New Nitrogen Bases with Severe Steric Hindrance Due to Flanking *tert*-Butyl Groups. *cis*-2,6-Di-*tert*-butylpiperidine. Possible Steric Blocking of Olfaction

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New severely hindered nitrogen bases, 2,6-di-*tert*-butyl-1,4-dihydropyridine (**2**), 2,6-di-*tert*-butyl-3,4-dihydropyridine (**3**), 2,6-di-*tert*-butyl-3,4,5,6-tetrahydropyridine (**5**), *cis*-2,6-di-*tert*-butylpiperidine (**6**), and a novel endoperoxide, 1,5-di-*tert*-butyl-8-aza-6,7-dioxabicyclo[3.2.1]octane (**7**), were obtained by lithium metal reduction of 2,6-di-*tert*-butylpyridine (**1**). Dihydropyridine **2** tautomerizes to **3** in deuteriochloroform at 38 °C. Pyridine **1** loses its characteristic "2,6-dimethylpyridine-like" odor upon silica gel column chromatography. The significance of this observation is discussed.

The great value in organic synthesis of sterically hindered bases[1] has recently become more and more apparent. Their unique ability to abstract protons in reaction media containing sites intrinsically more reactive toward nucleophilic attack has allowed the direct generation of a wide variety of carbanionic species. Alkylations, acylations, and carboxylations employing such carbanions are too numerous to cite.[2]

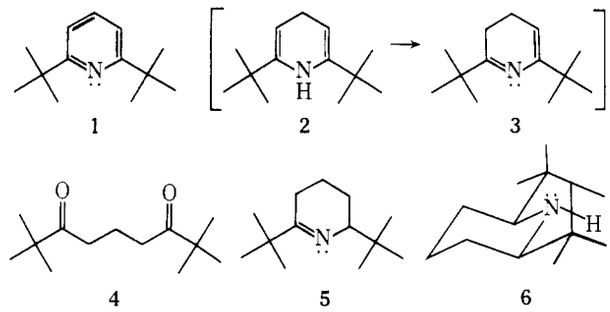
Steric inhibition of competing reaction routes has permitted the strong but severely hindered base lithium 2,2,6,6-tetramethylpiperidide to be used as proton abstracter in the generation of various benzyne and carbene (or carbenoid) species.[3] The Hünig base ethyldiisopropylamine[4] has been used as proton-specific base in a direct synthesis of di-*tert*-butyl ether by O-alkylation of *tert*-butyl alcohol with *tert*-butyl cation.[5]

Sterically hindered amines are routinely used as precursors of stable nitroxyl radicals employed as ESR probes in biologically oriented studies[6] and are also of interest as ganglionic blocking agents in the treatment of hypertension.[7] It has been suggested that "the degree of shielding of the basic nitrogen atom by substituents on the adjacent carbon atoms is the primary factor controlling ganglionic blocking activity".[7c] Sterically hindered amines have also been used to protect polypropylene from photodegradation.[8]

However, the use of sterically hindered bases to favor deprotonation at sterically more accessable sites relative to less accessable sites has met with very limited success. Bartsch and co-workers have clearly delineated the effects of steric hindrance and base strength on orientation in base-promoted eliminations of 2-substituted butanes.[9] Even the most severely hindered bases studied (including the potassium salts of tricyclohexylcarbinol, tri-2-norbornylcarbinol, and 1,1-di-*tert*-butylnonadecanol) yielded less than 30% 1-butene in the butene mixture produced upon reaction with 2-iodobutane in Me_2SO at 50 °C.[9b,c] The use of Corey–Pauling–Koltun space-filling models indicates that *existing bases are just not sterically hindered enough to effectively distinguish between protons at C-1 and C-3 in the 2-halobutanes.*

Results and Discussion

With the aim of extending the already successful applications of severely hindered bases and the future goal of simple, direct "Hoffmann orientation" control in base-promoted elimination reactions, we have synthesized bases **2, 3, 5,** and **6** in a preparative approach to these problems. They and their common precursor, 2,6-di-*tert*-butylpyridine[10] (**1**), share the feature of having two *tert*-butyl groups flanking the basic nitrogen. All of these bases are water-insoluble oils which readily dissolve in aqueous acid. The bulky *tert*-butyl groups effectively limit access to the basic lone-pair electrons since they are held in the proper orientation by a six-membered ring



