with step one as rate determining, and this step provides a contrained transition state with the corresponding negative $\Delta S^{\ddagger}$.

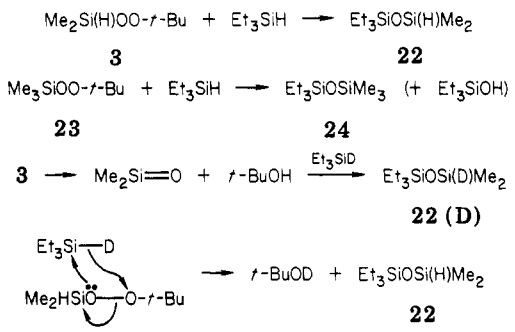
For a probe of this mechanistic possibility, dimethyl-*tert*-butoxysilanol (**15**) was synthesized and thermolyzed. Silanol **15** was prepared treating dichlorodimethylsilane sequentially with *tert*-butyl alcohol and water. This silanol proved to be quite stable at room temperature but at temperatures >100 °C reacted rapidly. Thermolysis of **15** in tridecane (3 h, 150 °C) resulted in complete consumption of **15**. The products were found to be dependent upon the concentration of the starting silanol. Pyrolysis of dilute solutions (5%) produced three major products—$D_4$, silanol **17**, and dimethyldi-*tert*-butoxysilane (**19**). Pyrolysis of 20% and 40% solutions also afforded three major products—**17**, **19**, and 5-*tert*-butoxyhexamethyltrisiloxan-1-ol (**20**)—and no detectable $D_4$ (Scheme III). It should be noted that these results are inconsistent with those reported[4] for hydridosilyl peroxide thermolysis where the yield of cyclosiloxane increased with increased initial concentration of peroxide.

(7) Kawazumi, K.; Murai, B. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1951.
(8) Noll, W. "Chemistry and Technology of Silicones"; Academic Press: New York; 1968; p 207.
(9) Eaborn, C. "Organosilicon Compounds"; Butterworths; London; 1960; p 103 ff.

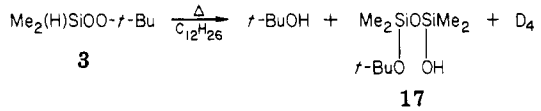
**Scheme IV**



**Scheme V**



It might be assumed that our observation of **17** as a major product in the thermolysis of **15** rules out **15** as an intermediate in the thermolysis of **3** since **17** was not observed by the Soviet group. However, in our hands when solutions of dimethylsilyl *tert*-butyl peroxide (**3**) (3–20% solutions in dodecane) were pyrolyzed (125–150 °C), there was observed by GCMS silanol **17** in addition to $D_4$. Silanol **17** was always formed in higher yield than $D_4$, and only minute traces of $D_3$ were ever seen. We note that on nonpolar GC columns (e.g., 6 ft, 5% SE30) $D_4$ and **17** had nearly identical retention times and produced one broad peak. Thus it is quite possible that this peak was mistakenly assumed to be composed entirely of $D_4$. It should also be noted that $D_3$ would be the expected product of intramolecular condensation of **20**.

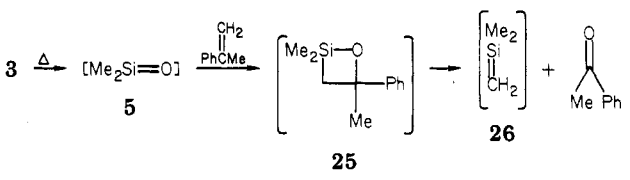


While our alternative mechanism (Scheme II) will account for observations A–D (vide supra), it does not obviously explain the trapping results E–G.

The trapping of silanone by reagents containing a Si–O $\sigma$ bond can be alternatively explained by condensation reactions of initial intermediate **15**. For example, it was reported that the thermolysis of silyl peroxide **3** in the presence of hexamethyldisiloxane resulted in a 2% yield of the product of silanone **5** insertion, trisiloxane **21**. A condensation route to this product is provided in Scheme IV.

