of **1**. For example, 2,4-di-*tert*-butylpyridine, an isomer of **1** coproduced in the synthesis of **1** by direct alkylation[10] using *t*-BuLi, may not have been entirely removed.

(19) L. Reggel, R. A. Friedel, and I. Wender, *J. Org. Chem.*, **22**, 891 (1957).

(20) The solid $CO_2$ reacts vigorously with the anhydrous 1,2-ethanediamine solvent.

(21) H. Booth, J. H. Little, and J. Feeney, *Tetrahedron*, **24**, 279 (1968).

(22) J. B. Lambert and S. I. Featherman, *Chem. Rev.*, **75**, 611 (1975); I. D. Blackburne, A. R. Katritzky, and Y. Takeuchi, *Acc. Chem. Res.*, **8**, 300 (1975); F. A. L. Anet and I. Yavari, *J. Am. Chem. Soc.*, **99**, 2794 (1977), showed a free energy preference of 0.36 kcal/mol for equatorial NH in piperidine at very low temperature (−172 °C, $CHClF_2/CHCl_2F$).

(23) F. Bohlmann, *Chem. Ber.*, **91**, 2157 (1958); P. J. Krueger and J. Jan, *Can. J. Chem.*, **48**, 3236 (1970), reported that *cis*-2,6-dimethylpiperidine exhibits Bohlmann bands at 2790 and 2701 $cm^{-1}$ while *trans*-2,6-dimethylpiperidine shows only weak CH stretching bands below 2840 $cm^{-1}$.

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# Sterically Hindered Silyl Perchlorates as Blocking Reagents

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Tri-*tert*-butylsilane, di-*tert*-butylmethylsilane, and *tert*-butyldimethylsilane were converted into the corresponding silyl perchlorates through a rapid and quantitative exchange with trityl perchlorate. Tri-*tert*-butylsilyl perchlorate proved somewhat difficult to prepare and was quite unreactive. *tert*-Butyldimethylsilyl perchlorate reacted with alcohols much more rapidly than did the usual reagent, *tert*-butyldimethylsilyl chloride. The ethers formed from di-*tert*-butylmethylsilyl perchlorate proved far more stable to acidic conditions than THP or *tert*-butyldimethylsilyl ethers.

In synthetic organic chemistry silylating agents are often used to protect hydroxyl functions. However, unhindered silyl groups such as trimethylsilyl are of limited value because of their extreme reactivity toward acid- and base-catalyzed solvolysis. Since 1972, one of the most popular protecting reagents has been *tert*-butyldimethylsilyl chloride.[1] Ethers formed from this hindered silyl chloride are many times more stable toward solvolysis than are trimethylsilyl ethers. The use of increasing steric bulk on silicon to provide increased solvolytic stability has recently been extended to *tert*-butyldiphenylchlorosilane by Hanessian and Lavallee.[2] Of course, the same steric bulk which affords the additional protection also resists the formation of the silyl ether in the first place. However, Corey[1] found *tert*-butyldimethylsilyl chloride to be satisfactory for primary and secondary alcohols when imidazole is utilized as a catalyst, though extended reaction times are sometimes required.

We wished to continue the replacement of methyl groups on silicon by *tert*-butyl groups to its logical conclusion. However, we anticipated that even two *tert*-butyl groups on silicon would render the silyl chloride ineffective in reactions with alcohols. Thus the need for a better leaving group than chloride was considered of prime necessity. We recently discovered that perchlorate is an extremely labile leaving group on silicon.[3] Thus, when triethylsilyl perchlorate is treated with sodium borohydride at room temperature, there is immediate and quantitative formation of triethylsilane. This reduction is particularly dramatic in view of the usual requirement of the more reactive $LiAlH_4$ for reduction of alkoxysilanes.

$$Et_2SiOClO_3 \xrightarrow{NaBH_4} Et_3SiH$$

In view of the striking reactivity of silyl perchlorates as demonstrated in the above example, we felt that the perchorate group might overcome any reactivity obstacles inherent for silyl chlorides. This paper will report the syntheses of *tert*-butyldimethylsilyl, di-*tert*-butylmethylsilyl, and tri-*tert*-butylsilyl perchlorates, and their reactions with alcohols.

## Results and Discussion

**Synthesis.** Silyl perchlorates were first prepared some 20 years ago by Wannagat and Liehr[4] through the reactions of silyl chlorides with silver perchlorate.

$$R_3SiCl + AgClO_4 \rightarrow R_3SiClO_4 + AgCl$$
$$(R = Me, Et, n\text{-}Pr, Ph, p\text{-}MeC_6H_4)$$

Their studies revealed no evidence for ionic character, and it was concluded that these compounds were simply covalent esters of perchloric acid.

While the above method of synthesis is quantitative, we were loath to become involved with a process requiring considerable amounts of an expensive silver salt. Thus, a less costly route was sought. We have found[3] that the long-established trityl salt–silyl hydride exchange reaction[5] works quite well when the organic salt is trityl perchlorate. Indeed, we have found that all silyl hydrides attempted to date, save the most highly hindered for which the reaction is slower, react with trityl perchlorate in methylene chloride to instantaneously decolorize the solution and afford triphenylmethane and silyl perchlorate.[6] For example, triethylsilane reacts with trityl perchlorate to produce triphenylmethane and triethylsilyl perchlorate, both in essentially quantitative yield. The silyl perchlorate can be distilled out as a colorless liquid.

$$Et_3SiH + Ph_3ClO_4^- \xrightarrow{CH_2Cl_2} Et_3SiOClO_3 + Ph_3CH$$

*tert*-Butyldimethylsilane (**1**) was prepared in 90% yield from chlorodimethylsilane and *tert*-butyllithium. Addition of **1** to a methylene chloride solution of trityl perchlorate yielded upon workup 91% of clear, odorless *tert*-butyldimethylsilyl perchlorate (**2**) [bp 35 °C (0.06 Torr)].