1 **2** **3**

4 **5** **6**

incorporating the nitrogen and both α carbons. The use of space-filling models clearly shows that in these species the basic site is located at the bottom of a deeper "well" than in such bases as 2,2,6,6-tetramethylpiperidine, and indeed in all the great variety of sterically hindered bases previously studied,[2-9,11] including the ganglionic blocker 1,2,2,6,6-pentamethylpiperidine.[7b,c] The great magnitude of the steric attenuation of nucleophilicity of **1** was demonstrated by the observation that it could be N-methylated only at very high pressures (5000–6000 atm).[12]

Reaction of **1** with 2 to 7 molar equiv of Li in NH_3 with excess *t*-BuOH as the proton source[13] yielded mixtures of **2** and **3** (various ratios, up to 60% **2**). These tautomeric dihydropyridines were identified by 60 MHz ^1H NMR spectroscopy and also by hydrolysis of such mixtures to the novel diketone 2,2,8,8-tetramethyl-3,7-nonanedione (**4**). Mixtures of **2** and **3** underwent tautomerization over a period of several hours to greater than 98% **3** when present at about 40% total concentration of **2** and **3** in $CDCl_3$ at 38 °C (as observed by ^1H NMR). The greater stability of the 3,4-dihydropyridine is possibly due to relief of steric compression strain present in the 1,4-dihydropyridine. This is not an argument that the N lone pair in **3** occupies less space than the N–H group in **2** since **3** must have a quite twisted conformation. The bis(vinyl)-amine structure has been shown for the parent 1,4-dihydropyridine,[14] but only postulated (30 years ago) for its 2,6-dimethyl derivative on the basis of the isolated hydrolysis product, heptane-2,6-dione.[15] In any case **3** appears to be the only observed 3,4-dihydropyridine[16] apart from earlier examples having additional oxygen or nitrogen substitution at the 2 position[17] (resonance stabilization of the carbon–nitrogen double bond). The rearrangement of **2** to **3** clearly illustrates the tautomerization process that probably accounts for the often observed Birch reduction of aromatic species past the 1,4-dihydro stage.[13]

Silica gel column chromatography (distilled pentane–diethyl ether gradient elution) of 2.00 g of a product thought by 60 MHz ^1H NMR analysis to consist of a 1 to 3 mixture of **2** to **3** together with about 6 to 8% of the starting pyridine **1**

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yielded 1.64 g of pure diketone **4** by adventitious hydrolysis and 0.137 g of a rapidly eluted compound having a 60 MHz ^{1}H NMR spectrum identical to that of precursor **1**. This liquid possessed only a faint "hydrocarbon-like" odor and no trace of the "lutidine-like" odor of all samples of **1** not subjected to silica gel column chromatography. Its thin layer chromatographic behavior and solubility in aqueous acid were indistinguishable from the corresponding properties of other samples of **1**. The absence in **1** of a lutidine-like odor[18] and the observation that 4,5-dimethylacridine lacks the severe lachrymatory and skin irritating properties of acridine itself[11] may both be due to steric blocking of coordination to relatively large electron-pair acceptors in the tissues affected. Possibly a transition metal serves in the olfaction of certain functional groups. Aliphatic amines seem highly resistant to the "steric masking" observed for **1** but these stronger bases are very likely detected as their conjugate acids at physiological pH.

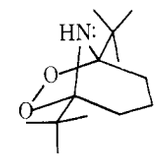
Reaction of **1** in ammonia with 5 molar equiv of Li and only 1 molar equiv of *t*-BuOH (insufficient to protonate all the strongly basic species generated) yielded a mixture from which successive vacuum distillation and silica gel column chromatography provided a 46% yield of pure 2,6-di-*tert*-butyl-3,4,5,6-tetrahydropyridine (**5**). This imine has its sp^2 hybridized nitrogen lone pair electrons enormously hindered by the flanking *tert*-butyl groups and can therefore be expected to show exceptional resistance to any potential coordinating metal or Lewis acid other than a proton.

