Journal of Organometallic Chemistry, 178 (1979) 95—103

TRI-t-BUTYLSILYLAMINES: SYNTHESIS, PHYSICAL PROPERTIES AND NEW SILYLAMINE DERIVATIVES *

PETER M. NOWAKOWSKI and LEO H. SOMMER **
Department of Chemistry, University of California, Davis, California 95616 (U.S.A.)

(Received April 4th, 1979)

Summary

Tri-t-butylsilylamine has been synthesized in excellent yield from the hydrogenation of tri-t-butylsilylazide. The pK_b values of the amine and its mono- and dimethyl derivatives have been quantitatively measured in 40% H_2O/60% THF solution. Stable silylammonium salts, $[(CH_3)_3C]_3SiN^+H_3X^-$ (X = Cl, Br, BF_4) have been isolated and characterized. In addition, boron trihalide adducts of the amine, $[(CH_3)_3C]_3SiNH_2 \rightarrow BX_3$ (X = F, Cl), have been isolated and studied.

Introduction

After almost thirty years of attempts [1—4], tri-t-butylsilicon compounds were first synthesized in 1975, almost simultaneously, by three research groups [5—7]. In spite of recent activity in this new field [8—13], no study has been done on the sterically motivated stabilizing effect that the tri-t-butylsilyl group would have on silylamino compounds. The apparent resistance of tri-t-butylsilyl compounds to S_N2—Si type displacement reactions [7,8] and the earlier successful measurement of the pK_b of a sterically hindered silylamine, 1-diethylamino-3,5,7-trimethyl-1,3,5,7-tetrasilaadamantane, $Me_3AdN(C_2H_5)_2$ [14], provided the incentive to develop a practical synthesis for tri-t-butylsilylamines and to explore some of their basic chemistry.

Results and discussion

Classical synthetic routes of formation of silylamines failed to produce any tri-t-butylsilylamine. Marshall and coworkers had developed a method of synthesis of silylamines involving tin hydride reduction of silyl azides [15]. Tri-t-butylsilylazide (I) was produced in 70% yield by the method of Audrieth [16], by the

---

* Dedicated to Professor E.G. Rochow on the occasion of his 70th birthday.

** Author to whom correspondence should be addressed.

reaction of tri-t-butylsilylchloride and sodium azide [17]. Compound I is a

$$[(CH_3)_3C]_3SiCl + NaN_3 \xrightarrow[\text{reflux}]{CH_3CN} \underset{(I)}{[(CH_3)_3C]_3SiN_3} + NaCl$$

white, waxy solid which gives spectra and analysis consistent with the proposed structure (Tables 2, 3). The tri-n-butyltin hydride reduction of I proceeded very slowly, the yield of tri-t-butylsilylamine (II) was low (26%) and purification from tin containing material proved difficult. Lithium aluminum hydride reduction of

$$\underset{(I)}{[(CH_3)_3C]_3SiN_3} + (C_4H_9)_3SnH \rightarrow \underset{(II)}{[(CH_3)_3C]_3SiNH_2} + (C_4H_9)_6Sn_2$$

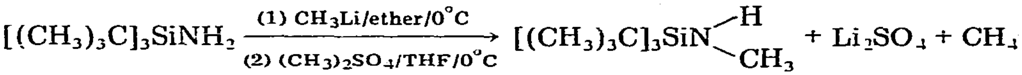
I yields very little II. The primary product is tri-t-butylsilane.

An easy, clean synthesis of II was achieved by the medium pressure hydrogenation of I in t-butyl alcohol over Raney Nickel active catalyst, following a procedure often used for the reduction of organic azides to amines [18,19]. Conversion to II is quantitative and removal of solvent yields a pure, white, waxy

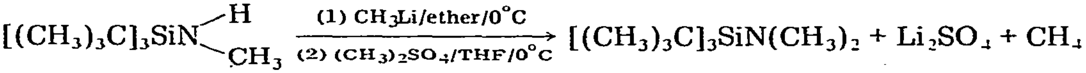
$$\underset{(I)}{[(CH_3)_3C]_3SiN_3} + H_2 \xrightarrow[\substack{t\text{-BuOH} \\ 1000\ \text{psig, r.t.}}]{RaNi} \underset{(II)}{[(CH_3)_3C]_3SiNH_2} + N_2$$

solid which gives the expected spectra and analytical data (Tables 2, 3). Less hindered silylamines and silylazides will undergo solvolysis in alcohols to yield alkoxysilanes via an S_N2—Si mechanism [20]. It is only the remarkable stability of compounds I and II in protic solvent, for at least several days, which allows this procedure to be used.