Di-*tert*-butylmethylsilane (**3**) was synthesized from methyldichlorosilane and *tert*-butyllithium in 82% yield. This material had a bp of 152–4 °C and had identical spectral properties with the impure **3** (bp 148–155 °C) prepared by the more tedious, multistep method of Doyle and West.[7] Conversion of **3** to di-*tert*-butylmethylsilyl perchlorate (**4**) was accomplished in 87% yield [bp 65 °C (0.1 Torr)] through exchange with trityl perchlorate.

The method of Dexheimer and Spialter[8] was used to prepare tri-*tert*-butylsilane (**5**). While tri-*tert*-butylsilyl perchlorate (**6**) could be prepared from reaction of **5** with trityl perchlorate, the reaction was quite sluggish and separation from triphenylmethane proved difficult. Thus **5** was converted

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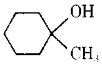
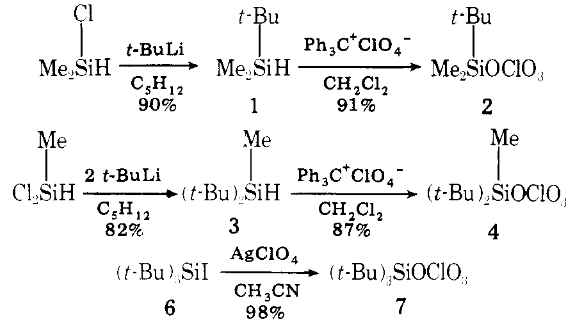
**Table I. Reactivity Comparison of *tert*-Butyldimethylsilyl Perchlorate and *tert*-Butyldimethylsilyl Chloride with Tertiary Alcohols**

| | registry no. | $t$-BuMe$_2$SiOClO$_3$ (2)[a] Py/CH$_3$CN | $t$-BuMe$_2$SiCl[b] imidazole/DMF |
|---|---|---|---|
| $t$-BuOH | 76-65-0 | $t_{1/2} \sim 30$ s<br>100% in 5 min | 30% in 3 days |
|  | 590-67-0 | $t_{1/2} \sim 3$ min<br>100% in 20 min | 10% in 3 days |

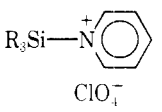
[a] Registry no.: 67124-66-7. [b] Registry no.: 18162-48-6.

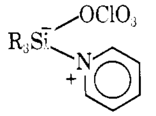
to the silyl iodide 7 by the method of Weiderbruch and Peter,[9] and then transformed with silver perchlorate in acetonitrile to 6 in 98% yield. Sublimation produced white, crystalline 6 in 91% yield (dec >150 °C).

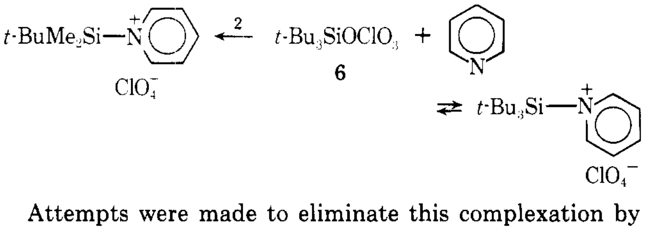


All the silyl perchlorates (2, 4, and 6) were found to react quite rapidly with water, so normal precautions for their handling must be taken.

**Reactions with Alcohols.** All reactions of silyl perchlorates were conducted in acetonitrile solution with 1 equiv of a pyridine present. It is unlikely that the silyl perchlorate is actually the ultimate reactant, as the NMR spectrum of this solution reveals the pyridine ring protons to be considerably shifted downfield. This could be accounted for by either 8 or 9. However, the pyridinium salt 8 most easily accounts for the downfield shifts of ~0.25 ppm observed for methyl on silicon for 2 and 4. While 2 and 4 exhibited similar behavior with regard to the formation of a pyridinium complex, the NMR spectrum of tri-*tert*-butylsilyl perchlorate (6) and pyridine was quite different with regard to the chemical shift and sharpness of the pyridine region. This part of the spectrum was reminiscent of the addition of 0.5 equiv of perchloric acid to pyridine, namely, the peaks were broad and their chemical shifts were between those of pyridine and pyridinium ion. If this was the result of an equilibrium situation it should be disturbed by the presence of 2. Indeed, when a slight excess of 2 was added to the system, the aromatic signals became identical with those observed for 2 alone with pyridine.

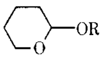

8


9



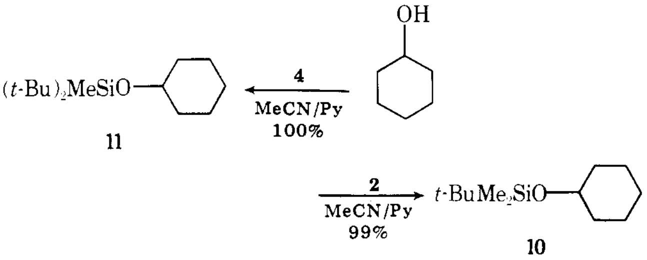
Attempts were made to eliminate this complexation by using 2,6-di-*tert*-butyl-4-methylpyridine in place of pyridine. Quite surprisingly NMR studies showed that all three silyl perchlorates reacted with this extremely hindered base.