Reaction of **1** in 1,2-ethanediamine[19] at 90 °C (oil bath temperature) with 18 molar equiv of concurrently added Li and *t*-BuOH gave a product whose ^{1}H NMR spectrum showed no peaks below δ 2.25 except for those due to the presence of 5 to 7% of imine **5**, the separation of which proved difficult. In the hope of carboxylating the conjugate base of the latter (and removing the expected zwitterionic imino acid side product by subsequent aqueous extraction), the procedure was modified to include the addition of 50 to 100 molar equiv of solid CO_2 to the cooled reaction mixture.[20] The resulting products, after aqueous extraction, drying, and evaporation of the volatile components, exhibited an ^{1}H NMR spectrum virtually identical to that of a subsequently prepared analytical sample of **6**. Vacuum distillation provided an 86% yield of the pure liquid *cis*-2,6-di-*tert*-butylpiperidine.

All spectral data are consistent with the assignment of the cis configuration to **6**. In view of proposed mechanisms[13] for Lithium amine reductions, in particular the configuration determining protonation step, the highly strained trans configuration would not be expected. Reduction of 2,6-dimethylpyridine with sodium in refluxing ethanol was reported to yield *cis*- and *trans*-2,6-dimethylpiperidine in a 74/26 ratio.[21] If one assumes staggered *tert*-butyl rotamers as shown for **6**, equatorial NH would have two additional peri CH_3/H interactions and axial NH would have two additional syn-axial interactions relative to piperidine itself, the conformational preference of which is clearly quite small, although controversial.[22] Thus the additional conformational interactions in **6** relative to piperidine appear to be equal with respect to the CH_3/NH and CH_3/N lone pair interactions, and the NH axial–equatorial equilibrium may be similar to that in the parent amine.

Uniquely hindered secondary amine **6** exhibits a tiny, barely detectable absorption at about 3375 cm^{-1} in its infrared spectrum (neat). However, the Raman spectrum (Ar laser, 514.5 nm) of neat **6** shows two separate peaks at 3376 and 3308 cm^{-1} with relative band area ratio intensities of about 3.0 to 1.0 at 20 °C. The more intense, high frequency Raman band at 3376 cm^{-1} may be due to equatorial NH stretching.[22] Prominent low-frequency CH stretching bands (expected for the axial lone pair conformation) are observed at 2774 and 2715 cm^{-1} in the Raman spectrum of **6**, and corresponding Bohlmann bands[23] are seen in its infrared spectrum. The smaller of the two Raman NH stretching bands (at 3308 cm^{-1}) may then be due to axial NH stretching, but confirmation of these tentative assignments must await further study.

Analysis of small crystals that appeared in the neck of a rotary evaporator during work-up of one of the NH_3/Li reaction products indicated the absence of vinyl protons and an apparent mass spectral parent peak of *m/e* 195, corresponding to an isomer of imine **5**. An initially considered bicyclic *cis*-di-*tert*-butylaziridine was ruled out when trial reactions led to the production of this compound in improved yield: Its microanalysis corresponded to $C_{13}H_{25}NO_2$ and its mass spectrum revealed a tiny parent peak at *m/e* 227. The downfield ^{13}C NMR peak at 102.7 ppm (bridgehead carbons) and all the other data now seem consistent only with the "ozonide-like" endoperoxide 1,5-di-*tert*-butyl-8-aza-6,7-dioxabicyclo[3.2.1]octane (**7**). Apparently a precursor adds dioxygen



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and readily eliminates it upon mass spectral fragmentation. Work is in progress to see if the precursor is the aziridine with compressed *cis*-di-*tert*-butyl groups considered initially.

