The Sr preparations contained six such lines; the Ca preparation eight. The *d*-spacings of four of the Sr lines agreed very roughly with the *d*-spacings of certain stronger lines common to γ-Sr[9] and to both tetragonal and hexagonal "Sr_8Li."[9] The Ca lines agreed very roughly with certain of the stronger lines of Laves-phase $CaLi_2$.[10] Hence, it is possible that these lines were due to small amounts of α-phase slightly hydrided metal.

The interionic distances in the perovskite phases have been calculated and are given in Table II along with the distances in related binary hydrides and fluorides.

TABLE II

INTERIONIC DISTANCES IN HYDRIDE AND FLUORIDE PHASES

X = H or F; M = Ca, Sr, or Ba

	d_{Li-H}, Å.	d_{M-H}, Å.	d_{Li-F}, Å.	d_{M-F}, Å.
LiX	2.04[a]	. . .	2.01[f]	. . .
CaX_2	. . .	2.32[b,c]	. . .	2.36[h]
SrX_2	. . .	2.49[c,d]	. . .	2.51[h]
$LiSrX_3$	1.92	2.71	. . .	. . .
BaX_2	. . .	2.67[c,e]	. . .	2.69[h]
$LiBaX_3$	2.01	2.84	2.00[g]	2.82[g]

[a] E. Staritzsky and D. J. Walker, *Anal. Chem.*, **28,** 1055 (1956). [b] J. Bergsma and B. O. Loopstra, *Acta Cryst.*, **15,** 92 (1962). [c] The distance given is that of the seven nearest H^- neighbors of a Ca^{+2} in the proposed structure.[b] [d] Assuming the H^- parameters to be the same as in CaH_2[b] and the lattice constant ratio of 1.074 ± 0.002 for SrH_2 to CaH_2[8] to hold for interatomic distances within the cell as well as for a_0, b_0, and c_0. [e] With similar assumptions; ratio 1.150 ± 0.008 for BaH_2 to CaH_2. [f] H. E. Swanson and E. Tatge, "Standard X-Ray Diffraction Patterns," National Bureau of Standards Circular 539, Vol. 1, U. S. Government Printing Office, Washington, D. C., 1953, p. 92. [g] Reference 2. [h] R. G. Wyckoff, "Crystal Structures," Vol. I, Interscience Publishers, New York, N. Y., 1948, Chapter IV, Table p. 14c.

The M–H distances are considerably higher in the perovskites than in the binary hydrides. This is probably the effect of the change in coordination number of H^- around M^{+2} from 7 in MH_2 to 12 in $LiMH_3$. This same effect is noted in the corresponding fluorides.

The Li–H distance in $LiBaH_3$ is close to that in LiH, but is considerably shorter in $LiSrH_3$. The Li–F distance is "normal" in $LiBaF_3$. This shortened distance in $LiSrH_3$, and the fact that $LiSrF_3$ could not be readily prepared,[3] may be attributed to the high polarizability of H^- relative to F^-. The rigid fluoride ions cannot adapt to the shortened distance requirements with strontium in this lattice; the deformable hydride ions can.

The uniformity of the lattice constant values of $LiBaH_3$ and $LiSrH_3$ suggests that departures from stoichiometry in these phases cannot be very large, at least not at room temperature.

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

Boron-Nitrogen Compounds. XV.[1,2] Preparation of Vinylated Aminoboranes

BY KURT NIEDENZU, PETER FRITZ AND JOHN W. DAWSON

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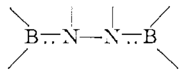
Recent investigations have demonstrated that hindered rotation about the B–N linkage of an aminoborane, R_2N-BR_2', is possible and appears to result from the participation of the free electron pair of the nitrogen in the B–N bond.[3] This behavior substantiates the analogy drawn between aminoboranes and their corresponding olefins as postulated by Wiberg.[4] On the other hand, considerable differences in the chemical behavior of both types of compounds have been observed; therefore an interpretation of physicochemical data has to be treated with extreme caution as has recently been illustrated by a detailed investigation of (methylphenylamino)methylphenylborane.[5] New interesting results contributing to the understanding of the boron–nitrogen bond should be realized through a study of (formal) inorganic dienic structures. Of the pure B–N combination, three structures can be formulated involving conjugated B–N π-bonding in addition to a normal covalent bond (I–III). Likewise two semi-inorganic structures illustrate a conjugation of formal bonds with B–N π-bonding (IV and V).



