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Hindered Organosilicon Compounds. Synthesis and Properties of Di-*tert*-butyl-, Di-*tert*-butylmethyl-, and Tri-*tert*-butylsilanes

Michael P. Doyle*[1] and Charles T. West

Contribution from the Department of Chemistry, Hope College, Holland, Michigan 49423. Received July 22, 1974

Abstract: Di-*tert*-butylchlorosilane, but not di-*tert*-butyldichlorosilane, reacts slowly with alkyllithium compounds to form di-*tert*-butylalkylsilanes. With methyllithium, substitution is the only observed process. With *tert*-butyllithium, reduction competes with and is favored over substitution by 2:1. Tri-*tert*-butylsilane is prepared from *tert*-butyltrichlorosilane by reaction with *tert*-butyllithium, followed by lithium aluminum hydride reduction of the resulting mixture of products that includes di-*tert*-butyldichlorosilane, di-*tert*-butylchlorosilane, di-*tert*-butylsilane, and tri-*tert*-butylsilane, and by selective chlorination of di-*tert*-butylsilane with subsequent reaction of di-*tert*-butylchlorosilane with *tert*-butyllithium. The nature of the *tert*-butyllithium reduction process is discussed. The spectral properties of di- and tri-*tert*-butylsilanes are presented; relatively severe crowding of the *tert*-butyl groups in tri-*tert*-butylsilane is implied from C–H stretching frequencies.

Organic compounds possessing bulky *tert*-butyl groups in close proximity have received considerable attention in recent years.[2-6] Such compounds possess unusual physical and chemical properties. Intramolecular crowding of the *tert*-butyl groups in tri-*tert*-butylmethane, for example, distorts bond angles and bond lengths from their normal equilibrium values.[2a] Rotation of the *tert*-butyl groups in tri-*tert*-butylmethane is restricted, and a strain energy of 33.5 kcal/mol for this compound has been calculated.[2b] The strain present in tri-*tert*-butylmethane and its derivatives is likewise evident in the chemical reactivities of these compounds.[5,6]

Few examples are known of compounds with three *tert*-butyl groups bonded to a central atom other than carbon. Tri-*tert*-butyltin derivatives[7a-c] and tri-*tert*-butylphosphine[7d] have been recently prepared but do not appear to be severely restricted in chemical reactions that would increase the steric bulk about the central atom.[7] A silicon analog of tri-*tert*-butylsilane, (Me₃Si)₃SiH, and even (Me₃Si)₄Si have been reported.[8] However, previous attempts to prepare tri-*tert*-butylsilane have not been successful.[9] We have found that, whereas di-*tert*-butyldichlorosilane is inert to substitution reactions by alkyllithium compounds, tri-*tert*-butyl- and di-*tert*-butylmethylsilane can be prepared from di-*tert*-butylchlorosilane and *tert*-butyl- or methyllithium.

The syntheses and spectral properties of these compounds are described.

Results and Discussion

tert-Butyltrichlorosilane was prepared by the procedure of Tyler, Sommer, and Whitmore.[9a] When the *tert*-butyltrichlorosilane was further treated with *tert*-butyllithium over a period of 11 days, while the reaction temperature was slowly increased from 38 to 105°, instead of observing only di-*tert*-butyldichlorosilane, five compounds were detected and analyzed (eq 1). One of these compounds was identified

$$(t\text{-Bu})SiCl_3 + t\text{-BuLi} \longrightarrow (t\text{-Bu})_2SiH_2 + (t\text{-Bu})_2SiHCl +$$
$$9\% \qquad 32\%$$
$$(t\text{-Bu})_2SiCl_2 + (t\text{-Bu})_3SiH + (t\text{-Bu})SiCl_2\text{-O-}t\text{-Bu} \quad (1)$$
$$47\% \qquad 5\% \qquad 7\%$$

as tri-*tert*-butylsilane. Nearly identical results were obtained in a duplicate experiment.

The source of the tri-*tert*-butylsilane could not have been di-*tert*-butyldichlorosilane since this compound is resistant to substitution by *tert*-butyllithium under these reaction conditions and does not form tri-*tert*-butylsilane even under more drastic conditions.[9a] Likewise, although hydride displacement from organosilanes by alkyllithiums is a known

process,[10] no tri-*tert*-butylsilane is produced after treating di-*tert*-butylsilane with *tert*-butyllithium for 53 hr under reaction conditions similar to that used with *tert*-butyltrichlorosilane in eq 1.
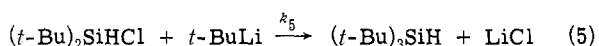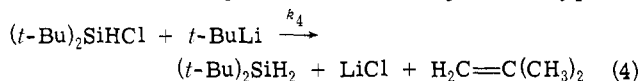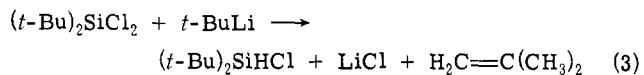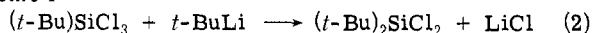
Di-*tert*-butyldichlorosilane was similarly resistant to substitution by methyllithium. However, di-*tert*-butylchlorosilane reacted with methyllithium at 50° to form di-*tert*-butylmethylsilane. In a small scale reaction, GLC analysis showed a nearly quantitative yield of di-*tert*-butylmethylsilane; on a larger scale, this compound was isolated in 91% yield. Thus the replacement of one chlorine on di-*tert*-butyldichlorosilane by hydrogen provides a dramatic change in the reactivity toward alkyl substitution at silicon!