Experimental Section

General. All chemicals were anhydrous reagent grade and used as supplied unless otherwise stated. Precursor **1** was used as received from Willow Brook Labs., Inc., Waukesha, Wis. Lithium (Alfa, 1/8 in. wire) contained 0.01% sodium. Ammonia vapor was passed through a 2 × 40 cm column of sodium hydroxide pellets prior to condensation. Baker silica gel (60–200 mesh) was used for column chromatography. Pentane was distilled and oxacyclopentane was distilled from lithium aluminum hydride and stored under nitrogen. Fisher 1,2-ethanediamine was heated with sodium at 85–90 °C for 48 h, distilled, and stored under nitrogen.

All reaction vessels used in the lithium reductions were flushed with nitrogen, but the nitrogen source was disconnected prior to addition of the lithium. Appropriate reflux condensers equipped with calcium chloride drying tubes were employed. Teflon-coated magnetic stirring bars were used except in the preparation of **6** which required an all-glass mechanical stirrer. Syringe techniques were used whenever possible.

Proton magnetic resonance spectra were recorded on a Varian A-60A spectrometer using deuteriochloroform with internal tetramethylsilane. Carbon and nitrogen NMR spectra were obtained in the Fourier transform mode on a JEOL PS/PFT-100 spectrometer in hexadeuteriobenzene taken as 128.5 ppm. Raman spectra were obtained on a Spex Industries Model 1401 spectrometer using an argon laser at 514.5 nm. Infrared spectra were recorded on a Perkin-Elmer infracord. Mass spectra were recorded on an AEI Model MS-9 spectrometer. Melting points were measured on a Mel-Temp apparatus and are uncorrected. Analyses were performed by Schwartzkopf Microanalytical Laboratories, Woodside, N.Y.

2,6-Di-*tert*-butyl-1,4-dihydropyridine (2) and 2,6-Di-*tert*-butyl-3,4-dihydropyridine (3). A solution of 9.56 g (50 mmol) of **1** in 50 mL (530 mmol) of dry *t*-BuOH was added to 100 mL of freshly condensed ammonia. Lithium (0.763 g, 110 mmol) was added in 16 approximately equal-sized pieces over a 10-min period, and after allowing the resulting mixture to gently reflux for another 60 min, 8.02 g (150 mmol) of ammonium chloride was added in portions. A water bath (40 °C) was used to evaporate the ammonia and 300 mL of diethyl ether was then added to the residue. The resulting ether solution was filtered, shaken with anhydrous sodium sulfate, filtered again, and evaporated under vacuum to yield 9.25 g of **2** and **3** (96%, crude). Analysis by 60 MHz ^{1}H NMR indicated the presence of a 3 to 2 ratio of **2** to **3** with about 15% of **1** remaining. **2:** δ 1.09 (s, 6 CH_3), 2.91 (t, J = 3.4 Hz, CH_2), 4.22 (m, 2 CH=), 4.33 (br s, NH). **3:** δ 1.10 (s, 3 CH_3), 1.15 (s, 3 CH_3), 1.97 (m, CH_2CH_2), 5.16 (m, CH=).

A 0.238-g portion of this product mixture was dissolved in 5.0 mL of 10% HCl and the resulting solution was allowed to stand at 25 °C

for 24 h. The resulting products were shaken with 20 mL of diethyl ether and 15 mL of water and the ether extract was washed, dried ($MgSO_4$), and evaporated under vacuum to yield 0.219 g of an oil consisting of 4 together with about 10% of 1 (60 MHz ^1H NMR analysis).

2,2,8,8-Tetramethyl-3,7-nonanedione (4). A 2.00-g portion of a product mixture thought by ^1H NMR spectroscopic analysis to consist of a 1 to 3 ratio of **2** to **3** together with 6 to 8% of 1 was subjected to silica gel column chromatography using a 0 to 10% diethyl ether gradient in distilled pentane to yield, in order of elution: (a) 0.137 g of pure 1 having only a faint "hydrocarbon-like" odor; (b) 0.022 g of impure **7**; (c) 1.64 g of pure **4**, mp 29.0–31.0 °C [60 MHz ^1H NMR δ 1.13 (s, 6 CH_3), 1.81 (p, CH_2), 2.53 (t, 2 CH_2); IR ($CDCl_3$) 1705 cm^{-1}; mass spectrum (*m/e*, 50 eV) 212 (M^+), 155, 127, 110, 109, 85, 71, 69, 57, 55. Anal. Calcd for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39. Found: C, 73.68; H, 11.55.].