Monomethyl- and dimethyl-amino derivatives of II were synthesized by conventional means. The parent amine, II, was treated with an equivalent of methyllithium in diethyl ether, and then reacted with excess dimethylsulfate in THF to give *N*-methyl tri-t-butylsilylamine (III) in 76% yield. Compound III was then treated in a similar manner to give 71% of *N*,*N*-dimethyltri-t-butylsilylamine (IV).



$$\underset{(II)}{[(CH_3)_3C]_3SiNH_2} \xrightarrow[(2)\ (CH_3)_2SO_4/THF/0^\circ C]{(1)\ CH_3Li/ether/0^\circ C} \underset{(III)}{[(CH_3)_3C]_3SiN\begin{smallmatrix} H \\ CH_3 \end{smallmatrix}} + Li_2SO_4 + CH_4$$



$$\underset{(III)}{[(CH_3)_3C]_3SiN\begin{smallmatrix} H \\ CH_3 \end{smallmatrix}} \xrightarrow[(2)\ (CH_3)_2SO_4/THF/0^\circ C]{(1)\ CH_3Li/ether/0^\circ C} \underset{(IV)}{[(CH_3)_3C]_3SiN(CH_3)_2} + Li_2SO_4 + CH_4$$

Both compounds are white, waxy solids, and they give spectra and analyses consistent with the suggested structures (Tables 2, 3).

The pK_b measurement of II, III and IV were done using the same technique used by Homer and Sommer on 1-diethylamino-3,5,7-trimethyl-1,3,5,7-tetrasila-adamantane(V) [14]. A 40% H_2O/60% THF solvent system was employed to ensure homogeneity during the determinations and to give data directly comparable to that obtained for V. Two organic amines, t-butylamine and 2,6-dimethylaniline, were chosen as reference compounds with some steric hindrance around nitrogen. All silylamines were reclaimed from the test solutions in 88% or greater isolated yield and no decomposition resulting from the experimental

TABLE 1

pK_b DETERMINATIONS IN 40% H_2O/60% THF AT 26°C

	pK_b	Reference
t-Butylamine	4.08 ± 0.02	This work
Tri-t-butylsilylamine (II)	8.25 ± 0.02	This work
N-Methyltri-t-butylsilylamine (III)	9.43 ± 0.02	This work
N,*N*-Dimethyltri-t-butylsilylamine (IV)	10.78 ± 0.02	This work
$Me_3AdN(C_2H_5)_2$ (V)	8.32 ± 0.02	14
2,6-Dimethylaniline	11.50 ± 0.02	This work

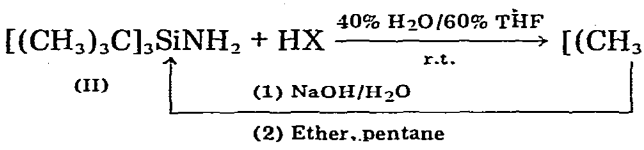
technique could be detected by IR or GLC. The values obtained are given in Table 1.

The complexity of structure—basicity relationships for amines in general leads one to conjecture that the near correspondence of basicity for silylamines II and V is a result of a fortuitous cancellation of the effects on basicity by the different structural features present in the two amines. The low basicity of both II and V relative to t-butylamine is most probably caused largely by *dπ—pπ* bonding between silicon and nitrogen [14]. The relatively large decrease in basicity, 340-fold, between amines II and IV can be rationalized as the result of greatly enhanced overall steric effects which affect solvation of the ammonium ion more than solvation of the amine.

Silylamines normally react with hydrogen halide acids to give disiloxanes, alkoxysilanes or silanols in protic solvent [21] or silylhalides in aprotic solvents [22]. Aylett and co-workers have reported unstable silylammonium compounds which decompose at or below room temperature [23,24], and Ebsworth and Emeleus have reported a possible unstable donor—acceptor complex [25]. *N*,*N*-Dimethyl(trichlorosilyl)amine, $(CH_3)_2NSiCl_3$, and bis(dimethylamino)dichlorosilane, $[(CH_3)_2N]_2SiCl_2$, have been reported to form stable compounds with hydrogen chloride by Coates and Cass, but no spectral or structural data were given [26].

