

studies⁷ is the position of $P(C_4H_9)_3$, which these results suggest is a stronger π -bonding agent than $P(OC_4H_9)_3$ or $P(C_6H_5)_3$. Likewise the absorption position of $Mn(CO)_5Br$ cannot be reconciled with this interpretation. These discrepancies indicate that other parameters are important in determining the positions of these absorption bands.

In the ultraviolet region, the monosubstituted com-

pounds investigated ($L = P(C_6H_5)_3$, $P(C_4H_9)_3$, and $P(OCH_2)_3CCH_3$) showed intense absorptions at 254 $m\mu$, whereas $Mn(CO)_5Br$ absorbs at 241 $m\mu$.

Acknowledgments.—This research was supported by a National Science Foundation Grant, NSF-G12872. The authors thank the National Science Foundation for a pre-doctoral fellowship to R. J. A. For many helpful discussions, we also thank Dr. A. J. Poë.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASSACHUSETTS

Vinyl Derivatives of Metals. XVI. Addition of Silicon and Tin Hydrides to B-Trivinyl-N-triphenylborazine¹

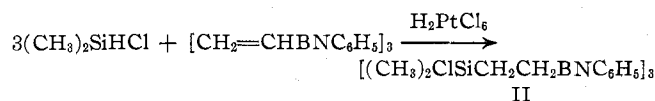
BY DIETMAR SEYFERTH² AND MINORU TAKAMIZAWA³

Received November 29, 1962

The addition of CH_3SiHCl_2 , $(CH_3)_2SiHCl$, $(CH_3)_3SiOSi(CH_3)_2H$, and $(CH_3)_3SiOSi(CH_3)HOSi(CH_3)_3$ to $[CH_2=CHBNC_6H_5]_3$ gave the respective B-tris-(β -silylethyl)-N-triphenylborazines. The reactions of those borazines containing Si-Cl bonds with water and with $(CH_3)_3SiOLi$ are described. The reaction of triphenyl- and triethyltin hydrides with $[CH_2=CHBNC_6H_5]_3$ gave $[R_3SnCH_2CH_2BNC_6H_5]_3$ ($R = C_6H_5$ and C_2H_5).

B-Trivinyl-N-triphenylborazine (I) was prepared recently by Pellon, *et al.*,⁴ and the radical-initiated polymerization and copolymerization of this new monomer were studied by these authors. Our interest in organofunctional, and especially in organosilicon-substituted, borazines has prompted this investigation of the addition of a number of silicon and tin hydrides to the vinyl groups of I.

Silicon Hydrides.—Although hydrogen chlorosilanes such as $HSiCl_3$ and CH_3SiHCl_2 did not react with I in the presence of radical initiators, they did add very readily to I in the presence of Speier's⁵ chloroplatinic acid catalyst.



The direction of addition of the Si-H bond to the vinyl side groups was determined by oxidation with alkaline hydrogen peroxide of the completely methylated borazine, $[(CH_3)_3SiCH_2CH_2BNC_6H_5]_3$, derived from II. Cleavage of the B-C bonds gave *only* β -trimethylsilylethanol, establishing the direction of addition as that given in the equation above. Had any $(CH_3)_3SiCH(CH_3)$ side groups been present in

the borazine, oxidation would have given α -trimethylsilylethanol as well, and the latter would have been detected in the gas chromatographic analysis of the alcohols produced.⁶