2,6-Di-*tert*-butyl-3,4,5,6-tetrahydropyridine (5). A solution of 1.913 g (10 mmol) of 1 and 0.741 g (10 mmol) of *t*-BuOH in 5.0 mL of oxacyclopentane was added to 35 mL of freshly condensed ammonia. Lithium (0.555 g, 80 mmol) was added in ten approximately equal-sized pieces over a 15-min period. The resulting mixture was allowed to gently reflux for another 2 h and then 4.28 g (80 mmol) of ammonium chloride was added in portions along with 20 mL of oxacyclopentane to facilitate stirring. A water bath (40 °C) was used to evaporate the ammonia and the residue was shaken with 50 mL of pentane and 35 mL of water. The separated pentane layer was washed with water, dried ($MgSO_4$), and evaporated under vacuum to yield 1.64 g of an oil which was subjected to silica gel column chromatography using a 0 to 6% diethyl ether gradient in distilled pentane to yield 1.37 g of crude **5**. Vacuum distillation of this product removed a substantial amount of high boiling impurity and yielded 0.895 g (46%) of pure **5**: bp 99–100 °C (16.5 mm); 60 MHz ^1H NMR δ 0.92 (s, 3 CH_3), 1.08 (s, 3 CH_3), ca. 1.00–2.25 (m, $CH_2CH_2CH_2$), 2.90 (m, CH); ^{13}C NMR 21.2 (CH_2), 23.0 (CH_2), 24.3 (CH_2), 27.4 (3 CH_3), 28.9 (3 CH_3), 35.6 (C), 40.5 (C), 66.9 (CH), 174.0 (=C); IR ($CDCl_3$) 1650 cm^{-1}; mass spectrum (*m/e*, 70 eV) 195 (M^+, 3), 180 (5), 155 (20), 138 (16), 109 (56), 84 (25), 69 (25), 57 (100, base), 55 (23), 43 (40), 41 (93). Anal. Calcd for $C_{13}H_{25}N$: C, 79.93; H, 12.90; N, 7.17. Found: C, 79.68; H, 12.78; N, 7.28.

Imine **5** is stored under nitrogen at room temperature to prevent discoloration and slow decomposition.

***cis*-2,6-Di-*tert*-butylpiperidine (6).** A solution of 4.78 g (25 mmol) of 1 in 5 mL of dry *t*-BuOH was added to 175 mL of anhydrous 1,2-ethanediamine. With vigorous stirring and heating of this mixture (90 °C oil bath) 3.12 g (450 mmol) of lithium was added over a 30-min period in 12 approximately equal-sized pieces alternating with approximately equal portions of dry *t*-BuOH, such that the total amount of *t*-BuOH used, including the initial 5 mL, was 33.4 g (450 mmol). After all the lithium metal had been consumed (2–3 min additional), the mixture was rapidly cooled to about 25 °C (water bath) and 60–90 g of dry ice was added to it in small portions (*exothermic* reaction). After another 15 min 700 mL of diethyl ether was added to the reaction products, followed by 32.1 g (600 mmol) of ammonium chloride (in portions and with ice-bath cooling). After an additional 10 min the resulting mixture was shaken with 350 mL of water, dried ($MgSO_4$), and evaporated under vacuum to yield 4.69 g (95%, crude) of **6**. Vacuum distillation of the product yielded 4.21 g (86%) of pure **6**: bp 95.0–97.0 °C (10 mm); 60 MHz ^1H NMR δ 0.88 (s, 6 CH_3), ca. 0.8–2.1 (m, $CH_2CH_2CH_2$), 1.13 (br s, NH, assignment by D_2O exchange), 2.14 (br d, J = 10.0 Hz, 2 CH); ^{13}C NMR 26.6 (C_4), 27.4 (6 CH_3), 27.6 (C_3, C_5), 34.5 (2 quaternary C), 67.4 (C_2, C_6), assignments confirmed by off-resonance proton decoupling; ^{15}N NMR (C_6D_6, downfield from external aqueous $^{15}NH_4Cl$) δ 30.0; mass spectrum (*m/e*, 70 eV) 197 (M^+, 0.3), 196 (1.3), 182 (9.4), 141 (18), 140 (100, base), 97 (15), 56 (33), 55 (28), 41 (29). Anal. Calcd for $C_{13}H_{27}N$: C, 79.11; H, 13.79; N, 7.10. Found: C, 79.36; H, 13.82; N, 7.07.