Both electronic and steric effects are important in reactions of organosilicon compounds.[11] Electronegative groups bonded to silicon facilitate the rate of nucleophilic substitution at silicon.[11,12] Thus, if electronic effects were dominant, alkyl substitution should have occurred more readily with di-*tert*-butyldichlorosilane than with di-*tert*-butylchlorosilane. However, exactly the opposite was observed. The difference in size between chlorine and hydrogen was sufficient to prevent even methyllithium from attacking di-*tert*-butyldichlorosilane.[13]

The mechanism of alkyllithium displacement of chloride from chlorosilanes is usually SN2-Si and involves inversion at silicon.[11] Steric hindrance by the *tert*-butyl groups of di-*tert*-butylchlorosilane would be expected to prevent backside approach and force displacement from the same side as the leaving group. The low reactivity of methyllithium toward di-*tert*-butylchlorosilane is consistent with this explanation; unstrained chlorosilanes for which an inversion mechanism cannot operate are very unreactive toward nucleophilic reagents.[11] In contrast, angle-strained organosilicon derivatives having C-Si-C angles less than normal react rapidly with even strong nucleophiles to give products with retention of configuration.[16,17]

The products from the reaction between *tert*-butyltrichlorosilane and *tert*-butyllithium can be explained by the process given in Scheme I. Di-*tert*-butyldichlorosilane,

Scheme I
$$(t\text{-}Bu)SiCl_3 + t\text{-}BuLi \longrightarrow (t\text{-}Bu)_2SiCl_2 + LiCl \quad (2)$$
$$(t\text{-}Bu)_2SiCl_2 + t\text{-}BuLi \longrightarrow$$
$$(t\text{-}Bu)_2SiHCl + LiCl + H_2C{=}C(CH_3)_2 \quad (3)$$
$$(t\text{-}Bu)_2SiHCl + t\text{-}BuLi \xrightarrow{k_4}$$
$$(t\text{-}Bu)_2SiH_2 + LiCl + H_2C{=}C(CH_3)_2 \quad (4)$$
$$(t\text{-}Bu)_2SiHCl + t\text{-}BuLi \xrightarrow{k_5} (t\text{-}Bu)_3SiH + LiCl \quad (5)$$

formed by displacement of chloride from *tert*-butyltrichlorosilane, is reduced to di-*tert*-butylchlorosilane by *tert*-butyllithium. Di-*tert*-butylchlorosilane reacts with *tert*-butyllithium to form both di-*tert*-butylsilane and tri-*tert*-butylsilane. Although we are unaware of similar reductions of chlorosilanes by *tert*-butyllithium, Grignard reagents possessing β hydrogens are noted for their ability to reduce chlorosilanes in a reaction process characterized by retention of configuration at silicon.[18] Similar processes also occur in alkylation reactions of haloorganoboranes.[19,20] In this study, we have found that *tert*-butylmagnesium chloride reduces di-*tert*-butyldichlorosilane under reaction conditions similar to those under which the dichlorosilane is reduced by *tert*-butyllithium (4 days, 95°).

In a separate experiment, a 2 M excess of *tert*-butyllithium was added to a mixture composed of 9% di-*tert*-butylsilane, 57% di-*tert*-butylchlorosilane, and 34% di-*tert*-butyldichlorosilane, and the reaction temperature was slowly

raised from 30 to 80° over a 4-day period. Analysis of the reaction mixture showed unreacted *tert*-butyllithium and only small amounts of di-*tert*-butyldichlorosilane (11%) and di-*tert*-butylchlorosilane (5%); di-*tert*-butylsilane and tri-*tert*-butylsilane were detected in a ratio of 2.6:1 (75% yield). The presence of higher molecular weight material was also observed but was not further analyzed. When an allowance was made for the amount of di-*tert*-butylsilane present in the starting material, the ratio of elimination to substitution for di-*tert*-butylchlorosilane (k_4/k_5) was calculated to be 2.1. Thus even with di-*tert*-butylchlorosilane, reduction by *tert*-butyllithium is the predominant reaction process.

2,2,3,3-Tetramethylbutane was observed as a reaction product from all reactions of chlorosilanes in which reduction by *tert*-butyllithium occurred. The presence of this compound, not observed in the stock *tert*-butyllithium solution, suggests that free-radical processes may be important in *tert*-butyllithium reactions with hindered chlorosilanes. An SNi-Si mechanism has been advanced for the reductions of chloro- and methoxysilanes by *tert*-butylmagnesium halides.[18] In these reactions, 2,2,3,3-tetramethylbutane was not an observed reaction product even when reaction times and reaction temperatures were comparable to or more severe than those in this study. Similarly, no tetramethylbutane was detected in the reaction products from the reduction of di-*tert*-butyldichlorosilane by *tert*-butylmagnesium chloride. The required use of excess amounts of *tert*-butyllithium and the comparable reactvities of *tert*-butylmagnesium chloride and *tert*-butyllithium toward di-*tert*-butyldichlorosilane are consistent with either a free-radical or SNi-Si process for reduction. However, the observed substitution by *tert*-butyllithium on di-*tert*-butylmethoxysilane without reduction (discussed below) and the production of tetramethylbutane point to a stepwise free-radical mechanism for reduction of hindered chlorosilanes by *tert*-butyllithium (Scheme II). If analogy can be drawn