The availability of II and of $[CH_3Cl_2SiCH_2CH_2BNC_6H_5]_3$ (III) in principle made possible the preparation of β -siloxanylethylborazines. However, neither of the two procedures tried gave wholly satisfactory results. Attempted cohydrolysis of trimethylchlorosilane and II in an ether-water system gave hexamethyldisiloxane and a white solid. This solid, m.p. 137°, also was obtained when II alone was hydrolyzed and was identified as the silanol, $[(CH_3)_2(OH)SiCH_2CH_2BNC_6H_5]_3$ (IV). Cohydrolysis of II with trimethylchlorosilane in an ether-15% HCl mixture gave an oil, which, however, still showed the presence of Si-OH linkages in its infrared spectrum. Most likely steric hindrance, probably due to the other ring substituents, serves to explain this rather difficultly effected condensation of IV. Cohydrolysis of III with trimethylchlorosilane gave a yellow, resinous solid, rather than the expected $\{[(CH_3)_3SiO]_2Si(CH_3)CH_2CH_2BNC_6H_5\}_3$. This is an indication that the borazinylsilanediol condenses at a much slower rate than trimethylsilanol. Hydrolysis of III alone in an aqueous sodium bicarbonate-ether system produced a white, crystalline solid, which appeared to be the silanediol, $[CH_3(OH)_2SiCH_2CH_2BNC_6H_5]_3$, although a satisfactory analysis could not be obtained. Treatment of II and III with lithium trimethylsilanoate resulted in poor yields of products.

The best route to the desired siloxanylethylbor-

(1) Part XV: D. Seyferth, D. E. Welch, and G. Raab, *J. Am. Chem. Soc.*, **84**, 4266 (1962). Also part III of the series, "Borazine Derivatives"; for part II see D. Seyferth, W. Freyer, and M. Takamizawa, *Inorg. Chem.*, **1**, 710 (1962).

(2) Alfred P. Sloan Research Fellow.

(3) Fellow of the M.I.T. School for Advanced Study, 1961-1962; on leave from the Shin-Etsu Chemical Industry Co. Ltd., Tokyo.

(4) J. Pellon, U. S. Patent 2,954,366 (1960); *Chem. Abstr.*, **55**, 4043 (1961); J. Pellon, W. G. Deichert, and W. M. Thomas, *J. Polymer Sci.*, **55**, 153 (1961).

(5) J. L. Speier, J. A. Webster, and G. H. Barnes, *J. Am. Chem. Soc.*, **79**, 974 (1957).

(6) D. Seyferth, *ibid.*, **81**, 1844 (1959).

azines used the chloroplatinic acid-catalyzed addition of Si-H containing siloxanes to the vinylborazine I. Thus addition of $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_2\text{H}$ gave $[(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{BNC}_6\text{H}_5]_3$, and the use of $[(\text{CH}_3)_3\text{SiO}]_2\text{Si}(\text{CH}_3)\text{H}$ resulted in $\{[(\text{CH}_3)_3\text{SiO}]_2\text{Si}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{BNC}_6\text{H}_5\}_3$. Higher polysiloxanyethylborazines should be easily accessible *via* similar addition of Si-H terminated polysiloxanes of the type $(\text{CH}_3)_3\text{SiO}[(\text{CH}_3)_2\text{SiO}]_n\text{Si}(\text{CH}_3)_2\text{H}$, although this point has not yet been investigated.

Tin Hydrides.—The addition of tin hydrides to olefins occurs readily in the absence of initiators, especially in the case of triphenyltin hydride.⁷ Trialkyltin hydrides are significantly less reactive than triphenyltin hydride. In agreement with this observation, we found that triphenyltin hydride reacted with I in refluxing toluene to give $[(\text{C}_6\text{H}_5)_3\text{SnCH}_2\text{CH}_2\text{BNC}_6\text{H}_5]_3$ in good yield. In contrast, triethyltin hydride did not react with I under these conditions, but a reaction to give $[(\text{C}_2\text{H}_5)_3\text{SnCH}_2\text{CH}_2\text{BNC}_6\text{H}_5]_3$ did take place in the presence of 2,2'-azobisisobutyronitrile. Radical initiation of the addition of alkyltin hydrides to olefins had been reported previously by Neumann, *et al.*⁸

