CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
DUKE UNIVERSITY, DURHAM, NORTH CAROLINA

Boron–Nitrogen Compounds. XIV.[1,2] The Preparation of Vinyldibromoborane and Some of Its Reactions with Amines

BY PETER FRITZ, KURT NIEDENZU, AND JOHN W. DAWSON

Received December 6, 1963

In the reaction of tetravinyltin with boron tribromide, mercury has been found to exhibit a twofold effect: (a) it ensures the utilization of all four organic groups for the conversion of the boron trihalide to an organodihalogenoborane and (b) one notes the complete absence of organoboron by-products. As a result, the isolation and characterization of vinyldibromoborane was accomplished. Reactions of the latter compound with various amines have been studied and B-vinylated bisaminoboranes, 1,3,2-diazaborolidines, and borazines have been prepared. B-Vinylation does not appear to influence the electronic nature of the B–N bond to any appreciable degree.

Previous publications[3,4] have illustrated that tetraorganotin compounds can react with boron trihalides to yield dihalogenoorganoboranes in accordance with eq. 1. It also has been reported that, by suitably

$$\mathrm{SnR_4 + 2BX_3 \longrightarrow R_2SnX_2 + 2RBX_2} \qquad (1)$$

choosing the proportions of reactants, it is possible to obtain diorganohalogenoboranes,[5] R_2BX. In one instance,[6] the utilization of all four organic groups of the SnR_4 at higher temperatures has been reported (eq. 2). More recent work[7] seems to indicate the general validity of eq. 1 even though either starting com-

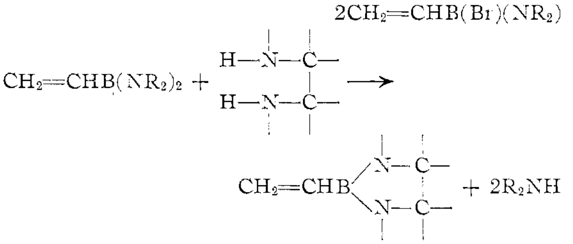
$$\mathrm{SnR_4 + 4BX_3 \longrightarrow SnX_4 + 4RBX_2} \qquad (2)$$

ponent may be present in excess. However, a mixture of vinylbromoboranes and trivinylborane always was obtained on treatment of tetravinyltin with boron tribromide, although the boron halide was employed in large excess. The boiling points of the boron-containing products in this latter reaction are so close that it has been impossible to separate them effectively by distillation. Therefore, no vinylbromoboranes have been characterized.[5] Since considerable amounts of a vinyldihalogenoborane were needed for future investigations in this laboratory, the reaction of tetravinyltin with boron tribromide was studied in more detail.

Previously cited results of Brinckman and Stone[5] were confirmed. Further, it was found possible to utilize all four vinyl groups of the tetravinyltin for the conversion of boron tribromide into vinyldibromoborane if the tin derivative was added to the boron tribromide in the presence of mercury at 0°. Moreover, under these circumstances, the reaction proceeds smoothly according to eq. 2, and virtually no organoboron by-products are found. Distillation of the reaction product afforded vinyldibromoborane in about 85% yield. Some of the reactions of vinyldibromoborane with amines have been studied; with dimethylamine, bis(dimethylamino)vinylborane is readily obtained. Disproportionation of vinyldibromoborane with bis(dimethylamino)vinylborane yields (dimethylamino)-bromovinylborane. With 1,2-diamines, bis(dimethylamino)vinylborane yields 1,3,2-diazaborolidines; ammonolysis of this same aminovinylborane affords B-trivinylborazine. These reactions are illustrated by eq. 3–6.

$$\mathrm{CH_2{=}CHBBr_2 + 4HNR_2 \longrightarrow CH_2{=}CHB(NR_2)_2 + 2R_2NH_2Br} \qquad (3)$$

$$\mathrm{CH_2{=}CHBBr_2 + CH_2{=}CHB(NR_2)_2 \longrightarrow 2CH_2{=}CHB(Br)(NR_2)} \qquad (4)$$



(5)

$$\mathrm{3CH_2{=}CHB(NR_2)_2 + 3NH_3 \longrightarrow (\text{—}BCH{=}CH_2\text{—}NH\text{—})_3 + 6R_2NH} \qquad (6)$$

The role of the mercury in the above preparation of vinyldibromoborane is not completely understood but it appears to function as a catalyst. A virtually quantitative recovery of the mercury was realized on processing the reaction mixture; about 90% of the calculated amount of tin tetrabromide was isolated. It also appears that mercury does not react with tetravinyltin at room temperature. Moreover, the effect of the mercury seems to be unique for the cited case, since, in a similar reaction with tetraethyltin, reaction occurred according to eq. 1 only.

