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TRI-*t*-BUTYLSILANE: SYNTHESIS, PHYSICAL PROPERTIES, DERIVATIVES, AND REACTIVITY TOWARDS OZONOLYSIS, CHLORINATION, FLUORINATION, AND HYDROLYSIS

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Summary

Tri-*t*-butylsilane has been synthesized in excellent yield from the condensation-reduction reaction of *t*-butyllithium on silicon tetrafluoride. The relative reactivity of this sterically crowded silane towards ozone, chlorine, and hydroxyl ion has been examined, relative to the behavior of less hindered silanes, and rationalized. The mechanistic path of the reaction determined whether its rate was significantly or negligibly affected by the nonbonded interactions of the bulky *t*-butyl substituents. Derivatives described include chloro-, fluoro-, and hydroxy-tri-*t*-butylsilanes.

Introduction

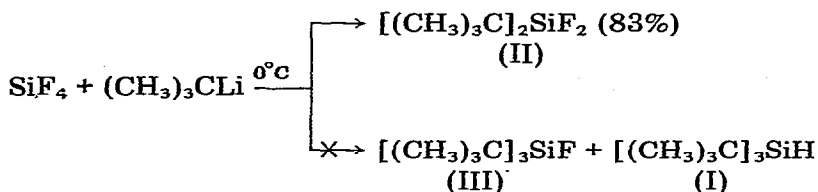
In 1948 Whitmore and his students reported an unsuccessful attempt to synthesize tri-*t*-butylsilane [1]. Since then there have been many other unsuccessful efforts [2] to prepare this compound**. There are a number of reasons for the interest in such a molecule. It represents an excellent model for the study of nonbonded interactions and reaction mechanisms in organosilanes; it could provide a reagent for adding a sterically-protected silicon atom to a substrate; and it presents a preparative challenge. Our recent fortuitous isolation of tri-*t*-butylsilane (I) [4] provided the incentive to develop a practical synthesis for this compound and to explore its basic chemistry.

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** Subsequent to initial submission of this manuscript, a low yield synthesis of I from SiCl₄ was reported by Doyle and West [3].

Results and discussion

Initial attempts to develop an efficient synthetic route to I employed either trichloro- or tetrachlorosilane. However, in all cases, reaction proceeded slowly and the yield of I remained low*. On the possibility that the presence of a small halogen atom and the lesser solubility of lithium fluoride, compared to lithium chloride, might provide more favorable steric and thermodynamic factors, it was decided to try tetrafluorosilane as the starting material**. In contrast to the sluggish reaction reported for SiCl_4 [4], SiF_4 reacted with *t*-butyllithium at 0°C to give an 83% yield of di-*t*-butyldifluorosilane (II). No formation of I or fluorotri-*t*-butylsilane (III) in this reaction could be found by VPC analysis.



That alkylation of SiF_4 at about 35°C stops cleanly after addition of the second *t*-butyl group was demonstrated by refluxing II with *t*-butyllithium in pentane for 113 h, effecting no reaction. Addition or in situ formation of anhydrous lithium fluoride showed no catalytic influence towards further alkylation. At higher temperatures, however, reaction of II with *t*-butyllithium in refluxing cyclohexane gave I in high yield (93%). As monitored by VPC analysis, no formation of III was observed either during the course of the reaction or in the resulting product mixture. It thus appears that reduction of the fluorosilane occurs only at elevated temperatures and is fast relative to alkylation. Moreover, such reduction of at least one fluoride substituent on silicon to hydride to give a less sterically-hindered substrate appears to be a prerequisite for further alkylation. Reduction of halosilanes by organolithiums has been reported previously only during the alkylation of hexachlorodisilane with isopropylolithium [8]. In that case it was shown that reduction did not involve, as the reducing species, lithium hydride which might have been generated in situ via initial thermal decomposition of the organometallic reagent. These preparative conditions of I from II were repeated in the presence of *N,N,N',N'*-tetramethylethylenediamine (TMEDA)***. At room temperature only a slight reaction was evident, even after 18 h. However at 35°C , after a 1 h induction period, a vigorous, strongly exothermic reaction occurred, forming I as the single isolable product. This route was not studied further since higher yields were obtained without TMEDA.

* Repeated efforts with commercial *t*-butyllithium failed to reproduce either the yields or product compositions reported by Whitmore [1].