The oxidation of the triphenyltin hydride-I reaction product with alkaline hydrogen peroxide gave β -hydroxyethyltriphenyltin in 54% yield. The n.m.r. spectrum of the latter in the aliphatic region, two triplets due to adjacent CH_2 groups at 1.73 and 3.89 p.p.m. downfield from tetramethylsilane, confirmed its structure. None of the other possible isomer, α -hydroxyethyltriphenyltin, could be detected. This experiment shows that at least 54% of the triphenylstannylethyl groups of the borazine formed had the $(\text{C}_6\text{H}_5)_3\text{SnCH}_2\text{CH}_2$ - structure. We believe that the product was wholly $[(\text{C}_6\text{H}_5)_3\text{SnCH}_2\text{CH}_2\text{BNC}_6\text{H}_5]_3$ because of the sharp melting point observed and because of the generally observed⁷ addition of organotin hydrides to terminal olefins to give a specific addition in which the stannyl group becomes attached to the terminal carbon atom of the olefin. On this basis we assume also that the triethyltin hydride-I product has the structure indicated above.

Experimental⁹

Addition of Hydrogenchlorosilanes to B-Trivinyl-N-triphenylborazine. (1) **Dimethylchlorosilane.**—To 2.0 g. (5.2 mmoles) of I in 25 ml. of dry toluene containing 0.1 ml. of 0.1% $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in isopropyl alcohol at 95–100° was added during 40 min. 6.0 g. (70 mmoles) of dimethylchlorosilane (Dow Corning Corp.) in 8 ml. of toluene. The mixture was heated for 5 hr. at 90–95°. Volatiles were removed at reduced pressure, leaving white, waxy solid. Recrystallization from dry hexane under nitrogen gave 2.8 g. (81%) of white, crystalline solid. Another recrystallization from hexane gave material of m.p. 163–164°, and a final short-path distillation gave m.p. 164–166°.

(7) G. J. M. van der Kerk, J. G. Noltes, and J. G. A. Luijten, *J. Appl. Chem.* (London), **7**, 356 (1957).

(8) W. P. Neumann, H. Niermann, and R. Sommer, *Angew. Chem.*, **73**, 786 (1961).

(9) All reactions were carried out under an atmosphere of prepurified nitrogen. Melting points are uncorrected. Analyses by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and by A. Schoeller, Kronach, Ofr.

Anal. Calcd. for $\text{C}_{30}\text{H}_{45}\text{N}_3\text{Cl}_3\text{B}_3\text{Si}_3$: C, 53.72; H, 6.76; N, 6.27. Found: C, 53.82; H, 6.96; N, 6.61.

(2) **Methyldichlorosilane.**—The reaction was carried out by the method described above using 2.6 mmoles of I and 26 mmoles of methyldichlorosilane (Dow Corning Corp.). Evaporation of toluene and excess methyldichlorosilane left 1.7 g. of light yellow, waxy solid. Recrystallization under nitrogen from dry hexane and short-path distillation *in vacuo* gave white, crystalline solid, m.p. 170–172°.

Anal. Calcd. for $\text{C}_{27}\text{H}_{38}\text{N}_3\text{Cl}_2\text{B}_3\text{Si}_3$: C, 44.30; H, 4.96; N, 5.74. Found: C, 44.76; H, 5.16; N, 5.78.

(3) **Methylation of $[(\text{CH}_3)_2\text{ClSiCH}_2\text{CH}_2\text{BNC}_6\text{H}_5]_3$ and Oxidation of the Product.**—Five grams (13 mmoles) of I and 10 g. (106 mmoles) of dimethylchlorosilane were allowed to react for 5 hr. in toluene solution as described above. Excess of dimethylchlorosilane was removed by distillation, and the clear solution remaining was added to the Grignard reagent prepared from 2.5 g. (0.11 g.-atom) of magnesium and 0.15 mole of methyl bromide in 50 ml. of ether. The ether was stripped from the resulting mixture, and the residual toluene solution was heated at reflux for 1 hr., cooled, and hydrolyzed with saturated ammonium chloride solution. The organic layer was separated, dried, and evaporated to leave a white, crystalline residue. Recrystallization from ether-methanol gave 6.0 g. (76.3%) of white needles, m.p. 157–159°, of $[(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{BNC}_6\text{H}_5]_3$.