Scheme II
$$(t\text{-}Bu)_2SiXCl + (CH_3)_3CLi \longrightarrow$$
$$(t\text{-}Bu)_2\overset{.}{Si}X + LiCl + LiCl + (CH_3)_3C\cdot \quad (6)$$
$$(X = H, Cl)$$
$$(CH_3)_3C\cdot + (t\text{-}Bu)_2\overset{.}{Si}X \longrightarrow$$
$$(CH_3)_2C{=}CH_2 + (t\text{-}Bu)_2SiHX \quad (7)$$
$$2(CH_3)_3C\cdot \longrightarrow (CH_3)_3C{-}C(CH_3)_3 \quad (8)$$
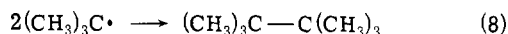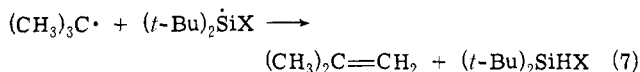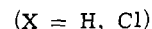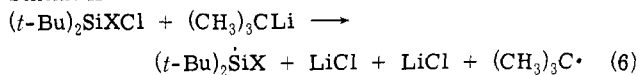
to the stabilities of *tert*-butylmethyl radicals,[6] $(t\text{-}Bu)_2\overset{.}{Si}X$ should be long-lived, allowing sufficient time for reactions such as that in eq 7 to occur. The reaction given by eq 6 may not be limited to chlorosilanes since 2,2,3,3-tetramethylbutane was also formed in the reaction between *tert*-butyllithium and di-*tert*-butylsilane. However, tetramethylbutane may have been formed in other, as yet unknown, reaction processes; further work is required to substantiate the validity of Scheme II.
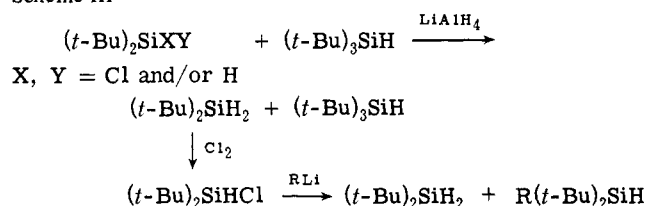
Numerous alternate routes to tri-*tert*-butylsilane were attempted. The reaction of trichlorosilane with a 4 M excess of *tert*-butyllithium at 70° for 6 hr gave, after work-up, a complex mixture of products consisting of di-*tert*-butylsilane, di-*tert*-butylsilanol, and more than six other unidentified compounds. Di-*tert*-butylmethoxysilane, prepared by the reaction of di-*tert*-butylchlorosilane with methanol in pyridine, was treated with an equivalent amount of *tert*-butyllithium for 2 days as the temperature was increased slowly from 30 to 90°; after work-up, di-*tert*-butylsilanol was isolated with tri-*tert*-butylsilane, which was formed in an overall yield of less than 2%. Product recovery from this

reaction was low (30–40%), and the major portion of the reaction products was insoluble in either ether or pentane. Although the methoxy group is a good leaving group in organosilicon chemistry,[11] and methoxyorganoboranes have been successfully alkylated without the occurrence of the elimination process evident with haloorganoboranes,[19,20] the reaction of di-*tert*-butylmethoxysilane with *tert*-butyllithium did not produce the desired product in a significant yield. The methoxysilane is resistant to reduction and is also resistant to alkylation by *tert*-butyllithium at silicon.

Limited success was achieved in improving the yield of tri-*tert*-butylsilane from that in eq 1 by treating di-*tert*-butylchlorosilane with *tert*-butyllithium in triethylamine at 50°. However, reaction times were extremely long; after 6 days, 25% of the chlorosilane reactant remained, and the yield of tri-*tert*-butylsilane was only 8%. When tetramethyldiaminomethane was used as the solvent in a separate experiment, *tert*-butyllithium was consumed but without any discernable production of tri-*tert*-butylsilane.

The preferred synthetic route to tri-*tert*-butylsilane and di-*tert*-butylalkylsilanes from *tert*-butyltrichlorosilane consisted of treating this compound with *tert*-butyllithium (eq 1), reducing the complex mixture with lithium aluminum hydride, and fractionally distilling the di-*tert*-butyl- and tri-*tert*-butylsilanes (Scheme III). Chlorination of di-*tert*-but-

Scheme III

$$(t\text{-Bu})_2\text{SiXY} \quad + \quad (t\text{-Bu})_3\text{SiH} \xrightarrow{\text{LiAlH}_4}$$

$$\text{X, Y} = \text{Cl and/or H}$$

$$(t\text{-Bu})_2\text{SiH}_2 + (t\text{-Bu})_3\text{SiH}$$

$$\downarrow \text{Cl}_2$$

$$(t\text{-Bu})_2\text{SiHCl} \xrightarrow{\text{RLi}} (t\text{-Bu})_2\text{SiH}_2 + \text{R}(t\text{-Bu})_2\text{SiH}$$

ylsilane gives di-*tert*-butylchlorosilane which is then treated with an alkyllithium reagent.[21]

Di-*tert*-butylchlorosilane was reduced to di-*tert*-butylsilane within 2 days in refluxing ether. Di-*tert*-butyldichlorosilane was resistant to reduction under comparable conditions; even over a 3-day period as the temperature of the reaction solution was raised from 35 to 85° and a large excess of the hydride reducing agent was used, less than 50% reduction of the di-*tert*-butyldichlorosilane was realized.

Selective chlorination of di-*tert*-butylsilane occurred when chlorine was slowly added to a carbon tetrachloride solution of di-*tert*-butylsilane at 0°. Analysis showed that, after complete consumption of di-*tert*-butylsilane, the ratio of di-*tert*-butyldichlorosilane to di-*tert*-butylchlorosilane was 1:5.1. Further addition of chlorine converts the monochlorosilane to the dichlorosilane. Chlorination of di-*tert*-butylsilane by reaction with *tert*-butyl chloride and catalytic amounts of aluminum chloride, although nearly instantaneous at 0°, was not as selective; the ratio of di-*tert*-butyldichlorosilane to di-*tert*-butylchlorosilane was 1:2.6.