1,5-Di-*tert*-butyl-8-aza-6,7-dioxabicyclo[3.2.1]octane (7). A solution of 1.913 g (10 mmol) of 1 and 3.71 g (50 mmol) of *t*-BuOH in 27 mL of diethyl ether was added to 25 mL of freshly condensed ammonia. With rapid stirring of the resulting heterogeneous mixture, lithium (0.347 g, 50 mmol) was added in eight approximately equal-sized pieces over a 10-min period. After another 30 min 15 mL of additional ammonia was condensed into the mixture, and after an additional 60 min ammonium chloride (2.94 g, 55 mmol) was added in portions. A water bath (40 °C) was used to evaporate the ammonia and the residue was shaken with 30 mL of pentane and 30 mL of water. The separated pentane layer was washed with water, dried ($MgSO_4$), and evaporated under vacuum to yield 1.851 g of an oil which was estimated by 60 MHz ^1H NMR analysis to consist of approximately equal parts of **1**, **3**, and **7**. Silica gel column chromatography of this mixture using a 0 to 8% diethyl ether gradient in pentane yielded in order of elution: (a) 0.509 g of pure **1** (^1H NMR analysis); (b) 0.552 g of **7** (24%), mp 90.0–92.5 °C; (c) 0.435 g of **4**. Vacuum sublimation yielded an analytical sample of **7**: mp 92.0–93.0 °C; 60 MHz ^1H NMR δ 1.04 (s, 6 CH_3), ca. 1.5–2.2 (m, $CH_2CH_2CH_2$), 3.45 (br s, NH); ^{13}C NMR 19.1 (CH_2), 25.5 (6 CH_3), 29.1 (2 CH_2), 35.8 (2 C), 102.7 (2 C, bridgehead); IR (CCl_4) 3365 cm^{-1} (w); mass spectrum (*m/e*, 70 eV) 227 (M^+), 195 ($M^+ - O_2$), 181, 180, 178, 57, 55, 41, 39, 29, 28. Anal. Calcd for $C_{13}H_{25}NO_2$: C, 68.68; H, 11.08; N, 6.16. Found: C, 68.59; H, 11.03; N, 6.03.

Acknowledgments. We thank Professor R. Lichter for obtaining the ^{13}C and ^{15}N NMR spectra and Dr. K. Krishnan for obtaining the Raman spectrum. Funds for a JEOL PS/PFT-100 NMR spectrometer were provided in part from NSF Instrumentation Grant No. GP-37025.

Registry No.—**1**, 585-48-8; **2**, 66922-14-3; **3**, 66922-15-4; **4**, 66922-16-5; **5**, 66922-17-6; **6**, 66922-18-7; **7**, 66966-53-8.

References and Notes

(1) Steric hindrance here refers to spatial limitations upon access to the lone pair electrons of a base by an approaching Lewis acid. The descriptive term "sterically crowded" implies internal congestion.
(2) The increasing popularity of the more severely hindered lithium dialkylamides (including lithium 2,2,6,6-tetramethylpiperidide) and of the lithium, sodium, and potassium salts of bis(trimethylsilyl)amine is seen by scanning the more recent volumes of M. Fieser and L. Fieser, "Reagents for Organic Synthesis", Wiley-Interscience, New York, N.Y., 1967–1977.
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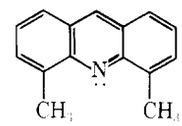

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of **1**. For example, 2,4-di-*tert*-butylpyridine, an isomer of **1** coproduced in the synthesis of **1** by direct alkylation[10] using *t*-BuLi, may not have been entirely removed.

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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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