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THE INTERACTION OF BORON HALIDES WITH 1,1,3,3-TETRAMETHYL-1,3-DISILACYCLOBUTANE *

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Summary

The exothermic reaction of BX_3 (X = F, Cl, Br) with 1,1,3,3-tetramethyl-1,3-disilacyclobutane (I) gave the ring-cleavage product $XMe_2SiCH_2Me_2SiCH_2BX_2$ (II) in almost quantitative yield. The order of activity was $BBr_3 > BCl_3 > BF_3$. Heating compounds of structure II at 180°C for 40 h did not affect IIa (X = F) but caused a complete rearrangement of IIc (X = Br) to $BrMe_2SiCH_2MeBrSiCH_2BMeBr$ (IIIc). Compound IIb (X = Cl) was incompletely (65%) converted to $ClMe_2SiCH_2MeClSiCH_2BMeCl$ (IIIb) under the stated conditions. It was concluded that the thermal rearrangement most likely proceeded by an intramolecular mechanism since only one isomer was found.

Introduction

The ring cleavage reactions of 1,1,3,3-tetramethyl-1,3-disilacyclobutane (I) with both electrophilic and nucleophilic reagents are well documented [2—5]. Of particular relevance to this work are the reactions of I with the Lewis acids $SnCl_4$ [4] and $AlCl_3$ [6] shown by eq. 1 and 2. In this paper are presented the

$$[Me_2SiCH_2]_2 + SnCl_4 \rightarrow ClMe_2SiCH_2Me_2SiCH_2SnCl_3 \quad (1)$$

$$2[Me_2SiCH_2]_2 + AlCl_3 \rightarrow (ClMe_2SiCH_2Me_2SiCH_2)_2AlCl \quad (2)$$

results from the interaction of I and boron trihalides.

Results and discussion

It was found that I reacts with boron trihalides according to eq. 3. Reaction of

$$\underset{(I)}{[Me_2SiCH_2]_2} + BX_3 \rightarrow \underset{\substack{(IIa)\ X = F \\ (IIb)\ X = Cl \\ (IIc)\ X = Br}}{XMe_2SiCH_2Me_2SiCH_2BX_2} \quad (3)$$

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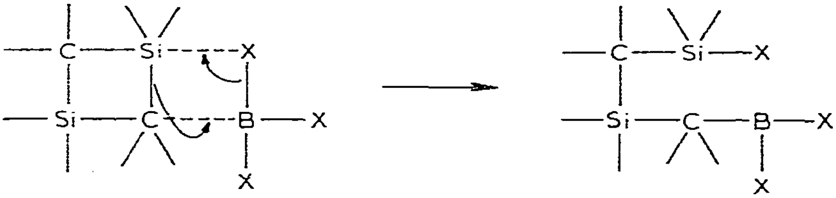
* Preliminary communication: ref. 1.

I under 4 atm pressure of BF_3 proceeded slowly at room temperature. Only about 30% uptake of BF_3 occurred in 6 h. When liquified BF_3 and I were rapidly mixed in a heavy walled glass bomb, a slight exotherm was noted. Both BCl_3 and BBr_3 react vigorously with I by either exposing I to the vapor of the trihalides or by slowly warming a mixture of the frozen reactants to room temperature. The moisture sensitive products, IIa, IIb and IIc are formed in essentially quantitative yields. A possible concerted mechanism for the interaction is proposed (eq. 4).



(4)

No further reaction of II with I was noted under reaction conditions where the temperature did not exceed room temperature. It was subsequently shown that IIb did not react with I even at 100°C. The interaction of aluminium trichloride and I, by comparison, yields only a diorganoaluminum compound (eq. 2). Apparently, the expected aluminum analog of IIb readily reacted with another molecule of I. The decreased activity of II toward I can probably be attributed to steric hindrance.