**Table II. Relative Solvolytic Stabilities of Blocked Alcohols**

| ether[a] | registry no. | 1% HCl in 95% EtOH | 5% NaOH in EtOH |
|---|---|---|---|
| $t$-BuMe$_2$SiOR | 67124-67-8 | 100% removal in 15 min at room temp | ~15% removal after 9 h at 80 °C |
|  | 709-83-1 | 100% removal in 15 min at room temp | stable |
| $t$-Bu$_2$MeSiOR | 67124-68-9 | no dec after 3 days at room temp<br>50% dec 24 h at 90 °C | no dec after 3 days at 80 °C |

[a] R = cyclohexyl.

To determine whether or not silyl perchlorates reacted in the desired fashion, to afford silyl ethers, 2 and 4 were reacted with cyclohexanol. Cyclohexanol was added to a stirred solution of 2 and pyridine in acetonitrile, and after 1.5 h, aqueous workup afforded a 99% yield (>95% pure by GC) of *tert*-butyldimethylsilyl cyclohexyl ether (10). A similar reaction using 4 produced a 100% yield (>95% pure by GC) of di-*tert*-butylmethylsilyl cyclohexyl ether (11).



In order to compare the relative reactivities of silyl chlorides and silyl perchlorates, the reactions of 2 and *tert*-butyldimethylsilyl chloride with two tertiary alcohols were examined and the results are shown in Table I. For the protection of these tertiary alcohols it is apparent that the silyl perchlorate/pyridine system is by far the more useful silylating agent, rapidly providing quantitative yields of the desired silyl ether at room temperature. No olefin formation was detected in these reactions of 2.

To compare the relative reactivities of the hindered silyl perchlorates, 2, 4, and 6 were each added to acetonitrile solution containing *tert*-butyl alcohol and 1 equiv of 2,6-di-*tert*-butyl-4-methylpyridine. The reactivity order of the series was observed to be 2 ($t_{1/2} < 30$ s) > 4 ($t_{1/2} < 60$ s) > 6 (no reaction). Thus it was decided that in view of both the considerable difficulty in preparation of 6 (drybox or Schlenk tube techniques and sublimation) and its extreme lack of reactivity that this hindered perchlorate was never likely to play a role in organic synthesis. Another disturbing feature of this comparison was the discovery that for the reaction of 4 a significant amount of isobutene was formed. This elimination was also observed in the reaction of 4 and *tert*-butyl alcohol in the presence of a 20% excess of pyridine, thus removing the possibility of 4 as a protecting reagent for tertiary alcohols and presumably others which can readily form a stabilized carbocation.

**Solvolytic Stability of Di-*tert*-butylmethylsilyl Ethers.** Di-*tert*-butylmethylsilyl ethers have been reported by Doyle and West[10] when they reduced cyclohexanones with di-*tert*-

butylmethylsilane; however, the stabilities of these ethers were not investigated. Thus we set out to compare the stability of di-*tert*-butylmethyl cyclohexyl ether (**11**) relative to the *tert*-butyldimethylsilyl cyclohexyl ether (**10**) under both acidic and basic conditions. These results are summarized in Table II.

In 5% ethanolic sodium hydroxide solution **10** is relatively stable, though it does decompose slowly, while **11** is totally inert under these conditions. However, this represents no improvement over the traditional THP blocked alcohol as it is also completely stable. More importantly, it was found that the di-*tert*-butylmethylsilyl system answered the frequent complaint on the acid lability of the *tert*-butyldimethylsilyl block. Indeed **11** was totally inert to acidic conditions which quickly and quantitatively solvolyzed both **10** and the THP derivative of cyclohexanol.

Since Doyle[10] had reported that tri-*tert*-butylsilyl ethers resisted cleavage, we were concerned that the di-*tert*-butylmethylsiloxy system would also have a cleavage problem. This fear was realized when cesium fluoride in $Me_2SO$ failed to react with **11** even at elevated temperatures. However, boron trifluoride in methylene chloride quickly and cleanly cleaved this ether even at 0 °C. Under these conditions the alcohol is never subjected to boron trifluoride as the hydroxylic functionality is protected as a borate ester until liberation by aqueous bicarbonate.

$$11 \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{BF_3}} t\text{-}\mathrm{Bu_2MeSiF} + \mathrm{F_2BOC_6H_{11}} \xrightarrow[\substack{\mathrm{H_2O} \\ 0\ ^\circ\mathrm{C},\ 30\ \mathrm{min}}]{\mathrm{NaHCO_3}} \underset{94\%}{\mathrm{C_6H_{11}OH}}$$

Of course it is expected that $BF_3$ would cause unwanted side reactions for some molecules of synthetic interest. On the other hand, one would probably not be interested in the di-*tert*-butylmethylsilyl blocking group unless protection against rather rigorous acidic conditions were required to effect the desired transformation(s).

## Conclusions

Silyl perchlorates are easily prepared by the trityl exchange reaction and, if normal precautions are taken, are stable reagents. However, since the compounds are perchlorates, it is highly recommended that safety shields be employed when using significant quantities. *tert*-Butyldimethylsilyl perchlorate represents a significant improvement over *tert*-butyldimethylsilyl chloride with respect to reactivity. For protection of primary and secondary alcohols di-*tert*-butylmethylsilyl perchlorate provides a block that is far more stable to acidic conditions.