It is interesting to note that nucleophilic reactions that "normally" occur with inversion at silicon, alkyllithium substitution, and lithium aluminum hydride reduction in this study are much slower for di-*tert*-butylsilyl derivatives than for comparable but less branched di- and trialkylsilyl derivatives.[11,22] In contrast, reactions that usually occur with retention of configuration at silicon, chlorination[11] and reduction by *tert*-butylmagnesium chloride,[18] are not apparently influenced to the same degree by the steric effects of alkyl groups bonded to silicon. Di-*tert*-butyldichlorosilane resists substitution by alkyllithium reagents but is reduced by *tert*-butylmagnesium chloride under conditions comparable with those used with less branched chlorosil-

Table I. Selected NMR Parameters of Alkylsilanes

Silane	δ, ppm[a]		$J^{29}{}_{\text{SiH}}$,[b]
	Si–H	(CH₃)₃C–Si	Hz
$(t\text{-Bu})_2\text{SiH}_2$	3.47	1.07	186
$(t\text{-Bu})_2\text{MeSiH}$	3.42	1.02	184
$(t\text{-Bu})_3\text{SiH}$	3.33	1.13	180
$(sec\text{-Bu})_3\text{SiH}$	3.52		181
Me_3SiH^c	4.00		190
$\text{Me}_2\text{SiH}_2{}^c$	3.82		190
$\text{MeSiH}_3{}^c$	3.58		194
$n\text{-BuSiH}_3$	3.55		194

[a] Relative to Me₄Si internal standard. [b] From ²⁹Si natural abundance, ±0.5 Hz. [c] Taken from ref 24c.

Table II. Selected Stretching Frequencies of Alkylsilanes

Silane	$\tilde{\nu}$, cm⁻¹ [a]	
	Si–H	C–H
$(t\text{-Bu})_2\text{SiH}_2$	2110	2965, 2950, 2935, 2890, 2865
$(t\text{-Bu})_2\text{MeSiH}$	2090	2960, 2940, 2890, 2860
$(t\text{-Bu})_3\text{SiH}$	2080	3000, 2980, 2945, 2890, 2860
Et_3SiH	2100	2960, 2940, 2920, 2895, 2880

[a] ±2 cm⁻¹.

anes; similarly, di-*tert*-butyldichlorosilane resists reduction by lithium aluminum hydride but is readily formed by chlorination of di-*tert*-butylchlorosilane under mild conditions. The implications of these observations for the synthesis of organosilicon compounds are not insignificant and will require further studies.

Selected NMR parameters for *tert*-butylsilanes are compared with those for less branched alkylsilanes in Table I. Relative to trimethylsilane, the Si–H protons of the *tert*-butylsilanes are more shielded with increased alkyl branching; similar effects have been observed for the C–H protons of *tert*-butylmethanes.[23] The $J^{29}{}_{\text{SiH}}$ values of *tert*-butylsilanes, although smaller than those reported for mono-, di-, and trialkylsilanes,[24] are not appreciably sensitive to steric factors from alkyl groups; both tri-*sec*-butylsilane and tri-*tert*-butylsilane, for example, have nearly identical J values.

The vibrational stretching frequencies of Si–H bonds for alkylsilanes have been correlated with σ^* values,[9c,25] implying that inductive effects on the Si–H bond are primarily responsible for changes in the Si–H stretching frequencies with changes in substituents. The Si–H frequencies for the di- and tri-*tert*-butylsilanes prepared in this study (Table II) similarly correlate well with σ^* and fall on the same line as those for less branched alkylsilanes.[9c] The C–H stretching vibrations of di-*tert*-butylsilane and di-*tert*-butylmethylsilane are normal when compared with triethylsilane and similar unbranched alkylsilanes; however, two of those for tri-*tert*-butylsilane are high, 3000 and 2980 cm⁻¹, and characteristic of tri-*tert*-butylsilyl derivatives, silanol and silyl ethers.[26] Recently Bartell and Burgi correlated C–H stretching frequencies with C–H bond lengths for the highly crowded tri-*tert*-butylmethane. If direct analogy can be drawn, the C–H bond lengths in tri-*tert*-butylsilane are also affected by intramolecular forces, although not to the same degree as tri-*tert*-butylmethane, and relatively severe crowding of the *tert*-butyl groups is implied. Similar interactions are not evident from the C–H vibrational frequencies of the di-*tert*-butylsilanes. Further structural information concerning tri-*tert*-butylsilane should provide a better understanding of the ability of silicon to accommodate bulky substituents relative to carbon.