The almost quantitative recovery of silylamines II, III and IV from acidic aqueous THF solution after several hours indicated that the corresponding ammonium salts were stable and could probably be isolated (see Scheme 1). All ammonium salts isolated were derivatives of tri-t-butylsilylamine (II) because of its availability. The reaction of a pentane solution of II with aqueous HCl yields an aqueous solution of tri-t-butylsilylammonium chloride (VI) which may be separated from the organic phase. White, powdery compound VI is obtained in 94% yield after removal of water. A similar procedure, using tetrafluoroboric acid

SCHEME 1



$$[(CH_3)_3C]_3SiNH_2 + HX \xrightarrow[\text{r.t.}]{40\%\ H_2O/60\%\ THF} [(CH_3)_3C]_3SiN^+H_3X^-$$

X = Cl(VI), BF_4(VII), Br(VIII)

TABLE 2

^{1}H NMR CHEMICAL SHIFT FOR NEW COMPOUNDS

Compound	Chemical shift (δ) relative to internal C_6H_6
I[a]	1.29 (t-Bu_3Si, s)
II[a]	1.17 (t-Bu_3Si, s), no NH_2 signal obs.
III[a]	1.20 (t-Bu_3Si, s, 27 H), 2.79 (N—CH_3, s, 3 H); no N—H signal obs.
IV[a]	1.24 (t-Bu_3Si, s, 27 H), 2.77 ($N(CH_3)_2$, s, 6 H)
VI[b]	1.20 (t-Bu_3Si, s); no N^+H_3 signal obs.
VII[b]	1.19 (t-Bu_3Si, s); no N^+H_3 signal obs.
VIII[b]	1.15 (t-Bu_3Si, s); no N^+H_3 signal obs.
IX[c]	1.22 (t-Bu_3Si, s); no NH_3 signal obs.
X[c]	1.24 (t-Bu_3Si, s); no NH_3 signal obs.

[a] In CCl_4. [b] In DMSO-d^6. [c] In acetonitrile-d_3/DMSO-d_6 4/1.

TABLE 3

IR SPECTRA, IMPORTANT MASS PEAKS AND ANALYTICAL DATA FOR NEW COMPOUNDS

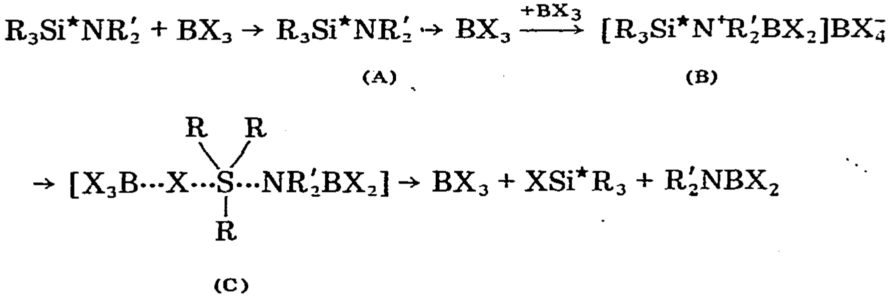
Compound	IR (cm^{-1})	Mass spectra[a] (relative intensity)	Analytical data		
				Calc.	Found
I[b]	2980m, 2960s, 2940s, 2900s, 2860s, 2150s, 1480s, 1390s, 1370m, 1330s, 1010w, 930w, 690m, 630s	184(31), 142(50), 100(100), 73(31), 57(35)	%Si %C %H %N	11.64 59.67 11.28 17.41	11.57 59.67 11.24 17.25
II[b]	3480w, 3410m, 2980s, 2940s, 2900s, 2860s, 1540m, 1480s, 1390s, 1360m, 1010w, 930w, 610s	158(46), 116(32), 74(100), 59(9), 57(11)	%Si %C %H %N	13.04 66.89 13.57 6.50	12.92 66.85 13.62 6.51
III[b]	3430w, 2980s, 2940s, 2900s, 2860s, 1460s, 1380s, 1340m, 1120s, 1100m, 1010w, 930w	172(56), 130(29), 88(100), 73(14), 59(24), 58(30), 57(23)	%C %H %N	68.04 13.62 6.10	67.98 13.50 6.20
IV[b]	2980s, 2960s, 2860s, 2800m, 1460m, 1390m, 1370w, 1270m, 1150m, 1070w, 980s, 930w, 670m	186(49), 144(36), 102(100), 88(5), 73(41) 72(49), 59(30), 57(29)	%C %H %N	69.05 13.66 5.75	69.01 13.57 5.76
VI[c]	3400w, 3140m, 2900s, 1580m, 1460s, 1440s, 1400s, 1370m, 1010w, 930w, 880w, 820m, 680s, 620m		%Cl	14.07	14.35
VII[c]	3400w, 3200s, 3170m, 3130m, 2960s, 2880m, 1590m, 1480m, 1430s, 1410s, 1370w, 1130s, 1030s, 930w, 850w, 820m, 770m, 650m, 620m		%F	25.06	24.89
VIII[c]	3400w, 3130m, 2940s, 2820s, 1570m, 1470s, 1430s, 1400s, 1370m, 1010w, 930w, 870w, 820s, 670s, 620s		%Br	26.96	26.98
IX[d]	3260s, 3220s, 3120m, 1590m, 1550m, 1400m, 1370s, 1230s, 1100s, 1030s, 950s, 820s, 750s, 720w, 670m		%F	20.12	19.98
X[d]	3220w, 3140w, 1390m, 1370m, 1260w, 1050w, 920w, 800s, 710m, 660m		%Cl	31.98	31.53

