The Preparation of Di-*tert*-butyl Ethyleneboronate *via* the Ethyleneboronic Anhydride–Pyridine Complex[1]

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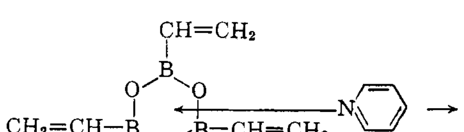
A *tert*-alkyl ester of ethyleneboronic acid was desired for studying the effects of steric hindrance about the boron atom on reactions involving the vinyl group.

Straightforward esterification of ethyleneboronic acid[2] with tertiary alcohols has been found to be impossible to carry out. Attempted azeotropic distillation of water from a solution of ethyleneboronic acid in *tert*-butyl alcohol and benzene at atmospheric pressure rapidly polymerized the vinyl compound even though a considerable quantity of radical inhibitor, phenothiazine, was present. Azeotropic distillation of water at 20 mm. through a 30-cm. packed column from ethyleneboronic acid in *tert*-amyl alcohol (which had first been freed from any primary or secondary alcohol contaminants by distillation from *tert*-amyl borate) yielded a small amount of liquid, b.p. below room temperature but above 15° at about 0.5 mm., which partially polymerized throughout the distillation apparatus during its distillation. This liquid was probably ethyleneboronic anhydride. If so, the yield was reasonably good, but no way could be found to preserve the material. An uninhibited sample (~10 ml.) polymerized explosively, breaking several pieces out of the container, a 100-ml. round-bottom flask, after short exposure to air and brief storage in the refrigerator.

It was then found possible to prepare the ethyleneboronic anhydride–pyridine complex[3] in nearly quantitative yield by treatment of dibutyl ethyleneboronate[2] with water, azeotropic distillation of the butanol at 20 mm., treatment of the residual ethyleneboronic acid with pyridine, and azeotropic removal of water at 20 mm. The distillable product, a low-melting solid, was stable on storage and required no inhibitor. Treatment of this boronic anhydride–pyridine complex with excess *tert*-butyl alcohol and azeotropic distillation of water with the aid of benzene at atmospheric pressure through an efficient column gave a good yield of the desired di-*tert*-butyl ethyleneboronate. No polymerization occurred. Apparently as a result of the temperature dependence of the rate, a small scale run (4 g. of pyridine complex) which allowed the various lower-boiling azeotropes to escape almost completely from the reaction flask into the fractionating column was completed in two days while the larger scale run described in detail required ten days.



$CH_2{=}CHB[OC(CH_3)_3]_2$

Experimental

Ethyleneboronic Anhydride–Pyridine Complex.—A stirred suspension of 92.1 g. (0.5 mole) of di-*n*-butyl ethyleneboronate[2] and 0.5 g. of phenothiazine in 250 ml. of water was distilled at 20 mm. through a 30-cm. vacuum-jacketed column packed with Podbielniak nichrome helices until the butanol–water azeotrope and most of the water had been removed. The residue of ethyleneboronic acid was treated with 175 ml. of pyridine and the pyridine–water azeotrope was distilled. The residue, ethyleneboronic anhydride–pyridine complex, was purified by rapid simple distillation, b.p. 50–80° (0.1 mm.), yield 39.5 g. (98%). This material was pure enough for use in the next step. It crystallized on seeding (by chilling with Dry Ice) and was stable on storage for several months at room temperature. The analytical sample was sublimed twice, m.p. 49–52.5°.

Anal. Calcd. for $C_{11}H_{14}B_3NO_3$: C, 54.89; H, 5.86; B, 13.48; N, 5.82. Found[4]: C, 54.87; H, 5.97: B, 13.64; N, 5.99.

Di-*tert*-butyl Ethyleneboronate.—A solution of 39.5 g. of ethyleneboronic anhydride-pyridine complex, 0.5 g. of phenothiazine, 320 ml. of *tert*-butyl alcohol, and 80 ml. of benzene was refluxed under nitrogen at atmospheric pressure (700 mm.) under the efficient fractionating column described above. The water which separated was drawn off. The total yield of water after 1 day was 3.8 ml.; 2 days, 5.5 ml.; 3, 6.7; 4, 7.1; 5, 8.1; 6, 8.6; 9, 9.5 (theory 9 ml. if pure water). The solution was then fractionated, first at atmospheric pressure, then with the water pump to yield 74.6 g. (81%) of di-*tert*-butyl ethyleneboronate, b.p. 55–56° (18 mm.), $n^{24}\text{D}$ 1.4050. In spite of its slow rate of formation, the *tert*-butyl ester hydrolyzes rapidly on contact with moist air. The infrared spectrum was consistent with the assigned structure. A center cut was analyzed.

Anal. Calcd. for $C_{10}H_{21}BO_2$: C, 64.24; H, 11.50; B, 5.88. Found: C, 64.40; H, 11.40; B, 6.13.

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[1] Supported by National Science Foundation Grant G-19906.

[2] D. S. Matteson, *J. Am. Chem. Soc.*, **82**, 4228 (1960).

[3] Pyridine–boronic anhydride complexes have been reported by H. R. Snyder and M. S. Konecky, *J. Am. Chem. Soc.*, **80**, 3611 (1958).

[4] Galbraith Laboratories, Knoxville, Tennessee.

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meso- and *dl*-1,2,3,4-Tetraphenylbutane

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Although symmetrical tetraphenylbutane can exist in a *meso* or *dl* form, no suggestion as to which form is which has appeared, even though two melting points, 86–90°[1] and 179–183,[2] have