## Experimental Section

**General.** Infrared spectra (IR) were recorded on a Beckman spectrophotometer. Routine NMR spectra were determined on a Varian HA-100 instrument and chemical shifts are reported as parts per million ($\delta$ scale) from tetramethylsilane, though it was not always used as the internal standard (benzene and methylene chloride were often used). $^{13}C$ and $^{29}Si$ NMR were recorded on a Bruker 90-MHz FT spectrophotometer as were the kinetic experiments of the silyl perchlorates with 2,6-di-*tert*-butyl-4-methylpyridine.

Routine and high-resolution mass spectra (MS) were recorded on an AEI MS-902. Gas chromatographic/mass spectral (GC/MS) analysis was accomplished on a Perkin-Elmer 270 mass spectrometer. Routine analytical gas chromatography (GC) was accomplished on a Varian aerograph 600-C flame ionization instrument using a $\frac{1}{8}$ in. diameter, 6-ft long column packed with 10% Dexel 300 on Chromosorb P. GC yields were accomplished by adding known amounts of an inert standard.

Solvents were dried by distillation from $P_2O_5$ under nitrogen, and were stored over molecular sieves.

Although the silyl perchlorates are covalent liquids, they should be treated as potential explosives with all proper safety equipment. Our only explosion occurred when a syringe, used for injecting a sample of triethylsilyl perchlorate into a reaction flask, exploded long *after* the addition was complete. The reaction itself was unharmed.

**Tri-*tert*-butylsilane (5) and Tri-*tert*-butylsilyl Iodide (7).** The method of Dexheimer and Spialter[8] was used to prepare **5**, and **7** was prepared from **5** by the method of Weiderbruch and Peter[9] and recrystallized from acetonitrile. All spectral and physical properties of the materials so prepared matched those previously reported for the two compounds. Some additional spectral data was obtained for **7**: $^{13}C$ NMR showed singlets at $\delta$ ($CDCl_3$,$^1H$-decoupled) 30.7 and 24.5 in the ratio of 4.1:1 and its $^{29}Si$ NMR ($CHCl_3$) showed a singlet at $\delta$ 47.9.

**Tri-*tert*-butylsilyl Perchlorate (6).** A sample of $AgClO_4$ was placed in a flask and dried by heating at 150 °C under vacuum overnight. This sample of $AgClO_4$ and a sample of **7** were placed in a "drybox" in which all subsequent manipulations were carried out. A quantity of **7** (2.25 g, 6.91 mmol) and $AgClO_4$ (1.30 g, 6.31 mmol) were placed in 40 mL of acetonitrile and heated to 75 °C with the immediate formation of a yellow precipitate presumed to be AgI. Heating was continued for 5 h. After the mixture had cooled it was filtered and the yellow precipitate (AgI) was washed with acetonitrile and allowed to dry (1.44 g, 98%). The filtrate was extracted several times with 15-mL portions of hexane and then evaporated to yield 1.83 g of a slightly yellow solid which was sublimed at 95 °C and 0.02-mm pressure to furnish white crystalline **6** (1.71 g, 5.74 mmoles, 91% based on $AgClO_4$). The material could also be prepared outside of the "drybox" using Schlenk tube, syringe, and rubber septum techniques.

The white cyrstalline **6** was found to soften and begin to decompose at 150 °C. It became completely black at 185 °C: $^1H$ NMR ($CD_3CN$) $\delta$ 1.27 (s); $^{13}C$ NMR ($CD_3CN$, $^1H$ decoupled) $\delta$ 29.18, 23.18; $^{29}Si$ NMR ($CD_3CN$) $\delta$ 29.27; IR ($cm^{-1}$, film was prepared by placing a small amount of a very concentrated $CH_2Cl_2$ solution between two salt plates, pressing the plates together, and evacuating them in a vacuum desiccator) 2960 m, 2910 m, 2880 m, 1486 m, 1476 m, 1399 m, 1374 m, 1270 m, 1231 s, 1034 s, 1021 w, 1014 w, 935 s, 820 s, 808 s, 743 s, 708 w, 690 w.

**Reaction of 7 with Alkali.** A quantity of **7** (40 mg, 0.12 mmol) was placed in an NMR tube with 0.5 mL of $CD_3CN$ and 5 $\mu$L (0.28 mmol) of water. After heating overnight at 75 °C there was no change in the NMR spectrum relative to the starting solution. To the reaction mixture was added 25 $\mu$L of a 50% aqueous KOH solution. After again heating overnight at 75 °C it appeared that the $^1H$ NMR absorption of **7** at $\delta$ 1.24 was being slowly replaced by a singlet at $\delta$ 1.15 and one at $\delta$ 1.06.

**Reaction of 6 with Water.** The NMR tube used to obtain the proton spectrum of **6** contained ~40 mg (0.13 mmol) in ~0.4 mL of $CD_3CN$. To this solution was added 3 $\mu$L (0.17 mmol) of water and the NMR spectrum was changed immediately from a singlet at $\delta$ 1.27 to a singlet at $\delta$ 1.08.