The essentially quantitative trapping of $Me_2Si{=}O$ by $Et_3SiH$ could also be explained by a condensation process. However, this is not required. Even though it was reported[4] that $Me_3SiOO$-*t*-Bu (**23**) did not react with $Et_3SiH$ under thermolysis conditions, in our hands this reaction *does* occur to afford mixed disiloxane **24** in 72% yield (Scheme V). This reaction was repeated several times, and, even when the reaction mixture was thoroughly degassed, the formation of **24** was accompanied by variable amounts of $Et_3SiOH$. Thus, the origin of **24** could either be direct reaction of peroxide **23** and $Et_3SiH$ or $Et_3SiOH$. However, the crucial point is that the reaction between

**Scheme VI**



silylhydride and silyl peroxide does not require the peroxide to possess a hydridosilyl group. Since there is a dramatic difference between our results for the reaction of $Et_3SiH$ and **23** and those reported earlier, it was decided to conduct a labeling experiment. If in the cothermolysis of **3** and $Et_3SiH$ the disiloxane product **22** is formed by silanone insertion, the resulting products will be *t*-BuOH and deuterated **22** if $Et_3SiD$ is employed. If, however, the reaction is simply between **3** and $Et_3SiD$, the alcohol will be deuterated and not the disiloxane (Scheme V). We find that thermolysis of **3** in an octane solution containing $Et_3SiD$ produces *t*-BuOD and only nondeuterated **22**. These results are not in keeping with silanone insertion.

Last, there is the reported observation that decomposition of hydridosilyl peroxides in $\alpha$-methylstyrene affords acetophenone.[4] This was interpreted as evidence for the intermediacy of silanones which cycloadded to the olefin to yield a silaoxetane (**25**) which in trun decomposed to silene **26** and acetophenone (10–12%) (Scheme VI). While we have produced no experimental data to comment on this reaction and the incredibly terse experimental section of the report[4] (no reaction conditions or spectral data) allows for many possible interpretations, we would make one comment. It has long been known[10] that $\alpha$-methylstyrene is readily oxidized to acetophenone by heating with free radical catalysts in the presence of even small amounts of oxygen. Indeed $\alpha$-methylstyrene oxidizes to acetophenone on storage,[10] particularly if ever opened to the atmosphere. Thus, one should be very leery of attaching too much significance to the formation of acetophenone from the thermolysis of a peroxide in $\alpha$-methylstyrene solution.

## Conclusion

While the thermolysis of hydridosilyl peroxides may to some degree involve silanone intermediacy, there is to date no experimental data demanding this interpretation.

## Experimental Section

**General Information.** All reactions, unless otherwise noted, were run under a nitrogen atmosphere. Routine proton NMR spectra were recorded on a Varian A60 or HA100 spectrometer. All chemicals shifts are reported as parts-per-million ($\delta$ scale) from tetramethylsilane. IR spectra were recorded on a Beckman IR 4250 spectrophotometer. UV spectra were recorded on a Cary Model 14 spectrophotometer. Mass spectra were recorded by using either a Finnigan Model 4000 (GCMS) or an AEI MS 902 spectrophotometer, with exact masses obtained on the latter instrument.

Gas chromatographic analyses and separations were performed on Varian Models 3700 and 920 and Aerograph Model A-90-P instruments. GC yields were determined with internal standards after determination of the relevant response factors. High-pressure liquid chromatography (HPLC) was performed on a Waters high-pressure liquid chromatograph equipped with UV and differential refractometer detectors.

**DABCO·Bis(*tert*-butyl hydroperoxide) Complex.** The DABCO·2HOO-*t*-Bu complex was prepared by a modification of the procedure of Fan and Shaw.[6] In a 250-mL flask equipped with a mechanical stirrer were placed DABCO (13.9 g, 0.123 mol)

(10) Mayo, F. R.; Miller, A. A. *J. Am. Chem. Soc.* **1958**, *80*, 2480.

and $Et_2O$ (200 mL). This slurry was cooled to 0 °C and *tert*-butyl hydroperoxide (25 mL, ca. 0.25 mol) was slowly added. After being stirred at 0 °C for 0.5 h, the solution was poured into 400 mL of pentane, at which time the DABCO·2HOO-*t*-Bu precipitated out. After being cooled in a freezer (−20 °C) for 2 h, the solution was filtered and the crystals were washed with pentane. The complex was dried overnight on a vacuum line to yield glistening white crystals (approximate yield of 70%).