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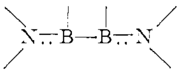

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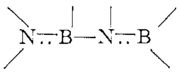
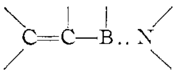
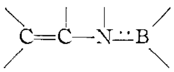


III



IV



V

Compounds containing the basic grouping as illustrated in structures I and II have recently been synthesized.[6,7] The route for the preparation of type III has recently been described[8] and the preparation of some B-vinylated boron–nitrogen compounds has been reported.[1,9] In the present paper, the syntheses of some representative compounds of types IV and V are described.

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B-Vinylated aminoboranes (IV) have been obtained through the reaction of aminoalkylhalogenoboranes with vinylmagnesium halide[9] and through the reaction of aminovinylhalogenoboranes[1] with alkyl (or aryl) magnesium halide.

(Vinylamino)boranes (V) were obtained through a transamination reaction involving the treatment of an aminoborane with the readily available (β-methyl-β-phenyl)vinylamine, $(CH_3)(C_6H_5)C{=}CH{-}NH_2$.[10]

$$>C{=}CH{-}NH_2 + R_2N{-}BR_2 \quad >C{=}CH{-}NH{-}BR_2 + R_2NH \qquad (1)$$

Thus five formal analogs of the organic diene system are now available for further studies. Moreover, it appears possible to synthesize inorganic and semiinorganic polyenes which can be considered to show varying degrees of conjugation by the reaction of aminovinylboranes with vinylamines, and there are experimental indications of the formation of longer chains of alternating boron and nitrogen atoms than is indicated in III.

Experimental[11]

(Dimethylamino)methylvinylborane, $(CH_3)_2N{-}B(CH_3)(CH{=}CH_2)$.—To a solution of 14 g. (0.134 mole) of (dimethylamino)-methylchloroborane[12] in 100 ml. of anhydrous ether, a solution of vinylmagnesium chloride in tetrahydrofuran (50 ml. of 2 *m* solution = 0.154 mole) was slowly added with vigorous stirring. The mixture was refluxed for about 30 min. and the ether and tetrahydrofuran were removed. (Dimethylamino)methylvinylborane, b.p. 90–91°, was distilled off the residue in a 39% yield (5 g.). *Anal.* Calcd. for BNC_5H_{12}: C, 61.9; H, 12.5; B, 11.15; N, 14.45. Found: C, 61.9; H, 12.5; B, 10.9; N, 14.4. An identical material was obtained through the reaction of (dimethylamino)vinylbromoborane[1] with methylmagnesium bromide in comparable yield.

(Dimethylamino)phenylvinylborane, $(CH_3)_2N{-}B(C_6H_5)(CH{=}CH)$.—In an analogous procedure, this compound was prepared from (dimethylamino)phenylchloroborane[8] and vinylmagnesium chloride in tetrahydrofuran solution. After evaporation of the solvent, a fraction, b.p. 60° (2 mm.), was collected in 30–40% yield. *Anal.* Calcd. for $BNC_{10}H_{14}$: C, 75.5; H, 8.9; B, 6.8; N, 8.8. Found: C, 75.7; H, 9.15; B, 7.05; N, 8.6. An identical material was obtained in 50% yield through the reaction of (dimethylamino)vinylbromoborane[1] with phenylmagnesium bromide in ether solution.

(Methylphenylamino)phenylvinylborane, $(CH_3)(C_6H_5)N{-}B(C_6H_5)(CH{=}CH_2)$.—Using the same molar ratios and technique as described above, this material was prepared in 35–40% yield from (methylphenylamino)phenylchloroborane[13] and vinylmagnesium chloride in ether–tetrahydrofuran solution, b.p. 108–111° (1 mm.), m.p. 55–58°. *Anal.* Calcd. for $BNC_{15}H_{16}$: C, 81.4; H, 7.3; B, 4.9; N, 6.3. Found: C, 81.3; H, 7.5; B, 5.0; N, 6.1. An identical material was obtained in about 70% yield by transamination of (dimethylamino)phenylvinylborane with N-methylaniline.