Anal. Calcd. for $\text{C}_{33}\text{H}_{54}\text{N}_3\text{B}_3\text{Si}_3$: C, 65.03; H, 8.93; N, 6.90. Found: C, 65.04; H, 8.70; N, 7.13.

The infrared spectrum of the product showed absorption characteristic of the trimethylsilyl group at 1260, 1250, 840, and 750 cm^{-1} and absorption due to the borazine ring system at ca. 1377 cm^{-1} .

To a mixture of 3.05 g. (5 mmoles) of this product, 0.5 g. of NaOH in 20 ml. of 95% ethanol, and 10 ml. of ether was added with stirring 3.0 g. of 30% hydrogen peroxide at such a rate that a mild reflux was maintained. A clear, yellow solution and viscous, white solid were formed. Water and ether (15 ml. of each) were added, and the mixture was agitated vigorously. The organic layer was separated and the aqueous phase extracted with ether. The dried ether solution was distilled to a head temperature of 38°. Gas chromatographic analysis of the residue (Dow Corning 710 silicone fluid on Chromosorb P, jacket temperature 125°, 16 p.s.i. He) showed that only β -trimethylsilylethanol (identified also by infrared spectrum) was present.

Addition of Si-H Containing Siloxanes to I. (1) **Pentamethyldisiloxane.**—To 1.0 g. (2.6 mmoles) of I in 12 ml. of toluene containing 0.1 ml. of platinum catalyst solution was added at temperatures slightly above 100° 3.7 g. (25 mmoles) of $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_2\text{H}^{10}$ in 5 ml. of toluene. The mixture was heated at reflux (103–105°) for 5 hr. Evaporation of volatiles left white, waxy solid, recrystallization of which from ether-methanol gave 1.22 g. (57%) of white crystals, m.p. 84–85°. These were purified by column chromatography (alumina, ether eluent) and another recrystallization from ether-methanol to give material of m.p. 86–87°.

Anal. Calcd. for $\text{C}_{39}\text{H}_{72}\text{N}_3\text{O}_3\text{B}_3\text{Si}_6$: C, 56.31; H, 8.73; N, 5.05. Found: C, 56.11; H, 8.79; N, 4.98.

The infrared spectrum of the product showed absorption at 1250, 840, and 750–760 cm^{-1} (trimethylsilyl group), 1065 cm^{-1} (Si–O–Si), and 1375 cm^{-1} (broad, due to borazine ring system).

(2) ***sym*-Heptamethyltrisiloxane.**—The same procedure was used in the H_2PtCl_6 -catalyzed addition of $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)\text{HOSi}(\text{CH}_3)_2$ (20 mmoles) to 2.6 mmoles of I in 16 ml. of toluene. Evaporation of volatiles left a yellow oil. Chromatography on alumina (hexane eluent) followed, and the oil which was isolated had the correct analysis for $\{[(\text{CH}_3)_3\text{SiO}]_2\text{Si}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{BNC}_6\text{H}_5\}_3$.

(10) B.p. 85–86°, prepared by cohydrolysis of dimethylchlorosilane and trimethylchlorosilane; b.p. 86° at 730 mm. reported by G. Greber and L. Metzinger, *Makromol. Chem.*, **39**, 189 (1960).

(11) B.p. 141–146°; prepared according to R. O. Sauer, W. J. Schreiber, and S. D. Brewer, *J. Am. Chem. Soc.*, **68**, 962 (1946).

Anal. Calcd. for $C_{46}H_{90}N_3O_3B_3Si_9$: C, 51.27; H, 8.61; N, 3.98. Found: C, 51.39; H, 8.65; N, 4.25.

The infrared spectrum showed the usual absorption attributable to the trimethylsilyl, siloxane, and borazine ring systems.