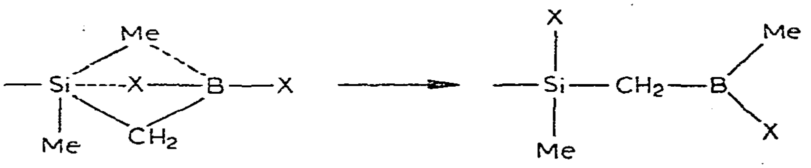
An interesting thermal isomerization of IIb and IIc, which was first noted on distillation of IIc, occurs as shown by eq. 5. Complete conversion of

$$\underset{\text{(IIb, IIc)}}{XMe_2SiCH_2Me_2SiCH_2BX_2} \xrightarrow[180^\circ C]{40h} \underset{\substack{\text{(IIIb) } X = Cl \\ \text{(IIIc) } X = Br}}{XMe_2SiCH_2MeXSiCH_2BMeX} \qquad (5)$$

$BrMe_2SiCH_2Me_2SiCH_2BBr_2$ (IIc) was accomplished at 180°C, however, only about 65% of IIb (based on integration of the PMR spectrum) was changed. No rearrangement of $FMe_2SiCH_2Me_2SiCH_2BF_2$ (IIa) was noted under the same conditions. Hanbold and Kraatz reported [7] that tetramethylsilane will exchange ligands with boron tribromide readily at temperatures above 100°C, whereas boron trichloride reacts slowly at 200°C. They also noted a methyl—bromine exchange between BBr_3 and $(Me_3Si)_3N$ (eq. 6). To explain the formation of IIIb

$$BBr_3 + (Me_3Si)_3N \xrightarrow{23^\circ C} MeBBr_2 + (Me_3Si)_2NSiMe_2Br \qquad (6)$$

and IIIc by an intermolecular four-centered interaction would suggest a very high reactivity of the Me_2Si group β to boron. A more probable mechanism is proposed in eq. 7. An intramolecular interchange involving the terminal silicon,



(7)

however, would require a bicyclic (six and four membered) ring formation which, although structurally reasonable, would probably be less likely to occur at elevated temperatures. More research is necessary to verify the proposed rearrangement path.

Spectroscopic data

Infrared spectra. The more essential absorption bands and their assignments are compiled in Table 1.

The Si—X stretching frequencies for all compounds were found to agree with those expected for a silicon containing only one halogen [8]. Although IIIb was not isolated, the IR of the mixture of IIb and IIIb showed only the 460 cm^{-1} band characteristic of $\equiv$Si—Cl [8].

A most notable feature in the spectra of II is a series of bands that occur in the 950—1200 cm^{-1} region for IIb and IIc and in the 1000—1350 cm^{-1} region for IIa. This has been assigned to the Si—CH$_2$—B deformation based on a similar pattern observed [10] in the spectrum of $(Me_3SiCH_2)_3B$. The isomerized product, IIIc, retains the general features of the Si—CH$_2$—B bands.

A strong Si—CH$_2$—Si band [11] at 1060 cm^{-1} was found in all the products.

Nuclear magnetic resonance spectra. The PMR data for the compounds prepared are listed in Table 2. Both IIb and IIc have similar patterns of intensity ratios 1/3/1/3 expected for the structures proposed. No ^{11}B splitting of the methylene protons adjacent to boron was observed, probably due to quadrupole relaxation of boron. A ^{19}F NMR carried out at 56.444 Mc on a neat sample of IIa showed a symmetrical multiplet, $J(^1H—^{19}F)$ 7.4 Hz, at 74.1 ppm from trifluoroacetic acid (TFA) as an external standard. This is consistent with reported values for F bonded to Me$_2$Si [12]. A braod, poorly resolved quartet was also

TABLE 1

INFRARED [a] BANDS (cm^{-1})