**Di-*tert*-butylsilyl *tert*-Butyl Peroxide (7).** In a 100-mL flask equipped with a magnetic stirrer were placed di-*tert*-butylbromosilane (7.958 g, 35.6 mmol), THF (80 mL), and DABCO·2HOO-*t*-Bu (5.71 g, 19.5 mmol). This solution was stirred at room temperature for 24 h before pouring into 150 mL of pentane. After being cooled to 0 °C, the solution was filtered. The solvents were removed with a rotary evaporator to leave behind a pale yellow liquid. This material was chromatographed (4-in. silica gel column, hexane eluent) to yield pure **7** (6.209 g, 75% yield): NMR ($CCl_4$) δ 1.05 (s, 18 H), 1.23 (s, 9 H), 4.12 (s, 1 H); IR (film) 2960 (s), 2930 (s), 2890 (s), 2855 (s), 2120 (s), 1470 (s), 1460 (sh), 1390 (m), 1365 (s), 1260 (w), 1240 (w), 1195 (m), 1060 (w), 1010 (m), 935 (w), 900 (m), 850 (s), 825 (s), 795 (s), 750 $cm^{-1}$ (w); mass spectrum, *m/e* (% relative intensity) (parent ion not seen), 217 ($P^+$ − Me, <1), 175 ($P^+$ − *t*-Bu, 1), 161 (1), 145 (1), 119 (2), 103 (4), 87 (1), 77 (36), 75 (25), 63 (100), 57 (82), 47 (5); exact mass for $C_{11}H_{25}O_2Si$ (parent ion −$CH_3$) calcd 217.1624, measd 217.1621; exact mass for $C_8H_{19}O_2Si$ (parent ion −*t*-Bu) calcd 175.1154, measd 175.1152.

**Thermolysis of Di-*tert*-butylsilyl *tert*-Butyl Peroxide (7).** A solution containing **7** (0.0432 g) and *n*-octane (0.50 mL) was placed in several capillary melting point tubes. These tubes were sealed and placed in an oven at 150 °C. A tube was removed every half hour, and the progess of the reaction was analyzed by GC. The reaction was complete after 3 h. The products formed were di-*tert*-butylsilanol (**11**) (2.5%), di-*tert*-butoxy-*tert*-butylsilane (**9**) (41.7%), di-*tert*-butyl-*t*-butoxysilane (**8**) (30.8%), and *sym*-tetra-*tert*-butyldisiloxane (**12**) (5.3%).

The reaction was repeated with 0.1 equiv of $Et_3N$ added. Under the same conditions, this reaction was complete in 1 h. The same products were formed but in slightly different yields (see Table I). Product **11** was identified by spectral comparison with an authentic sample. Product **12** was identified only by GC/MS. Products **9** and **8** were isolated by preparative GC (10-ft 15% SE30 column). The spectral characteristics of **8**, **9**, and **12** are summarized.

**9**: NMR ($CCl_4$) δ 0.85 (s, 9 H), 1.28 (s, 18 H), 4.48 (s, 1 H); IR (film) 2970 (s), 2925 (s), 2890 (m), 2855 (s), 2110 (m), 1470 (m), 1460 (m), 1385 (m), 1360 (s), 1235 (m), 1185 (m), 1050 (bd s), 1020 (m), 1000 (w), 935 (w), 865 (m), 835 (s), 795 $cm^{-1}$ (w); mass spectra, *m/e* (% relative intensity) 232 (parent ion, 1) 217 ($P^+$ − Me, 9), 207 (1), 175 ($P^+$ − *t*-Bu, 14), 161 (11), 133 (1), 119 (60), 103 (22), 89 (3), 77 (100), 63 (72), 57 (60); exact mass for $C_{12}H_{28}O_2Si$ (parent ion) calcd 232.1859, measd 232.1849; exact mass for $C_{11}H_{25}O_2Si$ (parent ion − $CH_3$) 217.1623, measd 217.1624; exact mass for $C_8H_{19}O_2Si$ (parent ion *t*-Bu) calcd 175.1154, measd 175.1152.