[a] No parent ions obs. for compounds I—IV and no mass spectra obs. for compounds VI—X. [b] 5% by wt. in CCl_4 soln. [c] KBr pellet. [d] Nujol mull.

gives an 88% yield of tri-t-butylammonium tetrafluoroborate (VII). Anhydrous HBr gas will react with a solution of II in pentane to give an immediate white precipitate of tri-t-butylsilylammonium bromide (VIII) which is isolated in quantitative yield by solvent removal. Compounds VI, VII and VIII are all white, powdery, water soluble solids with melting points in excess of 270°C. The spectra obtained and halide analyses are consistent with the proposed silylammonium structures (Tables 2, 3). The infrared spectra show a greatly broadened NH_2 stretching frequency shifted to lower energy than that observed in silylamine II.

Sommer and co-workers found that the reaction of optically active silicon compounds with boron trihalides results in displacement of the amino group and the formation of the inverted silylhalide, by an S_N2—Si mechanism [27] (Scheme 2). Aylett and Peterson have observed, at −78°C in a vacuum system, formation of solid borane and trimethylboron adducts of tris(dimethylamino)silane, $[(CH_3)_2N]_3SiH$, and bis(dimethylamino)silane $[(CH_3)_2N]_2SiH_2$, similar to structure A [28]. The adducts were postulated because of the isolation of alkylsilanes and aminoboranes after warming to room temperature. Silyl substituted aminoboranes, $(CH_3)_3SiN(H)BX_2$, have been isoalted in benzene solution by Becke-Goering and Krill from the reaction of boron trihalides and hexamethyldisilazane [29]. More recently, Haubold and Kraatz have observed silylamine-borane adducts similar to structure A in solutions of tris(trimethylsilyl)amine, $[(CH_3)_3Si]_3N$ and boron trifluoride or boron trichloride in ether [30]. The compounds were not isolated and are seen in solution only below −20°C.

SCHEME 2



$$R_3Si^{*}NR'_2 + BX_3 \rightarrow \underset{(A)}{R_3Si^{*}NR'_2 \rightarrow BX_3} \xrightarrow{+BX_3} \underset{(B)}{[R_3Si^{*}N^{+}R'_2BX_2]BX_4^{-}}$$

$$\rightarrow \underset{(C)}{[X_3B\cdots X\cdots \overset{R\ \ R}{\underset{R}{S}}\cdots NR'_2BX_2]} \rightarrow BX_3 + XSi^{*}R_3 + R'_2NBX_2$$

The stability of the silylammonium compounds VI, VII, and VIII indicated that an intermediate similar to A or B could be isolated by reaction of II with boron trihalide. A cold pentane solution of II gives an immediate white precipitate when either boron trifluoride or boron trichloride is bubbled into solution.

$$[(CH_3)_3C]_3SiNH_2 + BX_3 \xrightarrow[0°C]{pentane} [(CH_3)_3C]_3SiNH_2 \rightarrow BX_3$$

X = F(IX), Cl(X)

Compounds IX and X are white powdery substances with sharp odors. The elemental analyses and spectra are in agreement with the proposed structures. The yields of both are quantitative.