Hydrolysis of $[(CH_3)_2ClSiCH_2CH_2BNC_6H_5]_3$.—To 75 ml. of water and 50 ml. of ether at 0° was added slowly a solution of 26 mmoles of $[(CH_3)_2ClSiCH_2CH_2BNC_6H_5]_3$ in a toluene-ether mixture. The reaction mixture was stirred for 20 min., and the organic layer subsequently was separated, washed, and dried. Volatiles were distilled from the organic phase, and hexane was added to crystallize the product, $[(CH_3)_2(OH)SiCH_2CH_2BNC_6H_5]_3$, 1.2 g. (76%), m.p. 135–136°. Recrystallization from ether-hexane gave white crystals, m.p. 137°.

Anal. Calcd. for $C_{30}H_{48}O_2N_3B_3Si_3$: C, 58.55; H, 7.86; N, 6.83. Found: C, 59.03; H, 7.92; N, 7.23.

The infrared spectrum of the product showed absorption due to the presence of the dimethylsilyl group (1257 cm^{-1}) and the borazine ring system (broad, centered at 1377 cm^{-1}), and also a strong band at 3400 cm^{-1} , attributable to Si-OH groups. No Si-O-Si absorption between 1000 and 1100 cm^{-1} was observed.

Treatment of 4.6 mmoles of trimethylchlorosilane with 0.8 mmole of the product silanol-borazine in toluene in the presence of 6 mmoles of triethylamine at 50° resulted in precipitation of triethylamine hydrochloride. Hydrolysis, followed by drying and evaporation of the organic layer, gave a viscous oil.

Hydrolysis of $[(CH_3)_2ClSiCH_2CH_2BNC_6H_5]_3$.—To a solution of 1.5 g. (17 mmoles) of sodium bicarbonate in 100 ml. of water and 100 ml. of ether was added dropwise at 0–5° an ether-toluene solution containing 2.6 mmoles of this borazine. Some white, crystalline material (0.29 g.) precipitated. The latter was filtered, and the organic layer was separated, dried, and concentrated *in vacuo* to remove ether. Addition of hexane to the solution remaining precipitated 0.65 g. of white crystals; total yield, 0.94 g. (59%). The product was recrystallized from methanol-benzene to give white, crystalline solid, soluble in methanol, insoluble in hexane and benzene, decomposition point 143–145°. At this temperature water appeared to form in the m.p. capillary, and a resinous solid resulted. The infrared spectrum showed strong absorption at 3400 cm^{-1} (Si-OH), as well as at 1260 cm^{-1} (CH_3Si-) and at 1380 cm^{-1} (broad, borazine ring). No absorption due to the siloxane linkage was noted. Correct analyses could not be obtained, due to the apparent instability of the product on standing. The evidence above suggests, but does not prove, that the product is $[CH_3(OH)_2SiCH_2CH_2BNC_6H_5]_3$.

Reaction of Si-Cl Containing Borazines with Lithium Trimethylsilanolate.—*Ca.* 24 mmoles of lithium trimethylsilanolate¹² in ether-tetrahydrofuran medium was added slowly to *ca.* 7.8 mmoles of $[(CH_3)_2ClSiCH_2CH_2BNC_6H_5]_3$ in 35 ml. of toluene and 30 ml. of tetrahydrofuran. The resulting mixture was heated at reflux for 2 hr., cooled, and hydrolyzed with saturated ammonium chloride solution. Evaporation of the organic layer at reduced pressure left a brown, turbid oil (5.6 g.). The latter was chromatographed on an alumina column. Hexane eluted 3.3 g. of clear, colorless oil, which solidified to waxy crystals on standing. Chromatography of the latter (ether eluent) on alumina gave an oil which crystallized to give low-melting solid whose infrared spectrum was identical with that of the $(CH_3)_3SiOSi(CH_3)_2H$ -vinylborazine product, and whose analysis was nearly in agreement with that of the expected product.

(12) Prepared according to D. Seyferth and D. L. Alleston, *Inorg. Chem.*, **2**, 418 (1963).

Anal. Calcd. for $C_{38}H_{72}N_3O_3B_3Si_6$: C, 56.31; H, 8.73; N, 5.05. Found: C, 56.86; H, 8.46; N, 5.28.