** A referee has called our attention to supporting indications in the literature that SiF_4 would be a superior substrate: Me_3SiF couples cleanly with *t*-BuLi/TMEDA whereas Me_3SiCl undergoes metalation at a methyl group [5]; fluorine displacement from silicon can be either retentive or invertive depending on steric and polar requirements of the incoming nucleophile [6]; hindered alkoxysilanes such as $(\text{t-BuO})_4\text{Si}$ are most readily prepared from fluorosilanes [7].

*** For a review of tertiary amine catalysis of organometallic reactions, see ref. 9.

In order to determine some of the basic chemical properties of I, it was subjected to appropriate conditions for ozonolysis, chlorination, fluorination, and base-catalyzed hydrolysis.

In previous studies on the oxidation of hydrosilanes by ozone, correlations were reported between the relative rate of ozonolysis and the substrate's Si—H stretching frequency [10] and Taft σ^* values [11]. Because of the steric hindrance potential in I, it was of interest to test its behavior relative to these empirical correlations.

Competitive ozonolysis of I revealed a relative reaction rate of 153 for I compared to 100 for tri-*n*-butylsilane. From the herein observed Si—H stretching frequency of 2094 cm^{-1} for I, the predicted rate of ozonolysis of I would be 262. According to the correlation with Taft σ^* values, the calculated rate would be 536, based on the following equation [11]:

$$\log k_{\text{rel}} = 1.2513 + \sum_i^4 \sigma_i^* + 2.2166$$

The fact that I is ozonized much more slowly than would be anticipated from either correlation can be rationalized as being a consequence of steric factors. Firstly, the steric requirements of the three *t*-butyl groups around silicon may be great enough to raise the energy level of the five-centered intermediate postulated in the reaction mechanism [11] or even to alter the mechanism. Moreover, the ground state may be so perturbed by the *t*-butyl crowding that bond hybridizations and atom electronegativities are changed. This could lead to rationalizing the experimental observations as indicating a reaction-ineffective perturbation on a higher intrinsic Si—H stretching frequency or a smaller effective value for σ^* than was used in the calculations.

Hydrolysis of I under basic catalysis in a homogeneous medium was examined. With triethylsilane present as a reference compound, I in aqueous ethanolic KOH was refluxed for several days. Within the first half hour all of the triethylsilane had disappeared but none of I had reacted. After 68 h, 15% of I still remained. Assuming an analytical accuracy of 2% and, hence, 30 minutes as representing at least six half-lives, one can estimate the maximum half-life possible for triethylsilane under these conditions to be five minutes. The data for I imply a half-life of about 23 h. The maximum reactivity of I relative to triethylsilane is then $1/276$, or less than 3.6×10^{-3} . This may be compared with the value of 8.1×10^{-3} found for triisopropylsilane relative to tri-*n*-propylsilane, as reported by Schott and Harzdorf [12] under similar conditions.

A further probe of Si—H bond reactivity in I was made by treatment of the compound in CCl_4 solution with chlorine gas. The rate of chlorination was determined relative to that for tri-*n*-butylsilane by the same analytical technique used for ozonolysis. Chlorotri-*t*-butylsilane was the only isolable product from chlorination of I. The rate of chlorination of I was extremely rapid and identical to that of tri-*n*-butylsilane. The observed rapid chlorination of the Si—H bond is characteristic of trialkylsilanes [13].

In contrast to the observed facile chlorination, fluorination of I with standard fluorinating agents proved difficult. The silane was inert towards HF in polar and non-polar solvents, as well as toward PF_5 , a reagent effective in fluorinating

a wide variety of hydrosilanes [14]. Antimony pentafluoride, a reagent which, when employed neat, causes violent decomposition of I fluorinated I smoothly and quantitatively at room temperature when dissolved in hexafluorobenzene. A stoichiometric analysis of the reaction revealed that one-half mol of antimony pentafluoride will fluorinate one mol of I*. Hexafluorobenzene was chosen as the solvent after it was observed that use of methylene chloride led to the formation not only of III but also of chlorotri-*t*-butylsilane via apparent solvent interaction.

The preparation of I by reduction of III with LiAlH_4 provided an insight into the reactivity of III. No reduction of III occurred in ether at 25°C even after 48 h, yet reduction was complete within 20 h in refluxing THF. Other trialkylfluorosilanes readily undergo reduction with LiAlH_4 under far milder conditions [15], a contrast which again illustrates the considerable degree of steric hinderance provided by the three *t*-butyl groups on silicon.