Experimental Section

General. Instrumentation has been previously described.[27] Commercially available tert-butyllithium in pentane, methyllithium in ether, and silicon tetrachloride were used without further refinement. Ether solutions of lithium aluminum hydride were prepared and refrigerated for several months with no apparent loss of activity. tert-Butylmagnesium chloride in ether was prepared by the method of Whitmore and Houk.[28] After allowing solids to settle, a clear solution was obtained by transferring to a dry bottle under positive dry-nitrogen pressure and refrigerated until used. Pyridine was distilled from calcium hydride and stored over 4A molecular sieves. Tetramethyldiaminomethane was distilled from p-toluenesulfonyl chloride, then from calcium hydride, and stored over barium oxide. Triethylamine was purified in the same manner. For all the reactions described, oven-dried (140°) glassware, assembled while hot under a dry-nitrogen flow, was used. A mineral oil bubbler was used to seal the reaction apparatus from air. For transferring small quantities of material (<200 ml), oven-dried syringes and needles were used. Samples were removed using a positive dry-nitrogen pressure. For transferring larger quantities of air- and moisture-sensitive materials (>200 ml), a 1/8 in. stainless steel tube from reagent bottle to reaction vessel was used. Transfer was accomplished using a positive pressure of dry nitrogen at the reagent bottle. All GLC analyses made use of 5-ft 15% SE-30 columns.

tert-Butyltrichlorosilane. In a modification of the method of Tyler, Sommer, and Whitmore,[9a] approximately 600 ml of 1 M tert-butyllithium (0.6 mol) in pentane was added dropwise with stirring at room temperature under a slow dry-nitrogen flow to 170 g (1.0 mol) of silicon tetrachloride. The reaction solution turned only slightly cloudy and was heated at reflux for 4 days resulting in the formation of a white precipitate. After 4 days, tert-butyllithium was not evident in the mixture. The reaction mixture was centrifuged to remove lithium chloride which was washed twice with pentane then recentrifuged. The combined supernatant solution was distilled to give 118 g of material, bp 127–160°. GLC and ^{1}H NMR analyses indicated that the distillate mixture consisted of 15% 2,2,3,3-tetramethylbutane, 73% tert-butyltrichlorosilane (0.45 mol, 75% yield), 9% di-tert-butylchlorosilane (0.06 mol), and 3% tert-butyl-tert-butoxydichlorosilane. Each of the GLC peaks was collected and analyzed separately.

2,2,3,3-Tetramethylbutane: white solid, sublimes readily; ^{1}H NMR (CCl$_4$) δ 0.88 (s); mass spectrum m/e (rel intensity) 112 (0.3), 57 (100), 43 (27), 41 (53), 29 (31).

tert-Butyltrichlorosilane: waxy white solid, bp 133–138° after redistillation; ^{1}H NMR (CCl$_4$) δ 1.20 (s); mass spectrum m/e (rel intensity) 194 (0.007, P + 4), 192 (0.02, P + 2), 190 (0.02, parent ion), 57 (100), 41 (41), 29 (27).

Di-tert-butylchlorosilane: colorless liquid; ^{1}H NMR (CCl$_4$) δ 4.23 (s, 1 H), 1.11 (s, 18 H); ir (film) 2980, 2960, 2945, 2900, 2870 (C–H), 2135 (Si–H), 1360, and 1380 cm^{-1} (t-Bu); mass spectrum m/e (rel intensity) 180 (0.19, P + 2), 179 (0.08), 178 (0.51, parent ion), 123 (1.3), 121 (3.5), 95 (5.5), 93 (18), 81 (4.5), 79 (14), 57 (100), 56 (45), 41 (38), 29 (29).

Anal. Calcd for C$_8$H$_{19}$ClSi: C, 53.75; H, 10.71; Cl, 19.83. Found: C, 53.90; H, 10.80; Cl, 20.09.

tert-Butyl-tert-butoxydichlorosilane: colorless liquid; ^{1}H NMR (CCl$_4$) δ 1.43 (s, 9 H) and 1.05 (s, 9 H); ir (film) 2990, 2970, 2950, 2910, 2870 (C–H), 1385, and 1365 cm^{-1} (t-Bu); mass spectrum m/e (rel intensity) 228 (0.01, parent ion), 217 (1.7), 215 (5.5), 213 (8.0), 57 (100), 56 (75), 41 (42), 29 (29).

Anal. Calcd for C$_8$H$_{18}$Cl$_2$OSi: C, 41.92; H, 7.91; Cl, 30.93. Found: C, 42.13; H, 8.01; Cl, 31.10.

Tri-tert-butylsilane and Di-tert-butylsilane. To 118 g of crude tert-butyltrichlorosilane (previously described) was added 620 ml of 1 M tert-butyllithium in pentane at room temperature under a slow dry-nitrogen flow. No reaction was apparent. Over a period of 11 days, the pot temperature was slowly raised from 38 to 105° by slowly removing solvent. At this time, no tert-butyllithium remained. The reaction mixture was centrifuged to remove lithium chloride, and the light-orange solution was decanted. The inorganic salts were washed thoroughly three times with pentane. After each wash, the mixture was centrifuged to remove the finely divided lithium chloride. Pentane was removed from the combined supernatant solution by distillation. GLC analysis gave the following relative proportions of products: 7% tetramethylbutane, 8% di-tert-

butylsilane, 8% tert-butyltrichlorosilane, 27% di-tert-butylchlorosilane, 6% tert-butyl-tert-butoxydichlorosilane, 40% di-tert-butyldichlorosilane, and 4% tri-tert-butylsilane. Similar results were obtained when the reaction mixture was refluxed for 4 days as temperatures increased from 30 to 75°. The GLC peaks assigned to di-tert-butyldichlorosilane and to tri-tert-butylsilane were collected and analyzed separately.

Di-tert-butyldichlorosilane: colorless liquid; ^{1}H NMR (CCl$_4$) δ 1.18 (s), $J_{^{13}C-H}$ = 126 Hz; ir (film) 2985, 2960, 2950, 2910, 2880 (C–H), 1470 (Si–C), 1390, and 1365 cm^{-1} (t-Bu); mass spectrum m/e (rel intensity) 216 (0.03, P + 4), 215 (0.02), 214 (0.13, P + 2), 213 (0.03), 212 (0.21, parent ion), 159 (0.08), 157 (0.34), 155 (0.51), 117 (1.0), 115 (5.2), 113 (8.0), 57 (100), 56 (49), 41 (33), 29 (22).