**8**: NMR ($CCl_4$) δ 0.98 (s, 18 H), 1.32 (s, 9 H), the remaining H was not observed; IR (film) 3700 (w), 3600–3200 (bd w), 2970 (s), 2930 (s), 2890 (m), 2855 (s), 1470 (m), 1460 (sh), 1385 (m), 1360 (s), 1235 (w), 1195 (s), 1065 (bs), 1010 (w), 935 (w), 820 (s), 785 (m), 635 $cm^{-1}$ (m); mass spectrum, *m/e* (% relative intensity) 232 (parent ion, 1) 217 ($P^+$ − Me, 6), 175 ($P^+$ − *t*-Bu, 13), 159 (1), 145 (1), 133 (2), 119 (45), 103 (9), 89 (2), 77 (100), 75 (83), 63 (13), 57 (14), 56 (13); exact mass for $C_{12}H_{28}O_2Si$ (parent ion) calcd 232.1859, measd 232.1852; exact mass for $C_{11}H_{25}O_2Si$ (parent ion − $CH_3$) calcd 217.1623, measd 217.1626; exact mass for $C_8H_{19}O_2Si$ (parent ion − *t*-Bu) calcd 175.1154, measd 175.1150.

**12**: mass spectrum, *m/e* (% relative intensity) 302 (parent ion, 1), 245 ($P^+$ − *t*-Bu, 1), 203 (10), 189 (1), 165 (1), 149 (1), 141 (4), 125 (1), 109 (4), 57 (100).

**Attempted Synthesis of Pentamethyldisilanyl *tert*-Butyl Peroxide (13).** In a 100-mL flask equipped with a magnetic stirrer were placed DABCO·2HOO-*t*-Bu (2.0828 g, 7.12 mmol) and $Et_2O$ (75 mL). After the mixture was coded to 0 °C, chloropentamethyldisilane (2.1550 g, 12.9 mmol) was added, and the solution was stirred for 20 h at room temperature. The reaction mixture was poured into pentane and filtered, the solvent removed on a rotary evaporator, and the residue percolated through a short silica gel column with hexane to obtain disiloxane **14** in 73% yield: IR (neat) 2990 (s), 2915 (m), 2880 (sh), 1415 (w), 1390 (m), 1365 (s), 1255 (s), 1240 (sh), 1200 (s), 1055 (s, bds), 875 (sh), 840 (s), 810 (s), 788 (s), 750 (m), 685 (m), 615 $cm^{-1}$ (m); mass spectrum, *m/e* (% relative intensity) no molecular ion observed, 205 (M − Me, 28), 149 (100), 148 (12), 147 (68), 133 (29), 95 (17), 73 (20), 57 (18); exact mass for $C_8H_{21}Si_2O_2$ calcd 205.1080, measd 205.1078.

**Dimethyl-*tert*-Butoxychlorosilane.** In a 1000-mL three-necked flask equipped with an overhead stirrer were placed dimethyldichlorosilane (60.18 g, 0.466 mol), $Et_2O$ (500 mL), and pyridine (38 mL, 0.471 mol). The solution was cooled to 0 °C, and *tert*-butyl alcohol (34.6 g, 0.467 mol) in 50 mL of $Et_2O$ was slowly added via addition funnel. After all the alcohol was added, stirring was continued overnight at room temperature. After the solution was filtered, the $Et_2O$ was removed by distillation. Fractionation of the residue with a 12-in. Vigreux column yielded 53.9 g of pure dimethyl-*tert*-butoxychlorosilane (bp 119–122 °C, 69% distilled yield): NMR ($CCl_4$) 0.42 (s, 6 H), 1.33 (s, 9 H).