**Triethylsilyl Perchlorate.** Trityl perchlorate (10.39 g, 30 mmol) was placed in a flask equipped with a rubber septum and a magnetic stirrer. The The flask was cooled in an ice bath and 40 mL of methylene chloride was added (yellow-orange slurry). Triethylsilane (3,5 g, 30 mmol) was added dropwise via syringe. As the addition was completed the mixture became homogeneous and colorless. After warming to room temperature the rubber septum was removed and quickly replaced by a short-path distilling head (some fuming was observed). The system was heated to 50 °C at atmospheric pressure for 30 min to drive off the methylene chloride. The residue was then carefully evacuated (tends to bump and foam) and distilled at 10 mm to furnish 5.91 g (92% yield) of a clear, colorless liquid: bp 43–45 °C (0.5 mm) [lit. (4) bp 45–46 °C at (1 mm)]; 60-MHz $^1H$ NMR $\delta$ 0.95 (m); $^{29}Si$ NMR (neat with 10% $C_6D_6$) $\delta$ 45.6.

***tert*-Butyldimethylsilane (1).** Freshly distilled chlorodimethylsilane (9.46 g, 0.1 mol) was added to 20 mL of pentane cooled in an ice bath. Dropwise addition of *tert*-butyllithium in pentane (50 mL of 2.0 M solution, 0.1 mol) was accomplished using a syringe and after the addition was complete the reaction mixture was allowed to warm to room temperature overnight. The product mixture was poured into a mixture of ice and bicarbonate solution. After extraction with water the pentane solution was distilled to afford 10.4 g (90% yield) of *tert*-butyldimethylsilane: bp 81–83 °C; $^1H$ NMR ($CCl_4$) $\delta$ 3.61 (septet, 1 H, $J = 3.5$ Hz), 0.89 (s, 9 H), 0.01 (d, 6 H, $J = 3.5$ Hz); IR (film) 2950 s, 2925 s, 2895 m, 2880 m, 2855 s, 2099 s, 1460 m, 1420 w, 1382 w, 1358 m, 1252 s, 1060 m, 1004 m, 982 s, 872 s, 830 s, 791 w, 771 w, 751 m, 713 m; MS $m/e$ (rel intensity) 116 (14), 101 (2), 75 (20), 73 (30), 59 (100), 58 (34), 57 (43), 56 (49); MS Calcd for $C_6H_{16}S$, $m/e$ 116.1021; found $m/e$ 116.1022.

***tert*-Butyldimethylsilyl Perchlorate (2).** This compound was prepared from *tert*-butyldimethylsilane (1.16 g, 10 mmol) and trityl perchlorate (3.65 g, 10.5 mmol) in the same manner as triethylsilyl perchlorate to afford 1.95 g (91% yield) of clear, odorless **2:** bp 35 °C (0.06 mm); $^{1}$H NMR (CD$_3$CN) $\delta$ 0.99 (s, 9 H), 0.51 (s, 6 H); IR (film) 2955 m, 2935 m, 2885 w, 2865 m, 1471 m, 1465 m, 1394 s, 1367 w, 1226 s, 1101 m, 1032 s, 1011 s, 1001 s, 938 w, 850 m, 780 s, 708 m, 662 m.

**Di-*tert*-butylmethylsilane (3).** This compound was prepared from *tert*-butyllithium (110 mL, 2.1 M in pentane, 0.23 mol) and methyldichlorosilane (12.6 g, 0.11 mol) in the manner used to prepare *tert*-butyldimethylsilane except that aqueous NH$_4$Cl was used to neutralize the product mixture. Fractional distillation produced 14.39 g (82% yield) of di-*tert*-butylmethylsilane (bp 152–154 °C) which was found to have identical spectral properties with the impure material (bp 148–155 °C) prepared by the more tedious multistep method of Doyle and West.[7]

**Preparation of Di-*tert*-butylmethylsilyl Perchlorate (4).** This compound was prepared from **3** (7.21 g, 45.6 mmol) and trityl perchlorate (15.7 g, 45.6 mmol) in 30 mL of methylene chloride by the same method used for triethylsilyl perchlorate (except the reaction mixture was stirred 1 h at room temperature). Distillation furnished 10.2 g (39.8 mmol, 87% yield) of clear, colorless **4:** bp 65 °C (0.1 mm); $^{1}$H NMR (CD$_3$CN) $\delta$ 1.11 (s, 18 H), 0.57 (s, 3 H); IR (film) 2975 s, 2945 s, 2900 m, 2870 s, 1472 s, 1395 w, 1371 m, 1230 s, 1114 s, 1034 s, 1010 s, 938 w, 826 m, 790 s, 739 m, 680 m.

**NMR Tube Reactions of Silyl Perchlorates 2, 4, and 6.** A number of the reactions of **2, 4,** and **6** were conducted in essentially the same fashion. A small septum was placed on an NMR tube and the tube was purged with dry nitrogen via a long, syringe needle. Deuterioacetonitrile (CD$_3$CN, 0.5 mL) was injected into the tube along with 30 $\mu$L of methylene chloride as an internal lock. A quantity of silyl perchlorate (0.126 mmol) was injected into the tube and its spectrum then obtained. For the two liquid perchlorates **2** and **4** volumetric measurements of the pure materials were used based on the approximate densities of 1.15 g/mL for **2** and 1.08 g/mL for **4.** For the solid **6** a stock solution was prepared by diluting 0.74 g (2.5 mmol) of **6** to 5 mL with CD$_3$CN to provide a 0.5 M solution. The requisite volume (250 $\mu$L, 0.125 mmol) of this solution was injected into an NMR tube containing 0.280 mL of CD$_3$CN and 30 $\mu$L of CH$_2$Cl$_2$ to approximate the final concentrations used for **2** and **4.**