Tri-tert-butylsilane: colorless liquid; ^{1}H NMR (CCl$_4$) δ 3.33 (s, 1 H, $J_{^{29}SiH}$ = 180 Hz) and 1.13 (s, 27 H, $J_{^{13}CH}$ = 126 Hz); ir (film) see Table II; mass spectrum m/e (rel intensity) 200 (0.04, parent ion), 101 (3), 73 (100), 59 (45), 57 (16), 45 (12), 43 (13), 41 (14), 29 (15).

Anal. Calcd for C$_{12}$H$_{28}$Si: C, 71.91; H, 14.08; Si, 14.01. Found: C, 71.87; H, 13.85; Si, 13.86.

To this crude reaction material was added 600 ml of approximately 1.5 M lithium aluminum hydride in ether at room temperature with stirring and under a slow dry-nitrogen flow. Initially the addition was accompanied by an exotherm and the formation of a white precipitate. After complete addition, the reaction mixture was brought to reflux and, over a period of 150 hr, the temperature was raised to 85° by slowly removing the solvent. The reaction mixture was allowed to cool to room temperature and then was slowly poured into aqueous ammonium chloride in small portions. The organic phase was separated, and the aqueous portion was extracted once with pentane. The combined organic phase and pentane extract were washed once with water, filtered through anhydrous magnesium sulfate, then fractionally distilled through a 30-cm Vigreux column. A 29.5-g portion with a boiling range between 87 and 126° contained 67% di-tert-butylsilane (136 mmol). A 21-g portion (146 mmol) with a boiling range between 126 and 128° was 99% di-tert-butylsilane. A 16.3-g portion with a boiling range between 43 and 73° (1 Torr) was 61% di-tert-butyldichlorosilane (0.05 mol) and 11% tri-tert-butylsilane (0.009 mol). A 1.0-g portion with boiling point between 73 and 80° (1 Torr) was 93% tri-tert-butylsilane (0.005 mol). The recovered yield of di-tert-butylsilane based on tert-butyltrichlorosilane and di-tert-butylchlorosilane reactants (0.51 mol) was 55%; that for tri-tert-butylsilane was 3%. Di-tert-butylsilane was analyzed and gave the spectral parameters listed in Tables I and II: mass spectrum m/e (rel intensity) 146 (0.05), 145 (0.14), 144 (1.0, parent ion), 87 (19), 73 (12), 59 (74), 57 (100), 45 (26), 41 (43), 29 (39).

Chlorination of Di-tert-butylsilane. Chlorine was slowly bubbled into a rapidly stirred solution of 33.6 g (0.234 mol) of di-tert-butylsilane in 100 ml of carbon tetrachloride at 0° under subdued artificial light. Progress of the reaction was monitored by ^{1}H NMR spectroscopy. When nearly all of the di-tert-butylsilane had been consumed, the reaction material was fractionally distilled. A 7.1-g portion, having a boiling range of 110–155° consisted of 89% di-tert-butylchlorosilane and 11% di-tert-butylsilane. A 33.2-g portion having a boiling range of 165–177° consisted of 77% di-tert-butylchlorosilane and 23% di-tert-butyldichlorosilane. The overall yields of di-tert-butyl-, di-tert-butylchloro-, and di-tert-butyldichlorosilanes were 2, 78, and 15%, a 95% overall recovery.

Reaction of Di-tert-butylsilane with tert-Butyl Chloride and Aluminum Chloride. To a rapidly stirred mixture of 0.50 g (3.5 mmol) of di-tert-butylsilane and a catalytic quantity of aluminum chloride chilled in a salt–ice–water bath was added 0.30 g (3.5 mmol) of tert-butyl chloride in pentane. An immediate exotherm was noted. GLC analysis of the reaction mixture at this time showed 21% di-tert-butylsilane, 60% di-tert-butylchlorosilane, and 19% di-tert-butyldichlorosilane. An additional 0.10 g (1.17 mmol) of tert-butyl chloride in pentane was then added, again immediately giving an exothermic reaction. GLC analysis of the reaction mixture showed 10% di-tert-butylsilane, 65% di-tert-butylchlorosilane, and 25% di-tert-butyldichlorosilane.

Di-tert-butylmethylsilane. A 200-ml portion of 1.84 M methyllithium was transferred to a dry reaction vessel. To this stirred solution was slowly added 33.2 g of a 77% di-tert-butylchlorosilane (0.143 mol)–23% di-tert-butyldichlorosilane mixture. No reaction

was apparent at room temperature. The reaction solution was refluxed with the temperature slowly raised to 50° over a period of 3 days by slowly removing the solvent. The reaction was quenched with an aqueous solution of ammonium chloride. The organic layer was separated, and the aqueous portion was extracted once with pentane. The combined organic and pentane extract was dried over anhydrous magnesium sulfate and filtered, the filter cake was washed with pentane, and the combined washes, extract, and organic phase were concentrated under reduced pressure. A short-path distillation gave 3.38 g of a liquid with a boiling range of 148–155° (85% di-*tert*-butylmethylsilane, 15% solvent) and 7.41 g with a boiling range of 159–190° (86% di-*tert*-butylmethylsilane, 14% di-*tert*-butyldichlorosilane). The total recovered yield of the methylsilane was 0.130 mol (91% yield based on di-*tert*-butylchlorosilane); in a separate experiment, no apparent reaction between methyllithium and di-*tert*-butyldichlorosilane was observed.

