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

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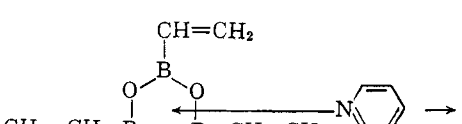
A *tert*-alkyl ester of ethyleneboronic acid was desired for studying the effects of steric hindrance about the boron atom on reactions involving the vinyl group.

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}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).

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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 been reported. The coupling reaction[2a] or reductions[1a,b, 2b,c] yielding symmetrical tetraphenylbutane would be expected to lead to isomer mixtures and it is therefore surprising that in only one study[2b] were two isomers reported. In this case the higher melting material was thought to be 1,2-diphenyl-3-benzylhydrindene.[3]

In this work both the sodium–alcohol reduction of 1,2,3,4-tetraphenylbutadiene and the magnesium metal coupling of *dl*-benzylphenylcarbinyl bromide yielded two products, m.p. 89–90° (I) and 183–185° (II), in about equal quantities. Both compounds had the correct elemental analysis for symmetrical tetraphenylbutane. No bands which could be attributable to a 1,2-substituted benzene ring were detectable in the infrared spectrum of II. Finally both I and II had the correct aromatic : aliphatic proton ratio as measured by n.m.r. (3.3:1). Thus, II is not a substituted hydrindene but rather is a diastereoisomer of I.

For several reasons it is suggested that II is *meso*-1,2,3,4-tetraphenylbutane while I is the *dl* mixture. In the absence of strong dipoles, the greater symmetry of the *meso* compound might be expected to be manifested in a higher melting point, as is in fact exhibited by II.[4]

The same reasoning could be used in arguing that the *meso* compound should be less soluble than the *dl* mixture. It was observed that I is much more soluble than II in ether, methyl and ethyl alcohol, deuterochloroform, and a three component mixture consisting of water, acetic acid, and isoamyl alcohol.

Since the methylene and methine protons in the symmetrical tetraphenylbutanes are not magnetically equivalent it might be expected that the proton magnetic resonance spectra of these compounds might be complex and this was found to be the case. The spectrum of I differed from that of II in that the former contained a broader region of peaks attributable mostly to methylene transitions on the one hand (downfield side) and mostly to methine transitions on the other (upfield side). This is probably a consequence of a larger chemical shift and/or greater spin-spin coupling constants in I. Finally the methylene signal in I was shifted downfield (τ 7.25 p.p.m.) from that in II (τ 6.88 p.p.m.). It is interesting to note that *meso*-2,3-diphenylbutane exhibits the same n.m.r. behavior when compared with *dl*-2,3-diphenylbutane[5] as I does when compared with II.

Experimental

All melting points were obtained on a Fisher-Johns melting point apparatus and are corrected. Elemental analyses were performed at Mellon Institute by Mr. James Kerns and co-workers. Infrared spectra were obtained using potassium bromide disks on a Perkin-Elmer Model 137 spectrophotometer. N.m.r. spectra were obtained on a Varian A-60 spectrometer using deuterochloroform as solvent and tetramethylsilane as internal reference.

The Reaction of *dl*-Benzylphenylcarbinyl Bromide with Magnesium.—A solution of 56 g. (0.214 mole) of *dl*-benzylphenylcarbinyl bromide in 50 ml. of ether was added dropwise to 5 g. (0.214 g.-atom) of magnesium turnings covered with 250 ml. of ether over a period of 2 hr. Reflux persisted throughout the addition. At the end of this period the solution in the flask was a dark yellow and a white voluminous precipitate had formed. A large amount of the original magnesium remained unchanged. Approximately 10 g. of anhydrous silver bromide[6] was added and the reaction mixture was stirred and refluxed for 0.5 hr. At the end of this period the solution was filtered. The precipitate was extracted twice with 200 ml. of boiling benzene and the extracts were combined and the benzene was stripped *in vacuo*. The residue, a white solid, was recrystallized from 200 ml. of ethanol–benzene (6:1) to yield 9.8 g. of white needles, m.p. 183–185° (sample I).

Anal. Calcd. for $C_{28}H_{26}$: C, 92.7; H, 7.3. Found: C, 92.40; H, 7.48.

Concentration of the mother liquor to *ca.* 50 ml. gave, upon cooling, a further 2.1 g. of white needles, m.p. 183–185°, which did not depress the melting point of the initial batch.

The filtrate was evaporated to dryness and then extracted with 250 ml. of boiling benzene. The benzene was stripped *in vacuo* leaving 18 g. of a viscous yellow oil which upon trituration with 25 ml. of petroleum ether gave a further 2.1 g. of white needles, m.p. 182–184°, which were found to be identical with the material described above (mixed m.p. 183–185°). The viscous residue was partially distilled and 1.4 g. of a colorless liquid, b.p. 100–135° at 0.1 mm., was collected. This crystallized in the receiver and was recrystallized from ethanol, m.p. 104°. This was not investigated further but was distinctly different from the material described below (mixed m.p. 72–76°).

The residue from the distillation was taken up in 100 ml. of hot methanol. Chilling in the ice bath caused crystals to deposit. These were recrystallized from cold methanol to give 11.5 of white needles, m.p. 89–90° (sample II).

Anal. Calcd. for $C_{28}H_{26}$: C, 92.7; H, 7.3. Found: C, 92.80; H, 7.50.

***meso*- and *dl*-Tetraphenylbutane from 1,2,3,4-Tetraphenylbutadiene.**—The procedure used was essentially that of Brook, Tai, and Gilman.[1b] From 2 g. of 1,2,3,4-tetraphenylbutadiene, 6 g. of sodium, and 75 g. of isoamyl alcohol there was obtained 0.74 g. of *meso*-1,2,3,4-tetraphenylbutane[7] (I) and 0.78 of the *dl* mixture (II). The isomers prepared in this way were identical in all respects with those prepared by the coupling reaction described above.

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[1] (a) E. Bergman, *J. Chem. Soc.*, 505 (1936); (b) A. G. Brook, K. M. Tai, and H. Gilman, *J. Am. Chem. Soc.*, **77**, 6219 (1955).

[2] E. S. Wallis and F. H. Adams, *ibid.*, **55**, 3850 (1933); (b) L. I. Smith and H. H. Hoehn, *ibid.*, **63**, 1184 (1941); (c) G. M. Badger, B. J. Christie, J. M. Pryke, and W. H. F. Sasse, *J. Chem. Soc.*, 4417 (1957).

[3] E. Bergman and W. Schreiber, *Ann.*, **122**, 500 (1933).

[4] The same argument might be employed in a discussion of *meso*- and *dl*-2,3-diphenylbutane. In this case the *meso* form melts at 125–126°, the *dl* forms melt at 12–13°; *e.g.*, F. D. Greene, *J. Am. Chem. Soc.*, **77**, 4869 (1955).

[5] A. A. Bothner-By and C. Naar-Colin, *ibid.*, **84**, 743 (1962).

[6] J. M. Gardner and P. Borgstrom, *ibid.*, **51**, 3375 (1929).

[7] The mixed melting point of this material with the starting butadiene (m.p. 183°) was 170–172°.