**Dimethyl-*tert*-butoxysilanol (15).** In a 100-mL Morton flask equipped with a magnetic stirrer were placed $Et_2O$ (75 mL), dimethyl-*tert*-butoxychlorosilane (2.193 g, 13.16 mmol), and pyridine (1.08 mL, 14.4 mmol). The solution was cooled to 0 °C, and $H_2O$ (0.26 mL, 14.4 mmol) was slowly added via syringe. The solution was stirred for 2 h while the temperature was allowed to slowly rise to room temperature. After being poured into 100 mL of pentane and dried over $Na_2SO_4$, the solution was filtered. Removal of the solvents with a rotary evaporator left behind a colorless, viscous liquid which was nearly pure **15** (yield ca. 90%). Product **15** was used without further purification: NMR ($CCl_4$) 0.08 (s, 6 H), 1.28 (s, 9 H), 2.60 (s, 1 H); IR (film) 3600–3000 (bd s), 2970 (s), 2915 (m), 2900 (m), 2870 (w), 1590 (w), 1470 (w), 1460 (w), 1440 (m), 1385 (m), 1360 (s), 1255 (s), 1240 (m), 1200 (s), 1050 (bd s), 1020 (w), 1000 (sh), 875 (s), 840 (s), 780 (s), 695 (w), 675 $cm^{-1}$ (w); mass spectrum, *m/e* (% relative intensity) 148 (parent ion, 1), 133 ($P^+$ − Me, 61), 117 (2), 115 (1), 103 (1), 77 (86), 75 (100), 59 (16), 47 (16).

**Thermolysis of Dimethyl-*tert*-butoxysilanol (15).** Solutions of **15** in tridecane were prepared (5%, 10%, 20%, and 40% solutions). Samples of each solution were placed in capillary tubes which were sealed. The tubes were then placed in an oven at 150 °C. Progress of the reaction was monitored by periodically removing sample tubes and analyzing the solutions by GC. The time required for complete reaction of **15** varied with concentration; the 4% solution required 1 h while the 40% solution required 2.5 h. The major products of the 5% solution were found to be 3-*tert*-butoxytetramethyldisiloxan-1-ol (**17**), dimethyldi-*tert*-butoxysilane (**19**), and $D_4$. The major products of the concentrated solutions (20% and 40%) were found to be **17**, **19**, and 5-*tert*-butoxyhexamethyltrisiloxan-1-ol (**20**). No $D_4$ was observed in these concentrated solutions. Products **19** and $D_4$ were identified by GC/MS, while **17** and **20** were isolated by preparative GC (10-ft. 15% SE30 column). The spectral characteristics of these products are summarized.

**17**: NMR ($CCl_4$) δ 0.00, 0.01 (s, s, 12 H), 1.18 (s, 9 H), 2.78 (s, 1 H); IR ($CCl_4$) 3700 (m), 2980 (s), 2930 (w), 2905 (w), 2870 (w), 1460 (w), 1390 (w), 1365 (m), 1255 (s), 1210 (sh), 1195 (s), 1050 (bd s), 910 (m), 665 (w), 630 $cm^{-1}$ (w); mass spectrum, *m/e* (% relative intensity) (parent ion not seen) 207 ($P^+$ − Me, 12), 191 (1), 167 (1), 151 (100), 149 (84), 135 (12), 133 (48), 119 (8), 105 (3), 103 (3), 96 (7), 89 (4), 75 (27), 57 (56), 47 (6).

**20**: NMR ($CCl_4$) δ 0.06 (bd s, 18 H), 1.22 (s, 9 H), 2.66 (s, 1 H); IR ($CCl_4$) 3700 (m), 2970 (s), 2930 (w), 2905 (w), 2870 (w), 1390 (w), 1360 (m), 1255 (s), 1200 (m), 1040 (bd s), 905 (m), 660 $cm^{-1}$ (w); mass spectrum, *m/e* (% relative intensity) (parent ion not seen), 281 ($P^+$ − Me, 1), 267 (1), 251 (1), 225 (10), 223 (12), 207 (32), 193 (8), 191 (7), 177 (2), 165 (1), 149 (2), 133 (9), 125 (3), 119 (2), 103 (3), 96 (4), 75 (12), 73 (8), 57 (100), 47 (2).