Experimental[8]

Vinyldibromoborane, $CH_2{=}CHBBr_2$.—A quantity (96 ml., 254.5 g., 1.015 moles) of boron tribromide was cooled to 0° in an

---

[1] Supported by the U. S. Army Research Office, Durham, N. C.

[2] For part XIII in this series see: H. Beyer, J. B. Hynes, H. Jenne, and K. Niedenzu, Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1963, p. 266; part XII: H. Jenne and K. Niedenzu, *Inorg. Chem.*, **3**, 68 (1964).

[3] F. E. Brinckman and F. G. A. Stone, Abstracts of Papers, 135th National Meeting of the American Chemical Society, Boston, Mass., 1959, p. 26M.

[4] K. Niedenzu and J. W. Dawson, *J. Am. Chem. Soc.*, **82**, 4223 (1960).

[5] F. E. Brinckman and F. G. A. Stone, *ibid.*, **82**, 6218 (1960).

[6] J. E. Burch, W. Gerrard, M. Howarth, and E. F. Mooney, *J. Chem. Soc.*, 4916 (1960).

[7] H. Nöth and P. Fritz, *Z. anorg. allgem. Chem.*, **322**, 297 (1963).

[8] Analyses reported herein were furnished by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y. Infrared spectra were recorded with a Perkin-Elmer Model 21 double beam spectrophotometer using sodium chloride optics. The ^{11}B nuclear magnetic resonance data were obtained on a Varian Model DP-60 spectrometer operated at 19.3 Mc., through the courtesy of Prof. R. Schaeffer, Indiana University, Bloomington, Ind.; p.m.r. spectra were obtained on a Varian Model A-60 spectrometer.

inert atmosphere and 30–40 g. of mercury was added. Tetravinyltin (58 g., 0.256 mole) then was added with vigorous stirring over a period of 40 min. The reaction mixture was allowed to warm to room temperature, solid materials were removed, and the product was distilled under an inert atmosphere to yield 164 g. (83%, based on the BBr_3 employed) of vinyldibromoborane, b.p. 93–94°, lit.[9] 35° (50 mm.). *Anal.* Calcd. for $C_2H_3BBr_2$: B, 5.5. Found: B, 5.2.

Bis(dimethylamino)vinylborane, $[(CH_3)_2N]_2BCH{=}CH_2$.—Dimethylamine was slowly and continuously bubbled into a solution of 167 g. (0.845 mole) of vinyldibromoborane in 1500 ml. of anhydrous ether at −15°. After about 15 min., a pale yellow solid precipitated. The cooling bath was removed, another 300 ml. of ether was added, and the introduction of amine was continued. Refluxing occurred as additional amine was added over 60 min.; cessation of the exotherm indicated that the reaction was essentially complete. After standing overnight, the reaction product was filtered and washed with ether, and the solvent was stripped from the combined filtrates. The residue was distilled under vacuum, yielding 69.5 g. (65%) of bis(dimethylamino)vinylborane, b.p. 29° (9 mm.). *Anal.* Calcd. for $C_6H_{15}BN_2$: C, 57.1; H, 12.0; B, 8.6; N, 22.2. Found: C, 57.1; H, 12.0; B, 8.5; N, 22.0.

(Dimethylamino)bromovinylborane, $(CH_3)_2NB(Br)(CH{=}CH_2)$.—A solution of 38 g. (0.305 mole) of bis(dimethylamino)vinylborane in 100 ml. of hexane was added to 60 g. (0.32 mole) of dibromovinylborane under cooling to −10°. After addition was complete, the cooling bath was removed and the mixture stirred for 1 hr. The reaction mixture was stripped through a 200-mm. Widmer column removing the solvent at n.t.p.; the residue distilled *in vacuo* to yield 78.5 g. (81%) of (dimethylamino)bromovinylborane, b.p. 39° (11 mm.). *Anal.* Calcd. for C_4H_9BNBr: C, 29.7; H, 5.6; B, 6.7; N, 8.65; Br, 49.5. Found: C, 29.5; H, 5.8; B, 6.9; N, 8.4; Br, 49.2.

B-Trivinylborazine, $(-BCH{=}CH_2NH-)_3$.—Dry ammonia gas was bubbled through 19.5 g. (0.155 mole) of bis(dimethylamino)-vinylborane at room temperature. While the ammonia was being added, the reaction vessel was slowly warmed to about 80–100° over 2 hr. The reaction product was then distilled under vacuum to yield 4 g. (49%) of B-trivinylborazine, b.p. 78–79° (7 mm.). *Anal.* Calcd. for $C_6H_{12}B_3N_3$: C, 45.7; H, 7.6; B, 20.5; N, 26.4; mol. wt., 158.65. Found: C, 45.5; H, 7.8; B, 20.8; N, 26.5; mol. wt., 158.8.