A similar reaction between lithium trimethylsilanolate (48 mmoles) and $[CH_3Cl_2SiCH_2CH_2BNC_6H_5]_3$ (7.8 mmoles) gave 7.1 g. of brown oil, which on purification by chromatography on alumina (hexane eluent) produced 3.7 g. of a clear, colorless oil. The infrared spectrum of the latter was identical with that of the oil obtained in the *sym*-heptamethyltrisiloxane-vinylborazine reaction.

Addition of Tin Hydrides to I. (1) Triphenyltin Hydride.—A solution of 1.0 g. (2.6 mmoles) of I and 3.0 g. (8.6 mmoles) of triphenyltin hydride¹³ in 15 ml. of toluene was heated at reflux for 4 hr. Some gray solid precipitated. Filtration was followed by evaporation of the filtrate at reduced pressure and addition of methanol to the residue. White, crystalline solid, m.p. 215–218°, 2.74 g. (73.5%), resulted. Recrystallization from toluene-methanol gave white needles, m.p. 219–221°.

Anal. Calcd. for $C_{78}H_{72}N_3B_3Sn_3$: C, 65.06; H, 5.04; N, 2.92. Found: C, 65.52; H, 5.20; N, 3.05.

The infrared spectrum of the product showed the B-N ring absorption at 1376 cm^{-1} and Sn-phenyl absorption at 1070 cm^{-1} .

(2) Triethyltin Hydride.—A mixture containing 2.6 mmoles of I, 2.1 g. (10 mmoles) of triethyltin hydride,¹³ and 0.05 g. of 2,2'-azobisisobutyronitrile in 13 ml. of toluene was heated at reflux for 5 hr. Evaporation of the clear solution under reduced pressure was followed by addition of methanol to the residue to give 2.2 g. (84%) of white solid, m.p. 73–81°. Recrystallization from ether-methanol gave white needles, m.p. 87–88°.

Anal. Calcd. for $C_{42}H_{72}N_3B_3Sn_3$: C, 50.06; H, 7.20; N, 4.17. Found: C, 50.19; H, 7.14; N, 4.80.

Oxidation of $[(C_6H_5)_3SnCH_2CH_2BNC_6H_5]_3$.—The borazine (1.92 g., 4 mmoles) was suspended in a mixture of 0.4 g. of NaOH in 95% ethanol (16 ml.) and 8 ml. of ether. Addition of 2.4 g. of 30% hydrogen peroxide to the refluxing mixture followed. The reaction mixture was stirred at the reflux temperature for 10 min. During this time an almost homogeneous solution resulted; later an oily precipitate formed. Twelve ml. each of water and ether was added and the mixture shaken vigorously. The organic layer was separated and dried; evaporation left a solid residue. Extraction of the latter with hot petroleum ether (b.p. 30–60°) gave 0.86 g. of white, crystalline $(C_6H_5)_3SnCH_2CH_2OH$ (54.4% yield), m.p. 67–69° (lit.¹⁴ m.p. 67–68°). N.m.r. (10% solution in CCl_4 ; recorded using a Varian Associates A60 n.m.r. spectrometer): triplets at 1.73 and 3.89 p.p.m. (CH_2 groups), singlet at 1.96 p.p.m. (OH), and complex phenyl absorption centered at 7.35 p.p.m., downfield from tetramethylsilane.

Acknowledgments.—This work was supported by the United States Air Force under Contracts No. AF 33-(616)-7124 and AF 33(657)-8532, monitored by Materials Central, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio. The authors are grateful to the Shin-Etsu Chemical Industry Company Ltd. for granting a leave of absence to M. T. and to Mr. Yasuhiko Sato for carrying out the experiment on the oxidation of $[(C_6H_5)_3SnCH_2CH_2BNC_6H_5]_3$.

(13) G. J. M. van der Kerk, J. G. Noltes, and J. G. A. Luijten, *J. Appl. Chem. (London)*, **7**, 366 (1957).

(14) H. Gilman and C. E. Arntzen, *J. Org. Chem.*, **15**, 994 (1950).