**Reactions of 2 and the 2–Pyridinium Complex with Water.** To each of the NMR tube reaction mixtures with and without pyridine was added 0.4 mL each of water and pentane. After vigorous shaking the pentane layer was removed and GC/MS of each product mixture was obtained and a single product was found from both reactions. The remaining pentane solutions were allowed to evaporate in open vials. A small amount of CCl$_4$ was added to the residue and solution IR and NMR spectra were obtained which showed the products of the two reactions to be identical and the structure was assigned as *tert*-butyl dimethylsil and: $^{1}$H NMR (CCl$_4$) $\delta$ 0.86 (s, 9 H), 0.01 (s, 6 H); IR (CCl$_4$) 3090 w, 3070 w, 3035 w, 2950 s, 2925 s, 2860 s, 1740 m, 1390 w, 1362 w, 1255 s, 1170 s, 1105 m, 940 w, 840 s, 675 s; GC/MS *m/e* (rel intensity) 246 (0.4, 231 (1), 189 (24), 147 (100), 133 (4), 132 (4), 117 (5), 73 (15), 66 (2), 59 (2), 57 (1), 45 (1), 41 (2).

**Reactions of 4 and the 4–Pyridinium Complex with Water.** Spectral data on the pentane extracts was obtained in identical fashion as for **2.** Again only one product was found for both reactions and its structure was assigned as di-*tert*-butylmethylsilanol: $^{1}$H NMR (CCl$_4$) $\delta$ 1.10 (s, 1 H) (for the reaction of the perchlorate itself this peak was seen at 0.91), 0.96 (s, 18 H), 0.01 (s, 3 H); IR (CCl$_4$) 3700 m, 3090 w, 3075 w, 3035 w, 2960 s, 2930 s, 2885 m, 2855 s, 2470 m, 1385 w, 1361 w, 1250 m, 1005 w, 981 w, 969 w, 670 s; GC/MS *m/e* (rel intensity) 174 (2), 117 (12), 75 (100), 61 (4), 60 (4), 57 (3), 56 (2).

**Reaction of 6 and the 6–Pyridinium Complex with Water.** Spectral data on the pentane extracts was obtained in identical fashion as for **2** and **4;** however, for **6** there was a significant difference between the reactions. The reaction of **6** with water produced a single product whose structure was assigned to be tri-*tert*-butylsilanol: $^{1}$H NMR (CCl$_4$) $\delta$ 1.09 (s); IR (CCl$_4$) 3700 m, 2980 m, 2955 s, 2905 m, 2875 s, 1480 m, 1385 m, 1368 w, 1010 s, 965 w, 620 m; GC/MS *m/e* (rel intensity) 159 (16), 117 (35), 87 (2), 75 (100), 61 (3), 57 (3), 41 (5). Silanol prepared by Dexheimer and Spialter[21] from the ozonolysis of tri-*tert*-butylsilane was reported to have the following spectral properties: $^{1}$H NMR (CCl$_4$) $\delta$ 3.12 (s, 1 H), and 1.10 (s, 27 H); IR 3448 w, 2950 s, 2874 s, 1481 m, 1393 w, 1368 w, 1075 w, 821 s; MS parent ion peak *m/e* 216.

The product mixture from the reaction of the **6**–pyridinium complex with water was found to be primarily tri-*tert*-butyl silanol and the GC/MS showed nothing more; however, the NMR showed some new absorptions at $\delta$ 1.22 and 1.19 and the IR showed new absorptions at 3410 w, 2210 m, 1620 m, 1593 w, 1455 m, 1445 m, 885 w, 693 w. The source of these new absorptions remains unidentified.

**Comparison of the Reactivities of the *tert*-Butyldimethylsilyl Perchlorate–Pyridine System to the Silyl Chloride–Imidazole System.** These reactions were conducted in NMR tubes in a fashion similar to previous descriptions. For the reactions of **2** with *tert*-butyl alcohol and 1-methylcyclohexanol a quantity of **2** (46 mg, 0.215 mmol) was injected into an NMR tube containing 0.75 mL of CD$_3$CN and 5 $\mu$L of benzene as an internal lock. Pyridine (20 mg, 0.25 mmol) was then added. To this solution was added 14.5 mg (0.196 mmol) of *tert*-butyl alcohol and the change in the O-*t*-Bu absorption was monitored by NMR. The *tert*-butyl alcohol peak at $\delta$ 1.22 was gradually replaced by the SiO-*t*-Bu peak at $\delta$ 1.26. The conversion was over 50% at 30 s and was complete at 5 min: $^{1}$H NMR (CD$_3$CN reaction solution) $\delta$ 1.26 (s, 9 H), 0.89 (s, 9 H), 0.12 (s, 6 H).

The reaction was repeated with 1-methylcyclohexanol (22 mg, 0.193 mmol) replacing *tert*-butyl alcohol. The methyl peak of the alcohol at $\delta$ 1.18 was gradually replaced by a peak at $\delta$ 1.26. The conversion was $\sim$50% at 3 min and complete at 20 min: $^{1}$H NMR (CD$_3$CN reaction solution) $\delta$ 1.49 (m, 10 H), 1.19 (s, 3 H), 0.87 (s, 9 H), 0.07 (s, 6 H).

Attempts to derivatize these tertiary alcohols using *tert*-butyldimethylsilyl chloride were then made to provide a strict comparison. The chloride (32 mg, 0.213 mmol) and imidazole (30 mg, 0.44 mmoles) in the proportions suggested by Corey and Venkateswarlu[1] were added to 0.75 mL of DMF. The same amounts of each of the two alcohols were added as before and the changes in NMR spectrum of the solution were monitored. After 3 days the conversion of *tert*-butyl alcohol to the ether was $\sim$30%; for 1-methylcyclohexanol it was $\sim$10%.