**19**: mass spectrum, *m/e* (% relative intensity) (parent ion not seen), 189 ($P^+$ − Me, 17), 133 (36), 117 (1), 115 (2), 101 (1), 87 (5), 77 (67), 75 (100), 57 (24), 47 (5).

**Dimethylsilyl *tert*-Butyl Peroxide (3).** In a 100-mL flask were placed DABCO·2HOO-*t*-Bu (6.862 g, 23.5 mmol) and $Et_2O$ (60 mL). This solution was cooled to 0 °C, and dimethylchlorosilane was added neat via syringe (5.0 mL, 44.9 mmol). A large amount of white precipitate formed immediately. Stirring was continued for 2 h while the temperature was gradually in-

creased to room temperature. The solution was then poured into 150 mL of pentane and was extracted. Removal of the solvents with a rotary evaporator left ca. 4.0 g of a colorless liquid which was nearly pure **3**. The recovered yield (ca. 60%) was quite low due to the high volatility of peroxide **3**. The peroxide was used without further purification. Attempted purification by column chromatography was unsuccessful as **3** decomposed on silica gel. The spectral properties of **3** are as follows: NMR ($CCl_4$) $\delta$ 0.18 (d, 2 H, $J$ = 2.5 Hz), 1.17 (s, 9 H), 4.58 (heptet, 1 H, $J$ = 2.5 Hz); IR (film) 2980 (s), 2935 (w), 2870 (2), 2140 (s), 1460 (w), 1385 (m), 1365 (s), 1255 (s), 1195 (s), 905 (bd s), 880 (s), 845 (s), 805 (w), 760 (m), 725 $cm^{-1}$ (m); mass spectrum, $m/e$ (% relative intensity) (parent ion not seen), 133 ($P^+$ – Me, 76), 119 (100), 117 (6), 103 (12), 87 (4), 73 (47), 66 (5), 59 (45), 47 (3).

**Thermolysis of Dimethylsilyl *tert*-Butyl Peroxide (3).** A 5% solution of **3** in dodecane was prepared and placed in several capillary tubes. After being sealed, these tubes were placed in an oven at 150 °C. The starting peroxide completely disappeared within a half hour. The major products, as observed by GC/MS, were $D_4$ and silanol **17**. As the initial concentration of **3** in dodecane was increased, the yield of **17** increased.

**Reaction of Dimethylsilyl *tert*-Butyl Peroxide (3) with $Et_3SiD$.** Deuteriotriethylsilane was prepared by treatment of triethylchlorosilane with lithium aluminum deuteride in $Et_2O$. The $Et_3SiD$ was purified by preparative GC (10-ft 15% SE30 column) just prior to use.

To a 5% solution of **3** in octane was added a threefold molar excess of $Et_3SiD$. This solution was placed in several capillary tubes. After being sealed, the tubes were placed in an oven at 135 °C. The reaction was complete within a half hour. The major products were *tert*-butyl alcohol and 1,1-dimethyl-3,3,3-triethyldisiloxane (**22**). The deuterated alcohol was only identified by GC/MS while **22** was isolated by preparative GC (6-ft. 30% SE column): NMR ($CCl_4$, 100 MHz) $\delta$ 0.16 (d, 6 H, $J$ = 2.5 Hz), 0.35–1.10 (complex multiplet, 15 H), 4.68 (heptet, SiH, 1 H, $J$ = 2.5 Hz); irradiation at $\delta$ 4.68 causes the doublet at $\delta$ 0.16 to collapse to a singlet; IR ($CCl_4$) 2965 (s), 2940 (sh), 2920 (m), 2880 (s), 2120 (s), 1465 (m), 1420 (m), 1380 (2), 1250 (bd s), 1065 (bd s), 1000 (s), 910 $cm^{-1}$ (s); the region of Si–D absorption (1520 $cm^{-1}$ for $Et_3SiD$) is clear; mass spectrum, $m/e$ (% relative intensity) 190 (parent ion, 1), 175 ($P^+$ – Me, 3), 161 ($P^+$ – Et, 100), 147 (4), 133 (82), 119 (5), 105 (67), 87 (7), 73 (13), 66 (13), 59 (41).