A sample of di-*tert*-butylmethylsilane was collected by GLC for analysis: colorless liquid; ^{1}H NMR (CCl$_4$) δ 3.42 (q, J = 4 Hz, 1 H), 1.02 (s, 18 H), 0.02 (d, J = 4 Hz, 3 H); mass spectrum m/e (rel intensity) 159 (0.07), 158 (0.88, parent ion), 101 (10.5), 85 (5.8), 73 (100), 59 (93), 57 (43), 45 (20), 31 (10).

Anal. Calcd for C$_9$H$_{22}$Si: C, 68.26; H, 14.00. Found: C, 68.48; H, 14.19.

Di-*tert*-butylmethoxysilane. A 6.0-g portion of di-*tert*-butylchlorosilane (89%) and di-*tert*-butyldichlorosilane (11%) was dissolved in 4.5 g of dry pyridine. Methanol (3.1 g), freshly distilled from sodium methoxide–methanol, was added and the mixture stirred rapidly overnight. The top organic layer was separated, washed once with water, aqueous sulfuric acid, and aqueous sodium bicarbonate. The organic solution was dried over anhydrous magnesium sulfate, filtered, then distilled to remove low-boiling components. The pot residue consisted of 90% di-*tert*-butylmethoxysilane, 6% di-*tert*-butyldichlorosilane, and 4% unknown. A pure sample was collected by GLC for analysis: colorless liquid; ^{1}H NMR (CCl$_4$) δ 3.97 (s, 1 H), 3.62 (s, 3 H), 1.00 (s, 18 H); ir (film) 3000, 2970, 2935, 2900, 2870 (C–H), 2120 (Si–H), 820 (Si–CH$_3$), 110 (Si–OCH$_3$), 1385, and 1363 cm^{-1} (*t*-Bu); mass spectrum m/e (rel intensity) 176 (0.04), 175 (0.11), 174 (0.64, parent ion), 89 (100), 75 (63), 59 (71), 57 (21), 45 (23), 41 (22), 29 (21).

Anal. Calcd for C$_9$H$_{22}$OSi: C, 62.00; H, 12.72; Si, 16.11. Found: C, 61.87; H, 12.63; Si, 16.26.

Reaction of Di-*tert*-butylsilane with *tert*-Butyllithium. To 2.0 g of di-*tert*-butylsilane was added 17 ml of 1 *M tert*-butyllithium with stirring under slow dry N$_2$ flow. No reaction was apparent. Over a period of 53 hr, the temperature was slowly raised to 90° by removing the solvent. The only products observed by GLC analysis were tetramethylbutane, di-*tert*-butylsilane, and traces of materials with longer retention times. An additional 20 ml of *tert*-butyllithium in pentane was added along with 20 ml of heptane. The temperature was raised to 82° and heated at that temperature for 48 hr. GLC analysis indicated no further reaction.

Reaction of *tert*-Butyl-, Di-*tert*-butylchloro-, and Di-*tert*-butyldichlorosilanes with *tert*-Butyllithium. To 1.5 g of a mixture containing 9% di-*tert*-butylsilane, 57% di-*tert*-butylchlorosilane, and 34% di-*tert*-butyldichlorosilane was added 20 ml of 1 *M tert*-butyllithium in pentane at room temperature under a slow flow of dry nitrogen. No reaction was immediately apparent. Over a period of 4 days, the reaction temperature was slowly raised to 80° by slowly removing the solvent. At this time, unreacted *tert*-butyllithium could be detected. GLC analysis of the reaction mixture gave 54% di-*tert*-butylsilane, 5% di-*tert*-butylchlorosilane, 2% unknown, 11% di-*tert*-butyldichlorosilane, 21% tri-*tert*-butylsilane, and 7% of an unknown (order of GLC elution).

Reaction of *tert*-Butyllithium with Di-*tert*-butylmethoxysilane. To 3.0 g of crude di-*tert*-butylmethoxysilane (90% pure, containing 6% di-*tert*-butyldichlorosilane and 4% unknown) was added 20 ml of 1 *M tert*-butyllithium in pentane at room temperature under a slow dry-nitrogen flow. The reaction mixture became exothermic and turned red upon addition of *tert*-butyllithium. Over a period of 2 days, the temperature was slowly raised to 90° by slowly removing the solvent. At this time, the dark reaction mixture was quenched in aqueous ammonium chloride, and the aqueous portion was extracted with ether. A solid that was insoluble in water, ether, and pentane accounted for the bulk of the organic material. The ether extract was dried over anhydrous magnesium sulfate and filtered, the filter cake was washed with ether, and the combined

ether extract and washes were concentrated under reduced pressure. After distilling the ether, 0.28 g of volatile material was collected at 0.1 Torr. GLC analysis of this mixture gave 28% di-*tert*-butylsilanol, 9% di-*tert*-butyldichlorosilane, 37% tri-*tert*-butylsilane, and 26% unknown. The material assigned to di-*tert*-butylsilanol was collected by GLC for spectral analysis: white crystalline solid, mp 65–66°; ^{1}H NMR (CCl$_4$), 4.05 (s, 1 H), 1.30 (s, 1 H), 1.02 (s, 18 H); ir (film), 3450 (broad), 3280, 3250 (O–H), 2975, 2940, 2900, 2870, 2790 (C–H), and 2050 cm^{-1} (Si–H).