	Si—X stretch	^{11}B—X stretch	SiCH$_2$Si	SiCH$_2$B	B—CH$_3$
$FMe_2SiCH_2Me_2SiCH_2BF_2$ (IIa)	880	1400s(*asym*) 1350s(*sym*)?	1060s	1320s 1290s 1000w	—
$ClMe_2SiCH_2Me_2SiCH_2BCl_2$ (IIb)	460m	870s(*asym*) 570m(*sym*)	1060s	1150s 1120s 995m	—
$BrMe_2SiCH_2Me_2SiCH_2BBr_2$ (IIc)	400m 370m	910w? 860s } (*asym*) 595w 562w } (*sym*)	1060s	1135s 1100s 985m	—
$BrMe_2SiCH_2MeBrSiCH_2BMeBr$ (IIIc)	400m 370m	600m 580m	1060s	1185s 1150s	1300s 930m?
$(Me_3SiCH_2)_3B$ [10]	—	—	—	1250s 1180s 980m	—

[a] Infrared data were obtained on a Perkin—Elmer 467 grating spectrometer using cells equipped with KBr or AgCl windows. Assignments were based on comparison to known compounds containing similar groups. Uncertainty of assignments are noted by (?). Abbreviations: s, strong; m, moderate; w, weak.

TABLE 2

PMR RESONANCES (In δ, ppm) [a]

1 2 3 4 5	1	2	3	4	5
$FMe_2SiCH_2Me_2SiCH_2BF_2$ (IIa)	0.25 [d] (J 7.4 Hz)	0.05 [d] (J 7.4 Hz)	0.19	[b]	—
$ClMe_2SiCH_2Me_2SiCH_2BCl_2$ (IIb)	0.43	0.28	0.24	1.46	—
$ClMe_2SiCH_2MeClSiCH_2BMeCl$ [c] (IIIb)	0.50	0.63	0.57	1.60	0.99
$BrMe_2SiCH_2Me_2SiCH_2BBr_2$ (IIc)	0.62	0.46	0.30	1.94	—
$BrMe_2SiCH_2MeBrSiCH_2BMeBr$ (IIIc)	0.70	0.95	0.80	2.02	1.20

[a] Obtained from carbon tetrachloride solutions using Varian T-60 and Varian A-60A spectrometers. All chemical shifts are reported relative to tetramethylsilane (TMS) as an internal reference. [b] Probably obscured by peak at 0.19 ppm. [c] Extracted from the spectrum of the mixture of IIc and IIIc. [d] Doublet.

observed at —5.9 ppm from TFA with a $J(^{11}B—^{19}F)$ of about 75 Hz. Others have observed a similar pattern for $F_2B—C$ compounds [13] around —1 to —6 ppm (from TFA) with J values around 70 Hz. Both ^{10}B coupling and quadrupole relaxation are considered as reasons for poor resolution [13a]. The combined data from the PMR and ^{19}F NMR justify the structure proposed for IIa.

The PMR spectrum of IIIc showed a five-line pattern of intensity ratios 2/3/2/3/6 which was expected for the proposed structure.

Experimental

Except where noted, all manipulations were carried out in a standard vacuum system equipped with Teflon® stopcocks (Fischer and Porter Co.). Commercially available boron trihalides were purified by fractional condensation. 1,1,3,3-Tetramethyl-1,3-disilacyclobutane was prepared as previously described [14]. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Ten. High resolution mass spectra were obtained on a Du Pont 492 mass spectrometer.

Reaction of 1,1,3,3-tetramethyl-1,3-disilacyclobutane (I) with boron trifluoride

Into a 25 ml heavy-walled glass vessel equipped with a Teflon® stopcock capable of withstanding 35 atm pressure was condensed, at —195°C, 3.74 g (25.9 mmol) I and 1.81 g (26.7 mmol) of boron trifluoride. The closed tube was immersed in a —78°C bath which was slowly warmed to room temperature. Separation of volatiles by trap-to-trap condensation in vacuo isolated 5.35 g (25.2 mmol), 97.3% yield, of a water-white liquid identified as $FMe_2SiCH_2Me_2SiCH_2BF_2$ (IIa). Vapor pressures were 4.0 mmHg and 5.0 mmHg at 19.5°C and 24.5°C, respectively, giving an extrapolated b.p. of 150 ± 3°C. A high resolution mass measurement showed a $(IIa - H)^+$ peak at m/e 211.0766, calcd.: 211.0758. (Found: C, 35.13; H, 7.62; B, 4.58; F, 24.85. $C_6H_{16}Si_2BF_3$ calcd.: C, 33.97; H, 7.60; B, 5.09; F, 26.86%).