**Reaction of Trimethylsilyl *tert*-Butyl Peroxide (23) with $Et_3SiH$.** A solution containing peroxide **23** (0.0728 g, 0.448 mmol), $Et_3SiH$ (0.188 g, 1.62 mmol), dodecane (0.514 g), and undecane (0.0344 g, GC standard) was prepared. Samples of this solution were placed in capillary tubes which were sealed and placed in an oven at 150 °C. The reaction was complete after 1.5 h. The major products formed were triethylsilanol (17%) and 1,1,1-trimethyltriethyldisiloxane (**24**) (72%). Triethylsilanol was identified by comparison with an authentic sample while **24** was isolated by preparative GC (6-ft 30% SE30 column). The spectral properties of **24** are as follows: NMR ($CCl_4$) $\delta$ 0.08 (s, 9 H), 0.40–1.20 (complex multiplet, 15 H); IR (film) 2980 (s), 2920 (s), 2885 (s), 1460 (m), 1415 (m), 1250 (s), 1240 (sh), 1065 (bd s), 1010 (s), 860 (s), 840 (s), 750 (s), 735 (s), 720 (s), 640 $cm^{-1}$ (w); mass spectrum, $m/e$ (% relative intensity) 204 (parent ion, 1), 189 ($P^+$ – Me, 6), 175 ($P^+$ – Et, 100), 161 (9), 147 (80), 133 (12), 119 (75), 117 (13), 105 (15), 103 (12), 87 (11), 80 (9), 73 (39), 66 (28), 59 (36).

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# Ligand Effects on the Reduction of Iron(III) Complexes by Alkyl Radicals. Formation of Alkyl Isocyanides and Chlorides from Cyanoiron(III) and Chloroiron(III) Species

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The reduction of the cyanoiron(III) complex $(NC)_2Fe(phen)_2^+$ by various alkyl radicals occurs readily by addition to the cyanide ligand to form an alkyl isocyanide coordinated to iron(II). The infrared and electronic spectra of analogous cyanoiron(II) and (alkyl isocyanide)iron(II) complexes are compared in the series: $(CH_3NC)_2Fe(phen)_2^{2+}$, $(CH_3NC)(NC)Fe(phen)_2^+$, $(NC)_2Fe(phen)_2$. Electron-rich alkyl radicals such as *tert*-butyl also reduce $(NC)_2Fe(phen)_2^+$ by an electron-transfer process which affords carbonium ion byproducts. For a particular alkyl radical, the competition between radical addition and electron transfer can be qualitatively related to its ionization potential. Various alkyl radicals also react readily with two series of chloroiron(III) complexes, tetrachloroferrate(III) and trichloroiron(III), to afford the reduced chloroiron(II) species and the corresponding alkyl chloride in essentially quantitative yield. The rates of chlorine atom transfer to alkyl radicals are measured by the competition method using $BrCCl_3$ as a bromine atom donor. The divergent trends in the reactivity pattern of alkyl radicals with tetrachloroferrate(III) and trichloroiron(III) are discussed in terms of $FeCl_4^-$ and $FeCl_2^+$, respectively, as the active chloroiron(III) species in acetonitrile solutions. The various pathways for the reduction of different iron(III) complexes by alkyl radicals are presented in the context of their reduction potentials.

## Introduction

Iron is an ubiquitous metal in various biological systems, especially those involving oxidative processes.[1] Coupled with the increasing realization that many oxidative enzymatic processes involve free radical intermediates,[2,3] it is important to delineate the oxidation–reduction reactions

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