**Preparative Scale Reaction of 2 with 1-Methylcyclohexanol.** To a flask equipped with a magnetic stirrer and a rubber septum was added 0.862 g (4.03 mmol) of **2** and 5 mL of acetonitrile. Pyridine (0.332 g, 4.2 mmol) was added slowly and finally 0.45 g (3.95 mmol) of 1-methylcyclohexanol was injected to the stirred solution. Just after the mixture became homogeneous a phase separation occurred. Stirring was continued for 1.5 h. The reaction mixture was then poured into a small separatory funnel containing 15 mL of pentane and 15 mL of saturated NaHCO$_3$ solution. The pentane layer was then extracted several times until the smell of pyridine could no longer be detected in the aqueous phase. Evaporation of the pentane solution then afforded 0.891 g (99% yield) of the desired silyl ether (>95% pure by GC): $^{1}$H NMR (CCl$_4$) $\delta$ 1.48 (m, 10 H), 1.18 (s, 3 H), 0.86 (s, 9 H), 0.05 (s, 6 H); IR (film) 2930 s, 2855 s, 1460 m, 1445 w, 1372 w, 1358 w, 1275 w, 1253 s, 1168 m, 1135 m, 1061 s, 1024 s, 1000 m, 831 s, 768 s; MS *m/e* (rel intensity) 228 (2), 213 (6), 185 (6), 177 (26), 95 (11), 75 (100), 59 (11), 57 (4); MS calcd for C$_{13}$H$_{28}$OSi *m/e* 228.1909, found *m/e* 228.1905.

**Preparative Scale Reaction of 2 with Cyclohexanol.** Silyl perchlorate **2** (0.854 g, 4.0 mmol) was reacted with pyridine (0.38 g, 4.8 mmol) and finally with 0.401 g (4.0 mmol) of cyclohexanol in the fashion described above. Workup as above furnished 0.848 g (99% yield) of the desired silyl ether (>95% pure by GC): $^{1}$H NMR (CCl$_4$) $\delta$ 3.58 (br s, 1 H), 1.47 (m, 10 H), 0.88 (s, 9 H), 0.02 (s, 6 H); IR (film) 2930 s, 2860 s, 1465 m, 1445 w, 1371 w, 1360 w, 1255 m, 1132 w, 1096 s, 1050 m, 1018 w, 1002 w, 992 w, 935 w, 883 w, 868 m, 834 s, 790 w, 771 m; MS *m/e* (rel intensity ) 214 (1), 199 (1), 157 (63), 75 (100), 73 (11); MS calcd for C$_{12}$H$_{26}$SiO *m/e* 214.1753, found *m/e* 214.1759.

**Preparative Scale of 4 with Cyclohexanol.** A quantity of **4** (5.60 g, 21.9 mmol) in 20 mL of CH$_3$CN was reacted with pyridine (1.9 g, 24 mmol) and finally with 2.19 g (21.9 mmol) of cyclohexanol. Again a phase separation occurred immediately after the dissolution of the cyclohexanol. After stirring the mixture for 1 h, 20 mL of pentane was added and the mixture extracted once with dilute HCl and twice with water. Evaporation of the pentane solution provided 5.62 g (100%) of the desired silyl ether (>95% pure by GC): $^{1}$H NMR (CCl$_4$) $\delta$ 3.62 (br s, 1 H), 1.50 (m, 10 H), 0.95 (s, 18 H), 0.04 (s, 3 H); IR (film) 2930 s, 2860 s, 1465 m, 1445 w, 1381 w, 1368 m, 1250 m, 1128 w, 1092 s, 1048 m, 1016 m, 1006 m, 992 w, 931 w, 883 w, 871 w, 856 m, 820 s, 776 m, 750 m, 692 m; MS *m/e* (rel intensity) 256 (6), 241 (3), 199 (36), 157 (48), 75 (100), 73 (18), 61 (12), 41 (15); MS calcd for C$_{15}$H$_{32}$OSi *m/e* 256.2222, found *m/e* 256.2210.

**Solvolytic Stability Comparison of *tert*-Butyldimethylsilyl (10), Di-*tert*-butylmethylsilyl (11), and Tetrahydropyranyl (THP) Ethers of Cyclohexanol.** For the acid stability test a stock solution of 1% HCl in aqueous ethanol was prepared by adding 2.9 g of concentrated (35%) aqueous HCl to 97.1 g of 95% ethanol. A sample of each ether (50 $\mu$L) was placed in a test tube containing 0.5 mL of the 1% HCl in aqueous ethanol solution and a septum placed over the mouth of the tube. The decomposition of the ethers was followed by GC. Both **10** and the THP ether were completely reacted in 15 min at room temperature; however, the DTBMS ether showed no decomposition after 3 days at room temperature. Upon heating some decomposition was observed, but after 24 h at 80 °C <50% decomposition had occurred.

For the alkaline stability test a stock solution of 5% NaOH in aqueous ethanol was prepared by dissolving 5 g of NaOH in 95 g of 95% ethanol. The THP ether was assumed to be stable under basic conditions, but samples of both silyl ethers (50 $\mu$L) were placed in NMR tubes containing 0.9 mL of the 5% NaOH in aqueous ethanol solution. The spectrum of 11 showed no change after heating at 80 °C for 3 days; however, **10** was found to decompose slowly under these conditions as ~15% of the silyl ether methyl absorption at $\delta$ 0.03 had been converted to a new peak at $\delta$ −0.07 after 9 h at 80 °C.