Although no obvious reaction was noted under the above conditions, a subsequent reaction in which melting BF_3 came in contact with stirred I at room temperature was exothermic.

Reaction of 1,1,3,3-tetramethyl-1,3-disilacyclobutane (I) with boron trichloride

In the same manner as was described above, 14.80 g (102.5 mmol) of I and 12.20 g (104.1 mmol) of boron trichloride were gradually warmed from −195°C until the melted boron trichloride reacted vigorously with I giving a sharp exotherm which was controlled by an ice bath. The excess boron trichloride was removed in vacuo by pumping on the mixture held at −23°C. The clear, water-white liquid remaining was determined to be 26.79 g (102.4 mmol) of $ClMe_2SiCH_2Me_2SiCH_2BCl_2$ (IIb), representing a 99.90% yield. A portion of IIb was distilled at 77°C/4 mmHg. The IR and PMR of the distillate and the undistilled IIb were identical. (Found: C, 27.86; H, 6.20; B, 3.75; Cl, 40.43; mol. wt. (cryoscopic in benzene), 263. $C_6H_{16}Si_2BCl_3$ calcd.: C, 27.55; H, 6.17; B, 4.13; Cl, 40.67%; mol. wt., 262).

Reaction of 1,1,3,3-tetramethyl-1,3-disilacyclobutane (I) with boron tribromide

Using the procedures described above, 4.400 g (30.48 mmol) of I and 8.036 g (32.07 mmol) of boron tribromide gave an exothermic reaction. Removal of excess boron tribromide at 0°C in vacuo left 11.95 g (30.26 mmol), 99.27% yield of a clear, slightly brown liquid, $BrMe_2SiCH_2Me_2SiCH_2BBr_2$ (IIc). The IR and PMR spectra of IIc closely resembled IIb. (Found: C, 17.91; H, 4.05; B, 2.60; Br, 60.95; mol. wt. (cryoscopic in benzene), 396. $C_6H_{16}Si_2BBr_3$ calcd.: C, 18.25; H, 4.08; B, 2.74; Br 60.70%; mol. wt., 395.)

A sample of IIc from another preparation was distilled in a spinning band column. The major fraction obtained at 111°C/4 mmHg had an IR spectrum which showed small but significant differences from that of IIc above and the PMR spectrum showed nine single peaks as opposed to the expected four peaks observed for IIb and IIc. Chemical analysis, however, was comparable to that obtained for IIc.

Thermal treatment of $XMe_2SiCH_2Me_2SiCH_2BX_2$

(a) $BrMe_2SiCH_2Me_2SiCH_2BBr_2$ (IIc) (4.642 g, 11.75 mmol) was introduced into a heavy-walled, 25 ml, glass tube, frozen and degassed in vacuo. The stopcocked vessel was heated at 180°C for 40 h. Separation of the volatiles by fractional condensation in vacuo gave a trace of BBr_3 (confirmed by IR) and a clear yellow liquid. The IR spectrum was distinctly different from that of IIc and the PMR spectrum gave a five peak pattern. The IR and PMR spectra of an equal volume mixture of the thermal product IIIc and undistilled IIc were essentially the same as those of the major fraction obtained in the distillation of IIc described above.

(b) $ClMe_2SiCH_2Me_2SiCH_2BCl_2$ (IIb) (1.835 g, 7.016 mmol) was heated in a like manner. Fractional condensation in vacuo gave a trace of BCl_3 (confirmed by IR) and a clear liquid. The IR and PMR spectra closely resembled the composite spectra obtained by mixing IIc and IIIc above. Integration of the PMR indicated a 65% conversion of IIb to IIIb.

(c) $FMe_2SiCH_2Me_2SiCH_2BF_2$ (IIa) heated under identical conditions was recovered unchanged (confirmed by IR and PMR).

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