

TABLE I
MELTING POINTS^a OF SOME LINEAR COMPOUNDS AND OF THE
CORRESPONDING INCLUSION COMPOUNDS WITH PHTP
M.p. pure PHTP = 128°

Included compound	M.p. of guest compound, °C.	M.p. of inclusion compound, °C.
Low-molecular weight polyethylene (mol. wt. 2000)	85	165
High-molecular weight polyethylene	135	181
<i>cis</i> -1,4-Polybutadiene	<0	158
<i>trans</i> -1,4-Polybutadiene	127	183
Polyoxyethylene glycol (Carbowax 1500)	40	139
<i>n</i> -Heptane	-91	127
Palmitic acid	64	157
Stearic acid	69	158
Undecilic acid	24	148
Adipic acid	151	165
Azelaic acid	106	154
Cetyl alcohol	49	148

^a Determined by a polarizing microscope.

gest applications in analytical as well as in separation methods. Moreover, we think that the PHTP-polymer crystalline systems will provide new information on the conformational structure of polymers by X-ray or by infrared studies; in particular, we emphasize that any chain-chain interaction will disappear in the presence of PHTP.

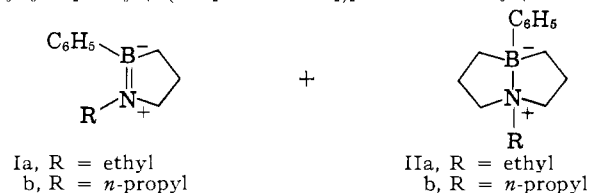
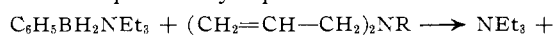
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A Novel Reduction of an Allylic Carbon-Nitrogen Bond

We wish to report a novel reduction of the carbon-nitrogen bond which was discovered during investigation of the reactions between triethylaminephenylborane and diallyl alkylamines. The amineborane complexes have been recently used as hydroborating agents for reaction with allyl amines to produce new boron-nitrogen heterocyclic systems.¹⁻³ In our attempt to use this procedure to prepare bicyclic systems, it was found that refluxing a dilute toluene solution of triethylaminephenylborane with a diallyl alkylamine resulted in two products, an air-sensitive liquid and a stable solid, to which we have assigned structures I and II, respectively. Bicyclic structures such as II have not been previously reported.



Thus use of diallylethylamine resulted in a colorless liquid (Ia), b.p. 72.5–74° (1.2 mm.), in 22% yield and a solid (IIa), m.p. 72.5–73.5° (from acetone), in 7% yield. *Anal.* (Ia) Calcd. for C₁₁H₁₆BN: C, 76.33; H, 9.32; N, 8.09; B, 6.25. Found: C, 76.27; H, 9.23; N, 8.06; B, 6.30. *Anal.* (IIa) Calcd. for C₁₄H₂₂BN: C, 78.16; H, 10.31; N, 6.51; B, 5.03. Found: C, 77.87; H, 10.38; N, 6.76; B, 4.87.

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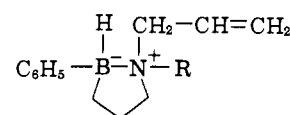
Use of diallyl-*n*-propylamine resulted in a colorless liquid (Ib), b.p. 87.5–90° (2.0 mm.), and a solid (IIb), m.p. 61–62° (from acetone), in 31 and 8% yields. *Anal.* (Ib) Calcd. for C₁₂H₁₈BN: C, 77.04; H, 9.69; N, 7.48; B, 5.78; mol. wt., 187. Found: C, 77.73; H, 9.35; N, 7.40; B, 5.62; mol. wt., 187 (mass spectrum). *Anal.* (IIb) Calcd. for C₁₅H₂₄BN: C, 78.61; H, 10.56; N, 6.11; B, 4.78; mol. wt., 229. Found: C, 78.49; H, 10.66; N, 6.27; B, 4.48; mol. wt., 239 (cryoscopic).

The mass spectrum of 1-*n*-propyl-2-phenyl-1,2-azaborolidine gave a parent ion peak at 187 mass units (m.u.). The most intense peak was at 158 m.u. corresponding to a loss of an ethyl group and consistent with the most probable mode of rupture of amines, the C–C bond β to the nitrogen atom. The intensities of the other peaks were considerably weaker, and they were found at 116 m.u. due to loss of the C₃H₇N–CH₂– group, 89 m. u., due to loss of C₃H₇NC₃H₆– group, 79, 63, 51, and 41 m. u. The last four peaks were very weak.

The infrared spectra of the products showed the absence of any olefinic or B–H units. The two 1,2-azaborolidines (Ia,b) showed strong peaks at 1512 cm.⁻¹ which have been attributed to –B=N⁺ bonds.^{2,4} The 1-aza-5-borabicyclo[3.3.0]octanes (IIa,b) showed strong bands at 1266 cm.⁻¹ which we are tentatively assigning to the –B–N⁺ coordinate bond. The boron-nitrogen bonds in diethanolamine esters of arylboronic acids and the boron-nitrogen bonds in complexes of boron halides with amine bases have been assigned to this region.^{5,6}

The boron resonance in the n.m.r. spectrum of 1-ethyl-2-phenyl-1,2-azaborolidine (Ia) was recorded at –23 and +8.9 p.p.m. for the 1-ethyl-5-phenyl-1-aza-5-borabicyclo[3.3.0]octane (IIa) relative to trimethyl borate. The p.m.r. spectrum of the former was also in accord with the structural assignment.

The bicyclic compounds are the result of intramolecular hydroboration of the two olefinic bonds by phenylborane. The 1,2-azaborolidines appear to be formed by the reduction of the allylic carbon-nitrogen bond and may be the result of the following intermediate, which apparently either does not undergo a



second hydroboration, or the rate of the second hydroboration is slow enough at the temperature of reflux (110°) so that the reduction is the predominant reaction. This reduction is somewhat analogous to hydrogenation of the benzyloxy bond in the Bergmann synthesis of polypeptides⁷ in that the groups which form relatively stable carbonium ions are easily reduced.

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