Compounds IX and X do not melt, but decompose at 240 and 190°C, respectively. They produce the parent silylamine, II, a halosilane, and a tarry or charred residue which is soluble in water.

$$[(CH_3)_3C]_3SiNH_2 \rightarrow BF_3 \xrightarrow[\Delta]{240^\circ C} [(CH_3)_3C]_3SiNH_2 + [(CH_3)_3]_3SiF + \text{tar}$$

(IX) (II)

(11%) (23%)

$$[(CH_3)_3C]_3SiNH_2 \rightarrow BCl_3 \xrightarrow[\Delta]{190^\circ C} [(CH_3)_3C]_3SiNH_2 + [(CH_3)_3C]_3SiCl + \text{tar}$$

(X) (II)

(36.5%) (8%)

The decomposition probably does not proceed according to the mechanism in Scheme 2 primarily because of the reluctance of tri-t-butylsilyl compounds to go through a transition state like C. The greater quantity of halosilane produced by IX compared with X may indicate that there is some steric effect in the decomposition pathway or it may only reflect the preference of silicon to bond to fluorine whenever possible.

In summary, the inability of tri-t-butylsilylamine to react by an S_N2—Si pathway lends it a stability which greatly affects its chemistry. It allowed the synthesis of the amine by an unorthodox route and it has permitted the first quantitative measurement of pK_b values for a series of silylamines. Previously unstable species, silylammonium salts and silylamine—boron trihalide donor—acceptor complexes, could be isolated and characterized. This stability may also provide a route to other unknown silicon containing species such as silyldiazonium salts.

Experimental

^{1}H NMR spectra were determined with a Varian Model A60A spectrometer in various solvents containing a small amount of benzene as an internal reference signal. Mass spectra were measured on a Varian Model M-66 spectrometer, with an ionizing voltage of 70 eV for all compounds. Infrared spectra were determined as 5% solutions in carbon tetrachloride or as KBr pellets or Nujol mulls as noted. Spectra were run using a Beckman Model IR-8 Grating infrared spectrophotometer.

Analytical gas chromatography was done on a Hewlett—Packard Model 7620A Chromatograph with a flame ionization detector using a 10% UCW-98 column (6′ × 1/8″). Preparative GLC was done on a Varian Aerograph Model 920 with a thermal conductivity detector using an 8% SF-96 column (10′ × 3/8″) for all separations.

Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn. All melting points are uncorrected but were determined in air-free sealed capillaries. Hydrogenation was done in a Parr Model 4052 Pressure Reactor fitted with a Parr Model 134HClO Glass liner.

Tri-t-butylchlorosilane was prepared as reported in the literature [5,7,8]. All solvents were dried by distillation from an active metal hydride or by use of 3A molecular sieves TM. Methyllithium (Alfa) and dimethyl sulfate (Aldrich) were used as received. Hydrogen bromide, boron trifluoride, and boron trichloride (Matheson Gas) were all used directly from the lecture bottle.

Tri-t-butylsilylazide (I)

A mixture of 16.6 g (71 mmol) of tri-t-butylchlorosilane, 9.1 g (140 mmol) of sodium azide and 250 ml of acetonitrile were refluxed for 18 h. The reaction was cooled and 100 ml of pentane was added to precipitate sodium azide from solution. The salts were removed by filtration under nitrogen and the solvent was removed to yield a yellow syrup which gave 12.08 g (70%) of tri-t-butylsilylazide by preparative GLC. M.p. 114—116°C.