**Cleavage of the Di-*tert*-butylmethylsilyl Ether of Cyclohexanol (11) with BF$_3$.** A sample of 11 (0.278 g) was placed in a flask with 10 mL of methylene chloride. Decane (0.081 g) was added as an internal GC standard. The flask was cooled in an ice bath and BF$_3$ was slowly passed over the stirred solution for 30 min. Saturated aqueous NaHCO$_3$ (15 mL) was added to the mixture and it was allowed to stir at room temperature for 5 h. The mixture was placed in a separatory funnel and the methylene chloride layer drained off. The aqueous layer was then extracted once with 10 mL of diethyl ether and the ether extract combined with the methylene chloride layer. After stirring the solution was found (by GC) to contain di-*tert*-butylmethylfluorosilane and cyclohexanol (94% yield; cyclohexanol was further identified by comparison of GC/MS with authentic material).

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**Registry No.**—**1,** 29681-57-0, **3,** 56310-20-4; **4,** 67124-69-0; **5,** 18159-55-2; **6,** 61150-01-4; **7,** 56348-26-6; triethylsilyl perchlorate, 18244-91-2; **2**–pyridinium complex, 67124-71-4; **4**–pyridinium complex, 67124-73-6; **6**–pyridinium complex, 67124-75-8; *tert*-butyl dimethylsilanol, 18173-64-3; di-*tert*-butylmethylsilanol, 56889-84-0; tri-*tert*-butylsilanol, 56889-90-8; cyclohexanol, 108-93-0; boron trifluoride, 7637-07-2; silver perchlorate, 7783-93-9; potassium hydroxide, 1310-58-3; water, 7732-18-5; trityl perchlorate, 3058-33-1; triethylsilane, 617-86-7; chlorodimethylsilane, 1066-35-9; *tert*-butyllithium, 594-19-4; methyldichlorosilane, 75-54-7.

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# Enones with Strained Double Bonds: The Bicyclo[3.3.1] System[1]

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Since examination of models suggests that bridgehead enones of the types **17** and **18** may have unusual chemical and physical properties, a variety of methods (Schemes III–VI) have been explored to form the enone **18**. Although various base-catalyzed elimination reactions (Scheme III) and pyrolytic elimination reactions (Schemes IV–VI) appear to generate the desired enone **18**, the tendency of this strained enone to undergo conjugated addition of nucleophiles or thermal rearrangement has thus far prevented us from isolating it.

An earlier investigation[2] of the structure of the $C_{27}H_{38}O$ compound formed from isophorone and hot aqueous alkali had suggested the intermediacy of the dienone 1 (Scheme I) with a bridgehead C=C. A stepwise synthesis of this $C_{27}$ compound was effected utilizing as one step the base-catalyzed dehydrohalogenation of the chloro enone 2 to generate the dienone 1 that underwent a rapid Michael reaction. To learn whether this ready dehydrohalogenation 1 → 2 was dependent on the presence of an allylic chloride (albeit a twisted allylic system) in the chloro ketone **2,** we have now examined an analogous reaction with the saturated chloro ketone **3.** This ketone 3 was prepared from dimer 4[3] of 3,5-dimethylcyclohexenone (**5**) by reduction to the ketol **6** and subsequent reaction with $SOCl_2$. Reaction of this chloro ketone **3** with $NaNH_2$ in a liquid $NH_3$–THF mixture formed the amino ketone **8.** As in our earlier study,[2] it seems most improbable that the conversion 3 → 8 occurs by either an $S_N1$ or an $S_N2$ process. Instead, we presume that a base-promoted dehydrohalogenation formed the enone intermediate 7 that was rapidly trapped by the conjugate addition of either ammonia or amide anion.

The ability to form, and in many cases isolate, bridgehead olefins of the type **10** (Scheme II) is now well established through the efforts of many investigators.[4] Several systems containing a bridgehead C=C that is part of a conjugated enone are also known.[4a,b] These include enones **11,**[5a–c] **12,**[5d–f] **13,**[5d,g] and **14.**[5h] The enone systems **11** appear to be relatively unstrained, while the systems **12** in part minimize strain by some distortion of the C=C accompanied by twisting about the C–C bond of the enone system so that the C=C and C=O functions are not coplanar.[5d] The failure of the enones **12** to undergo Michael additions is attributable both to this nonplanarity (and resultant poor conjugation) in the enone system and to the fact that the enolate anion **15** formed by Michael addition to the enones **12** would be more strained than the starting enone.[5d,f] Other examples of enone systems with considerable internal strain energy are the trans cyclic enones **16**[6] formed by photochemical isomerization.

In examining molecular models of these various bridgehead enone systems, we were impressed by the observation that while enones such as **12–14** seemed unlikely to have their C=C and C=O functions coplanar, such coplanarity appeared to add little strain to enones such as **17** (the parent system of intermediates **1** and **7**) and **18.** The main relief of strain in these latter two enones appeared to result from allowing the molecules to twist at the center of the C=C functions (indicated with arrows in structures **17** and **18**). A twist at this location would correspond to the geometry that might be expected for the photochemically excited states[7] or the radical anions derived from these enone systems. Consequently, it was of interest to seek preparative routes to enones such as **17** or **18** to learn whether these systems would exhibit unusual