(Methyl-*n*-butylamino)phenylvinylborane, $(CH_3)(C_4H_9)N{-}B(C_6H_5)(CH{=}CH_2)$.—A mixture of 9.0 g. (56.6 mmoles) of (dimethylamino)phenylvinylborane and 5.42 g. (62.3 mmoles) of methyl-*n*-butylamine was refluxed for about 2 hr. By that time the evolution of dimethylamine had almost ceased. Rectification of the reaction material afforded the desired (methyl-*n*-butylamino)phenylvinylborane, b.p. 74–75° (0.5 mm.); yield 17 g. (76%). *Anal.* Calcd. for $BNC_{13}H_{20}$: C, 77.5; H, 10.0; B, 5.4; N, 6.95. Found: C, 77.6; H, 10.3; B, 5.3; N, 7.0.

(β-Methyl-β-phenylvinylamino)dimethylborane, $(CH_3)(C_6H_5)C{=}CH{-}NH{-}B(CH_3)_2$.—A solution of 34 g. (297.5 mmoles) of (dimethylamino)dimethylborane and 33 g. (297.5 mmoles) of β-methylβ-phenylvinylamine[10] in 100 ml. of benzene was refluxed for 8 hr. After the solvent was stripped off, the product was rectified under vacuum to yield 25.7 g. (50% yield) of a colorless liquid, b.p. 71–78° (3 mm.). *Anal.* Calcd. for $BNC_{11}H_{16}$: C, 76.4; H, 9.3; B, 6.3; N, 8.1 Found: C, 76.7; H, 9.6; B, 6.0; N, 8.0.

Discussion

It has previously been postulated[1] that the effect of a B-attached vinyl group on the B–N bond order as reflected in infrared spectral shifts appears to be very small. This is in agreement with the present data on B-vinylated monoaminoboranes as illustrated in Table I.

TABLE I

B–N STRETCHING FREQUENCIES OF SOME MONOAMINOBORANES

Compounds	ν_{BN}, cm.$^{-1}$
(Dimethylamino)methylphenylborane	1410
(Dimethylamino)vinylphenylborane	1419
(Methylphenylamino)methylphenylborane	1385
(Methylphenylamino)vinylphenylborane	1384

On the other hand, it has also been suggested[1] that N-vinylation of an aminoborane should result in an increase of the B–N bond order as evidenced by the infrared absorption. This now can be confirmed, since the B–N stretching frequency is unusually high in N-vinylated aminoboranes. For instance, in (β-methyl-β-phenylvinylamino)dimethylborane, an absorption at 1471 cm.$^{-1}$ with a shoulder (denoting a ^{10}B effect) at 1480 cm.$^{-1}$ was assigned to ν_{BN}. Since this band disappears on hydrolysis of the material, the assignment appears to be reasonable.[14]

Other features of the spectra of (vinylamino)boranes include very strong C=C modes near 1665 cm.$^{-1}$, compared with 1667 cm.$^{-1}$ for the free β-methyl-β-phenylvinylamine, and a weak-to-medium NH stretching near 3400 cm.$^{-1}$ as compared with a doublet at 3390/3400 cm.$^{-1}$ in this same amine.

The experimental observations appear to be reasonable. Since any conjugation effect of vinyl and B–N groups should be exhibited through the free electron pair of the nitrogen and since the vinyl group is directly adjacent to the nitrogen atom, the effect of the N-attached vinyl group should be much stronger. It should result in an increase of the B–N bond order as evidenced by the infrared spectra.

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[11] Infrared spectra of the materials were recorded on a Perkin-Elmer Model 21 double beam spectrophotometer using sodium chloride optics. Analyses were furnished by the Schwazkopf Microanalytical Laboratory, Woodside 77, N. Y.

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