Tri-t-butylsilylamine (II)

(A) By tin hydride reduction of I. A solution of 0.16 g (0.64 mmol) of II and 0.46 g (1.6 mmol) of tri-n-butyltin hydride was heated to 104 ± 2°C. After 2 weeks all of the tin hydride had been consumed, the reaction was stopped and the products were collected by preparative GLC. The yield of isolated tri-t-butylamine, m.p. 70—72°C, was 0.032 g (26%), and 0.017 g (11%) of unreacted I was recovered.

(B) By catalytic hydrogenation with Raney Nickel. A solution of 4.65 g (19.3 mmol) of I in 20 ml of dry t-butyl alcohol was placed in a glass hydrogenation vessel along with 0.3 g of Raney Nickel active catalyst which had been washed free of water with three portions of dry t-butyl alcohol. The vessel was placed in the pressure reactor and the reactor was placed in the rocker mechanism. The system was flushed several times with hydrogen before final pressurization to 1000 psig. The mixture was rocked under pressure for 16 h at 30°C. The contents were then filtered under nitrogen to remove the catalyst and the solvent was removed at reduced pressure yielding 4.01 g (96.4%) of pure II.

N-Methyltri-t-butylsilylamine (III)

A solution of 1.50 g (6.97 mmol) of II in 20 ml of THF at 0°C was reacted with 4.5 ml of a 1.71 *M* solution of methyllithium in ether. After 30 min, 0.96 g (7.7 mmol) of dimethylsulfate in 2 ml of THF was added and the reaction was allowed to warm to room temperature and stirred overnight. An aqueous work-up with dilute NaOH solution was used, followed by extraction into pentane. After drying and solvent removal, preparative GLC yielded 1.21 g (76%) of *N*-methyltri-t-butylsilylamine, m.p. 157—158°C.

N,N-Dimethylaminotri-t-butylsilylamine (IV)

A similar procedure to that used for III and work-up employing 0.80 g (3.5 mmol) of III yielded 0.58 g (71%) of *N,N*-dimethylaminotri-t-butylsilylamine, m.p. 238—239°C.

pK_b Measurement — general method

The pK_b values of amines II, III, IV and the organic reference amines were determined using the half-neutralization technique on a Beckman Expandomatic pH meter fitted with glass and calomel electrode and calibrated with the appropriate standard buffer solutions. The temperature was maintained at 26.0 ± 0.5°C throughout the measurements.

A sample of the amine was carefully weighed into a 50 ml volumetric flask and exactly half an equivalent of 0.5070 *N* aq. HCl was added using a precision burette. Then 40%/60% THF solution was added to dilute to the mark and the resultant solutions were inspected for homogeneity. Measurements were made in an open beaker and calibration was rechecked periodically to minimize error.

Recovery of the amines after measurements were completed, involved addition of dilute aq. NaOH, followed by satd. NaCl solution and extraction into pentane. Pentane extracts were dried and solvent removal yielded 88 to 99% recovery of amine. IR spectra and m.p.'s were identical to pure starting materials.

Tri-t-butylsilylammonium chloride (VI)

A solution of 0.24 g (1.11 mmol) of II in 10 ml of pentane was shaken with 20 ml of 0.1 *N* aq. HCl for several minutes. The aqueous layer was separated and the organic layer was washed twice with 10 ml portions of distilled water. The aqueous extracts were combined and the water was removed at reduced pressure yielding a white solid. The solid was dried at room temperature over P_2O_5 at 1 torr for 24 h. This yielded 0.26 g (94%) of tri-t-butylsilylammonium chloride, m.p. >270°C.

Tri-t-butylsilylammonium tetrafluoroborate (VII)

A similar procedure to that used for VI employing 0.20 g (0.9 mmol) of II and aq. HBF_4 yielded 0.25 g (88%) of the theoretical amount of tri-t-butylammonium tetrafluoroborate, m.p. >270°C.

Tri-t-butylsilylammonium bromide (VIII)

A solution of 0.17 g (0.8 mmol) of II in 10 ml of pentane was cooled to 0°C. Anhydrous HBr gas was bubbled through the solution for 1 min causing immediate precipitation of a white solid. Solvent and excess HBr were removed under reduced pressure yielding 0.23 g (99%) of tri-t-butylsilylammonium bromide, m.p. >270°C.