Reaction of a Mixture of Di-*tert*-butylchlorosilane and Di-*tert*-butyldichlorosilane with *tert*-Butyllithium in Triethylamine. To 3.4 g of material containing 23% di-*tert*-butylchlorosilane, 14% unknown, and 63% di-*tert*-butyldichlorosilane was added 2.0 g of dry triethylamine followed by the dropwise addition of 15 ml of 1 *M tert*-butyllithium. The reaction temperature was slowly raised to 52° over a period of 150 hr, at which time no *tert*-butyllithium remained. The resulting mixture was quenched with aqueous sulfuric acid and extracted twice with pentane. The combined pentane extract was filtered through anhydrous magnesium sulfate, then concentrated under reduced pressure to give 1.2 g of material. GLC analysis gave 1% di-*tert*-butylsilane, 18% di-*tert*-butylchlorosilane, 22% unknown, 36% di-*tert*-butyldichlorosilane, and 24% tri-*tert*-butylsilane (order of GLC elution).

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Macro Rings. XLVII. Syntheses and Spectral Properties of Heteroannularly Disubstituted [2.2]Paracyclophanes[1]

Hans Allgeier,[2a] Merrell G. Siegel, Roger C. Helgeson, Erika Schmidt,[2b] and Donald J. Cram*

Contribution No. 3334 from the Department of Chemistry of the University of California at Los Angeles, Los Angeles, California 90024. Received August 19, 1974

Abstract: The syntheses and structure determinations of 39 new, disubstituted [2.2]paracyclophanes are reported in which each benzene ring contains one substituent. No transannular directive effects were observed in the nitration of either 4-cyano- or 4-acetyl[2.2]paracyclophane. At 200°, pseudo-*o*- and pseudo-*p*-cyanonitro[2.2]paracyclophanes equilibrated to give an equilmolar mixture. The transannular effects of the positions of the substituents on the ¹H NMR and uv spectra of these compounds are described. Unlike their monosubstituted counterparts, the [2.2]paracyclophanes with a nitro group in one ring and an amino in the other are colored orange to red. The end absorption of the longest wavelength band of the isomers decreases in intensity in the order pseudo-gem > pseudo-meta > pseudo-para > pseudo-ortho. Transannular canonical charge transfer resonance structures can be drawn for the two most colored isomers, but not for the other two.

Former papers in this series reported the syntheses,[3a,b,c,d] substituent directive effects,[3b,d] and spectral properties[3a,3e] of a number of disubstituted [2.2]paracyclophanes. In bromination of monobromo-, mononitro-, monoacetyl-, and monocarbomethoxy[2.2]paracyclophanes, transannular substituent directive influences were found to be associated with inter-ring proton transfer as the rate-determining step.[3b] In bromination of 4-cyano[2.2]paracyclophane, or nitration of 4-nitro[2.2]paracyclophane, these directive effects were absent.[3b,d] The structures of the disubstituted [2.2]paracyclophane derivatives were determined by thermal interconversion through benzyl–benzyl diradical intermediates[3c] or from the patterns of ¹H NMR chemical shifts.[3e] Particularly useful were the downfield chemical shifts of the protons pseudo-gem to the halogen and cyano groups, and the unusually large ortho and small para chemical shifts compared to open-chain model compounds. Transannular substituent effects on the ultraviolet spectra and pK_a's of monosubstituted [*m.n*]paracyclophanes were found to be small.[3a]

The present paper reports the synthesis and spectral properties of 39 new disubstituted [2.2]paracyclophanes with one substituent in each ring. These compounds were prepared for the following reasons: (1) to examine the possibility of observing intramolecular charge-transfer effects on the uv spectra of appropriately substituted compounds; (2) to extend the knowledge of pseudo-gem ¹H NMR chemical shifts to substituents not yet examined; (3) to test further the generalizations about transannular, substituent-directing effects on electrophilic substitution; (4) to prepare compounds for a study of transannular substituent effects on the pK_a's of [2.2]paracyclophanecarboxylic acids and [2.2]paracyclophanylammonium ions. The results of this study are reported elsewhere.[4]

Results and Discussion

Syntheses. The new compounds reported here, and those disubstituted [2.2]paracyclophanes that served as starting materials, are formulated in a way (Chart I) that emphasizes the positions of the substituents relative to one another, and that names those relationships. Reduction with hydrogen and platinum of bromonitro isomers **1–4**,[3b] gave bromoamines **5–8**, respectively. With 2 mol of cuprous cyanide in *N*-methylpyrrolidone[5] at 205° for 24 hr, pseudo-gem-bromonitro compound **1** gave 14% of starting material, 24% of rearranged pseudo-meta-bromonitro compound **2**, 3% of pseudo-gem-cyanonitro compound **9**, and 27% pseudo-meta-cyanonitro isomer **10**. Under the reaction conditions, isomerizations **1 ⇌ 2** and **9 ⇌ 10** appear to occur. At equilibrium, [**2**]/[**1**] > 4.6 at 200°,[3c] but in the reaction mixture, [**2**]/[**1**] ~ 2. The total yield of cyanated product (~30%) exceeded that of isomerized starting material (24%). Thus the cyanation appears to occur slightly faster than the isomerization of starting material. Nitration of 4-cyano[2.2]paracyclophane[3e] gave a mixture of products from which pseudo-para- and pseudo-ortho-cyanonitro compounds **12** and **11** were isolated (8 and 4%, respectively). When heated at 200° in *N*-methylpyrrolidone for 30 hr, **11** equilibrated with **12**, and $K = k_1/k_2 \sim 1$. The reaction was followed by ¹H NMR integration of the doublets of H_a in **11** and **12**, and $k_1 \sim k_2 \sim 3 \times 10^{-5}$ sec⁻¹. Both the rate and equilibrium constants resemble those obtained for the

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