In summary, for tri-*t*-butylsilane, chlorination is facile, ozonolysis appears to be influenced somewhat by steric hinderance, while fluorination and hydrolysis are made extremely difficult. It can be seen from the above results that I exhibits a wide range of relative reactivities and that these reactivities probably are a function of the specific mechanism of the reaction in question and its susceptibility to perturbation by steric features of the substrate silane. This susceptibility suggests, in turn, that the relative reaction rates of I and some simple hydrosilane, such as triethylsilane, towards a particular reagent may provide a clue to the reaction mechanism involved.

Experimental

All IR spectra were recorded on either a Perkin—Elmer 21 or 521 spectrophotometer. A Varian A-60A spectrometer was used to measure PMR spectra. The ^{13}C NMR spectrum was recorded on a Varian XL-100-15 spectrometer operating in the pulsed FT mode. The chemical shifts are reported relative to internal TMS. Mass spectra were obtained from a CEC-21-110B mass spectrometer interfaced with an AEI DS-30 data system. Ozone was generated from a pure oxygen stream by a Welsbach T23 ozonator. Except for the chlorination and ozonolysis reactions, vapor phase chromatography was performed with a Series 1700 Varian Aerograph using 0.25 in \times 10 ft copper columns packed with 20% SE-30 or 5% QF-1 on 60/80 mesh Chromosorb W. The rates of chlorination and ozonolysis were monitored with a Perkin—Elmer F30 chromatograph using a 0.01 in \times 100 ft stainless steel column coated with DX-300. Solutions of *t*-butyllithium in pentane came from PCR, Inc. and Ventron Corporation, while silicon tetrafluoride was obtained from Matheson Gas Products. Microanalyses were performed by Galbraith Laboratories Inc., Knoxville, Tenn.

*Di-t-butyl*difluorosilane (II)

A solution of 0.5 mol of *t*-butyllithium in 700 ml of pentane was cooled to 0°C in an ice bath and gaseous silicon tetrafluoride (~ 300 ml/min) was passed

* This observation suggests that HF, formed by hydrosilane reduction of SbF_5 , may be capable of fluorinating I in this reaction system.

into the solution through a capillary tube. Gas flow was discontinued after 1.5 h, at which time the solution gave a negative Gilman color test* and a neutral aqueous solution upon hydrolysis of an aliquot.

The colorless solution was then filtered, concentrated on a rotary evaporator, and distilled to give 38.0 g (83% yield) of II, b.p. 130-131°C. IR, μm : 3.38s, 3.51m, 6.80m, 7.20w, 7.34m, 11.24s, 11.78s, 12.04s, and 12.33m. PMR: δ 1.08s. (Found: C, 53.30; H, 10.09. $\text{C}_8\text{H}_{18}\text{F}_2\text{Si}$ calcd.: C, 53.29; H, 10.06%.)

*Attempted synthesis of fluorotri-*t*-butylsilane (III) from II*

To 0.15 mol of a 1.8 M solution of *t*-butyllithium in pentane was added 50 ml of pentane and 18.0 g (0.10 mol) of II. The solution was refluxed for 113 h but no formation of III could be detected by VPC. To test whether LiF might act as a catalyst, SiF_4 was passed through the solution until the lithium salt began to precipitate. Addition of SiF_4 was discontinued and the solution was refluxed for 20 h. No formation of III was detected by VPC.

Synthesis of III by fluorination of I

Antimony pentafluoride (0.6 g, 0.003 mol) was dissolved in 5 ml of hexafluorobenzene, producing a bright green solution. This solution was added dropwise to a rapidly stirred solution of 0.5 g (0.0025 mol) of I, 5 ml of hexafluorobenzene, and 0.3 g of dodecane as an internal reference. Aliquots were withdrawn periodically and analyzed by VPC. Quantitative conversion of I to III was complete after addition of one-half of the antimony pentafluoride solution.

Compound III gave the following analytical data: IR, μm : 3.41 s, 3.50s, 6.76m, 7.18w, 7.33w, 9.83w, 9.92w, 10.65w, 10.74w, 12.03s, 12.15s, and 12.33s; PMR: δ 1.08s; ^{13}C NMR: 29.799 ppm (s, CH_3) and 22.523 ppm (d, J 12.7 Hz, CMe_3). (Found: C, 65.83; H, 12.27. $\text{C}_{12}\text{H}_{27}\text{FSi}$ calcd.: C, 65.98; H, 12.46%.)

When the procedure was repeated at -50°C with methylene chloride as a solvent, a 1/1 mixture of III and chlorotri-*t*-butylsilane resulted.