Boron trifluoride adduct of tri-t-butylsilylamine (IX)

Boron trifluoride gas was bubbled for 1 min through a solution of 0.198 g (0.92 mmol) of II in 10 ml of dry pentane causing immediate precipitation of a white powder. Solvent and excess boron trifluoride were removed at reduced pressure yielding 0.24 g (93%) of tri-t-butylsilylamine-boron trifluoride adduct, decomposes at 240°C.

Boron trichloride adduct of tri-t-butylsilylamine (X)

A similar procedure to that employed for IX, using 0.21 g (0.97 mmol) of II and boron trichloride gas yielded 0.32 g (99%) of tri-t-butylsilylamine-boron trichloride adduct, decomposes at 190°C.

Acknowledgement

We thank the National Science Foundation for generous support of this work.

References

1 L.J. Tyler, L.H. Sommer and F.C. Whitmore, J. Amer. Chem. Soc., 70 (1948) 2876.
2 L.H. Sommer and L.J. Tyler, J. Amer. Chem. Soc., 76 (1954) 1030.
3 G. Schott and J. Meyer, Z. Anorg. Allgem. Chem., 313 (1961) 107.
4 V.G. Kessler and K. Kriegsman, Z. Anorg. Allgem. Chem., 342 (1966) 51.

5 M.P. Doyle and C.T. West, J. Amer. Chem. Soc., 97 (1975) 3777.
6 L. Spialter and E.M. Dexheimer, Tetrahedron Lett., (1975) 1771.
7 M. Wiedenbruch and W. Peter, Angew. Chem., Int. Ed. Engl., 14 (1975) 642.
8 E.M. Dexheimer, L.D. Smithson and L. Spialter, J. Organometal. Chem., 102 (1975) 21.
9 M.P. Doyle and C.T. West, J. Org. Chem., 40 (1975) 3821.
10 C.T. West and M.P. Doyle, J. Org. Chem., 40 (1975) 3829.
11 M. Wiedenbruch, W. Peter and C. Perrard, Angew. Chem., Int. Ed. Engl., 15 (1976) 43.
12 L. Rösch and H. Müller, Angew. Chem., Int. Ed. Engl., 15 (1976) 620.
13 H. Müller and L. Rösch, J. Organometal. Chem., 133 (1977) 1.
14 G.D. Homer and L.H. Sommer, J. Organometal. Chem., 67 (1974) C10, for an earlier report on the methiodide of $Me_3Ad\ NEt_2$, m.p. 170—200°C, see: C.L. Frye and J.M. Klozowaki, J. Amer. Chem. Soc., 94 (1972) 7186.
15 T.T. Tsai, W.L. Lehn and C.J. Marshall, J. Organometal. Chem., 22 (1970) 387.
16 L.F. Audrieth, Chem. Rev., 15 (1934) 169.
17 D.R. Parker, Ph.D. Thesis, University of California, Davis, Calif., 1976, p. 70, 71.
18 R.L. Augustine, Catalytic Hydrogenation, Marcel Dekker, New York, 1965, p. 90.
19 T. Sheradsky, in S. Patai (Ed.), *The Chemistry of the Azido Group*, Interscience, New York, 1971, p. 334.
20 L.H. Sommer, Stereochemistry, Mechanism and Silicon, McGraw-Hill, New York, 1965, p. 175.
21 L.H. Sommer, Intra-Science Chem. Rept., 7 (1973) 1.
22 L.H. Sommer and J.D. Citron, J. Amer. Chem. Soc., 89 (1967) 5797.
23 B.J. Aylett, H.J. Emeleus and A.G. Maddock, J. Inorg. Nucl. Chem., 1 (1955) 187.
24 B.J. Aylett and J. Emsley, J. Chem. Soc. (A), (1967) 652.
25 E.A.V. Ebsworth and H.J. Emeleus, J. Chem. Soc., (1958) 2150.
26 G.E. Coates and R. Cass, J. Chem. Soc., (1952) 2347.
27 L.H. Sommer, J.D. Citorn and G.A. Parker, J. Amer. Chem. Soc., 91 (1969) 4729.
28 B.J. Aylett and L.K. Peterson, J. Chem. Soc., (1965) 4043.
29 M. Becke-Goering and H. Krill, Chem. Ber., 94 (1961) 1059.
30 W. Haubold and U. Kraatz, Z. Anorg. Allgem. Chem., 421 (1976) 105.