2-Vinyl-1,3,2-benzodiazaboroline, $C_6H_4(NH)_2BCH{=}CH_2$.—A solution of 9 g. (83.5 mmoles) of *o*-phenylenediamine and 10.5 g. (83.2 mmoles) of bis(dimethylamino)vinylborane in 30 ml. of benzene was refluxed for 2 hr. and filtered while hot. On cooling, a white solid precipitated; a second fraction of crystals was obtained upon partial evaporation of the solvent. Repeated crystallization from benzene–hexane yielded a pure material, m.p. 119–121°. *Anal.* Calcd. for $C_8H_9BN_2$: C, 66.7; H, 6.25; B, 7.5; N, 19.45. Found: C, 66.5; H, 6.5; B, 7.4; N, 19.2.

1,3-Dimethyl-2-vinyl-1,3,2-diazaborolidine, $(-CH_2NCH_3-)_2BCH{=}CH_2$.—A solution of 17.1 g. (194.5 mmoles) of N,N′-dimethylethylenediamine and 24.5 g. (194.5 mmoles) of bis(dimethylamino)vinylborane in 200 ml. of hexane was refluxed for 90 min. The solvent was stripped off and the residue distilled under vacuum to yield 20.5 g. (85%) of the desired compound, b.p. 35–36° (11 mm.). *Anal.* Calcd. for $C_6H_{13}BN_2$: C, 58.1; H, 10.6; B, 8.7; N, 22.6. Found: C, 58.2; H, 10.8; B, 8.7; N, 22.4.

Discussion

In view of the difficulties encountered by previous authors[5] in attempting to purify vinylbromoboranes, the quality of the vinyldibromoborane prepared as described above was checked by ^{11}B n.m.r spectroscopy. The ^{11}B resonance of vinyldibromoborane was recorded as a singlet at −55.2 p.p.m. (relative to boron trifluoride etherate); the sample was found to be contaminated by small amounts of boron tribromide. No other boron-containing species could be detected. The proton magnetic resonance spectrum of the material showed a relatively broad resonance of τ 2.99 due to the vinyl protons.

The reactions of vinyldibromoborane with amines are analogous to those of other organodihalogenoboranes. It is of interest, however, to evaluate some spectral data. The B–N infrared stretching frequency of some B-vinylated boron–nitrogen compounds are compared with those of similar B-alkylated derivatives in Table I. From these data it appears that conjugation of a B-attached vinyl group with a boron–nitrogen linkage does not produce an appreciable shift in the infrared spectrum. This finding is in agreement with previous reports[10] that organic substituents on the boron have little influence on the electronic transitions in borazines. This situation is reinforced by similar data on substituted aminoboranes.[11] On the other hand, based upon previous reports,[10,11] it can be anticipated that, in N-vinylated boron–nitrogen compounds, the vinyl group will influence participation of the free electron pair of the nitrogen in the B–N linkage. Considering the available information on the infrared spectra of substituted borazines, it might be assumed that structures such as that postulated for B-trifluoro-N-trivinylborazine should exhibit one of the strongest B–N linkages.

TABLE I

B–N STRETCHING FREQUENCIES OF SOME BORON–NITROGEN COMPOUNDS

Compound	ν_{BN}, cm.$^{-1}$
B-Trivinylborazine	1483
B-Trimethylborazine[a]	1485
(Dimethylamino)bromovinylborane	1428
(Dimethylamino)chloromethylborane[b]	1415
Bis(dimethylamino)vinylborane	1382
Bis(dimethylamino)methylborane[b]	1381

[a] R. I. Wagner and J. L. Bradford, *Inorg. Chem.*, 1, 93 (1962).
[b] P. Fritz, Ph.D. Thesis, University of München, Germany, 1963.

Some nuclear magnetic resonance data were obtained for B-trivinylborazine. The ^{11}B resonance was recorded at −31.8 p.p.m. (relative to boron trifluoride etherate) with a line width at half maximum peak height of 276 c.p.s. The value of the chemical shift seems to be of the correct order of magnitude compared with the one from B-trimethylborazine, namely, −32.4 p.p.m. The proton resonance of B-trivinylborazine consisted of a complex multiplet structure due to the vinyl protons and centered at a value of τ 4.2; the N-attached hydrogens were evidenced by a broad singlet, τ 5.05.

---

(9) B. Bartocha, C. M. Douglas, and M. Y. Gray, *Z. Naturforsch.*, **14b**, 809 (1959).

(10) D. W. Davies, *Trans. Faraday Soc.*, **56**, 1713 (1960).

(11) G. M. Wyman, K. Niedenzu, and J. W. Dawson, *J. Chem. Soc.*, 4068 (1962).