Attempted fluorination of I

Following the procedure of Sommer [17], 10 ml benzene was added to 1.0 g I and 0.2 g 10% palladium on carbon. Anhydrous HF was passed through the solution for 20 min. VPC analysis of the solution showed no formation of III and no loss of I.

The experiment was repeated with PF_5 , producing identical results.

When anhydrous HF was passed through a solution of 0.5 g I and 10 ml anhydrous ether for 1.5 h, no loss of I nor formation of III could be detected by VPC.

*Tri-*t*-butylsilane (I) from II*

Method A. A solution of 0.06 mol of *t*-butyllithium in 30 ml of pentane was added to 8.1 g (0.045 mol) of II in 40 ml of cyclohexane. Pentane was removed by distillation to a vapor temperature of 63°C and the reaction system

* A negative Gilman color test [16] has not proven completely reliable for demonstrating the consumption of *t*-butyllithium.

was then refluxed for 18 h. At this time VPC analysis indicated that only I had formed and that 50% of II had been consumed. An additional 0.06 mol t-butyl-lithium in pentane was added, pentane removed by distillation, and refluxing continued for 21 h. After cooling, the reaction mixture was worked up by acidification with HCl, washing, drying, and distillation to give 8.4 g (93% yield) of I, b.p. 105°C/20 mmHg. IR, μm : 3.42s, 3.48s, 3.52s, 4.81s, 6.81s, 7.21m, 7.34m, 9.85m, 10.49w, 12.17m, and 12.50s; PMR: δ 3.36 (s, 1H, SiH) and δ 1.12 (s, 27H, CH₃). (Found: C, 71.96; H, 14.00. C₁₂H₂₈Si calcd.: C, 71.91; H, 14.08%.)

Method B. A solution of 18.0 g (0.1 mol) of II, 1.0 g *N,N,N',N'*-tetramethylethylenediamine and 0.11 mol t-butyl-lithium in 56 ml pentane was stirred for 21 h at 20°C. There was no noticeable disappearance of starting material, as determined by VPC analysis. After refluxing for 1 h, a strong exotherm occurred. Upon cooling, the solution set to a thick gel. Workup with HCl, followed by concentration on a rotary evaporator gave a 1/1 mixture of I and II. No other products could be detected by VPC analysis.

Preparation of I by reduction of III with LiAlH₄

A solution of 0.13 g III, 0.2 g lithium aluminum hydride, 5 ml ether, and 0.1 g dodecane as internal reference was stirred at 25°C for 48 h. No decrease of III could be detected by VPC. Ether was removed under vacuum and replaced with 5 ml THF. After refluxing 20 h, quantitative reduction to I was complete.

Ozonolysis

The ozonolysis of I was conducted according to the method of Spialter et al. [7]. Tri-*n*-butylsilane was employed as the reference silane and the internal standard was decane. Preparative VPC was used to isolate, as the only detectable product, tri-*t*-butylsilanol, m.p. 34-35°C. IR, μm : 2.9w, 3.39s, 3.48s, 6.75m, 7.18w, 7.31w, 9.3w, 12.18s, NMR: δ 3.12 (s, 1H, OH) and δ 1.10 (s, 27H, CH₃). Mass spectrum: parent ion peak 216.

Chlorination

Chlorine was slowly passed through a capillary tube into a solution of 0.2 g of I, 0.2 g tri-*n*-butylsilane, 0.1 g *n*-decane, and 10 ml CCl₄. The flow of chlorine was adjusted to give a convenient rate of chlorination, which was monitored by VPC analysis. The only products of the reaction were the corresponding chlorosilanes. Chlorotri-*t*-butylsilane, isolated by preparative VPC, possessed the following properties: m.p. 121-122°C; IR, μm : 3.41s, 3.50s, 6.77m, 7.20w, 7.33w, and 12.23s; PMR: δ 1.17s. (Found: C, 61.13; H, 11.32. C₁₂H₂₇ClSi calcd.: C, 61.36; H, 11.59%.)

Hydrolysis

To a 0.2 *N* KOH solution of 5 ml ethanol and 0.4 ml water was added 1 ml THF, 0.10 g (0.005 mol) of I and 0.12 g (0.01 mol) of triethylsilane as a reference. Hydrogen evolution was immediately apparent and within 0.5 h, all of the triethylsilane was hydrolyzed, as determined by VPC analysis. After 1 h no significant loss of I was observed but after 68 h, ~85% of I was consumed. A VPC retention time check indicated the formation of tri-*t*-butylsilanol as the hydrolysis product.

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