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NOTE

DIBUTYL *cis*- AND *trans*-1-BUTENE-1-BORONATE

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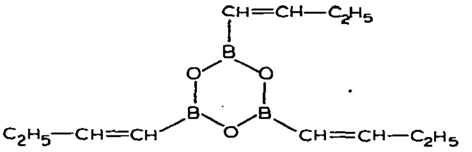
The *cis* and *trans* isomers of dibutyl 1-butene-1-boronate have been prepared and the allylic bromination of this system has been investigated.

1-Butenylmagnesium bromide was prepared from 1-bromo-1-butene according to the procedure of Ramsden *et al.*[1]. Treatment of this previously unreported Grignard reagent with trimethyl borate followed by the usual work-up procedure[2] yielded a mixture of the desired dibutyl 1-butene-1-boronate and the inevitable by-product, butyl borate. Separation of these compounds by distillation proved to be impossible due to the similarity in boiling points. However, this difficulty was circumvented by preparation of 1-butene-1-boronic anhydride, (I), from the crude reaction mixture.



(I)

This transformation was accomplished by hydrolysis of the mixture to the crude acid and subsequent formation of the anhydride by treatment with refluxing benzene and azeotropic removal of water. Distillation of (I) yielded a product free of butyl borate. The identity of (I) was established by elemental analysis, molecular weight determination, IR and NMR spectra, and transformation to the corresponding esters.

Treatment of anhydride (I) with 1-butanol and benzene resulted, after azeotropic removal of water and removal of solvents, in a mixture of dibutyl *cis*- and *trans*-1-butene-1-boronate which were separated by fractional distillation. This represents the first separation of such α,β-unsaturated boronic esters into geometric isomers. The structure of these isomers was established by IR analysis. The *trans* isomer exhibited a strong IR band at 10.1 μ characteristic of *trans* alkenes[3]. This band was absent in *cis* isomer. In addition the *cis* isomer exhibited a strong band at 10.9 μ which was entirely absent in spectra of the *trans* isomer. Both compounds gave quantitative yields of butyraldehyde 2,4-dinitrophenylhydrazone upon oxidative deboronation. The NMR spectra of these compounds were complex in the vinyl region but the position of peaks was sufficiently different to ascertain the purity of the samples. The *trans* isomer appeared to be virtually uncontaminated by the *cis*, while integration of the vinyl region in the *cis* isomer indicated approximately 80% of purity.

Allylic bromination of the dibutyl esters with either *N*-bromosuccinimide or small concentrations of bromine vapor yielded products containing both bromine and the alkene bond as evidenced by IR and NMR analysis, but a satisfactory elemental analysis could not be obtained. In an attempt to minimize side reactions, the di-tert-butyl ester was prepared and halogenated with similar results. NMR analysis of the crude products indicated a product distribution of approximately 50% of di-tert-butyl 1-bromo-2-butene-1-boronate and 50% di-tert-butyl 3-bromo-1-butene-1-boronate. This was established by integration of the area under the peaks resulting from the bromine-bearing carbon. In the 1-bromo isomer this was assigned as a doublet appearing at 3.85 while in the 3-bromo isomer it was assigned as a complex multiplet center at 4.35. Attempted dehydrohalogenation of such mixtures lead to butyl borate as the only identifiable product.

EXPERIMENTAL

General

Melting points are uncorrected. IR spectra were taken on Beckman IR-10 and Perkin–Elmer 137 spectrophotometers and NMR spectra on Varian A-60 and T-60 spectrophotometers.

1-*Butene*-1-*boronic anhydride*

A solution of 1-butenylmagnesium bromide prepared from 100 g (0.74 mole) of freshly distilled 1-bromo-1-butene and 18.0 g (0.75 g-atom) of magnesium turnings in 500 ml of tetrahydrofuran was added dropwise to a well stirred mixture of 78.0 g (0.75 mole) of trimethyl borate in 400 cc of absolute ether below −60°. The reaction mixture was worked up in the usual fashion[2] and the final distillation yielded 113.8 g of crude dibutyl 1-butene-1-boronate, b.p. 49–51° at 0.4 mm. A stirred suspension of 53.0 g (0.25 mole) of the crude dibutyl 1-butene-1-boronate and 0.3 g of phenothiazine in 200 ml of water was distilled at 40 mm through a 30 cm vacuum jacketed column packed with Podbielniak helices until all the butanol/water azeotrope and most of the water had been removed leaving a moist suspension of the boronic acid. Benzene, 100 ml, was added and the mixture refluxed and water was removed via a Dean–Stark trap. After separation of water ceased, the mixture was distilled to yield 8.0 g (39%) of 1-butene-1-boronic anhydride, b.p. 73–78° (0.15 mm), n_D^{24} 1.4650, λ_{max}^{film} 3.27 (H–C=C), 6.15 (C=C), 7–8 (B–O), 10.05, 10.58 and 12.00 μ. (Found: C, 58.93; H, 8.90; B, 12.94; mol.wt., 276. $C_{12}H_{21}B_3O_3$ calcd.: C, 58.63; H, 8.61; B, 13.21%; mol.wt., 246.)

Dibutyl cis- and trans-1-*butene*-1-*boronate*

1-Butene-1-boronic anhydride, 2.89 g (0.0118 mole), 100 ml of 1-butanol and 50 ml of benzene were refluxed through the previously described 30 cm column equipped with a Dean–Stark trap. The theoretical yield of water was collected in about 1 h. The solvents were then removed by distillation under reduced pressure and the residue fractionated with a Teflon Annular Spinning Band Column to yield two main fractions. Fraction one was 2.19 g of dibutyl *cis*-1-butene-1-boronate, b.p. 37–38° (0.05 mm), n_D^{24} 1.4254, λ_{max}^{film} 3.27 (HC=C), 6.16 (C=C), 7–8 (B–O), and 13.28 μ. (Found:

C, 67.79; H, 11.92; B, 5.14. $C_{12}H_{25}BO_2$ calcd.: C, 67.92; H, 11.88; B, 5.10%.) Fraction two was 3.96 g dibutyl *trans*-1-butene-1-boronate, b.p. 39–40° (0.05 mm), n_D^{24} 1.4280, λ_{max}^{film} 3.26 (H–C=C), 6.15 (C=C), 7–8 (B–O), 10.10 (*trans*-C=C), and 13.22 μ. (Found: C, 67.93; H, 11.88; B, 5.24. $C_{12}H_{25}BO_2$ calcd.: C, 67.92; H, 11.88; B, 5.10%.) A small center cut of 0.21 g consisting of a mixture of *cis* and *trans* was also taken. The overall yield is 79%.

Di-tert-butyl 1-butene-1-boronate

1-Butene-1-boronic anhydride, 7.0 g (0.028 mole), 100 ml of tert-butyl alcohol and 50 ml of benzene were refluxed for 60 h under the conditions described for the preparation of the n-butyl esters. Distillation yielded 12.7 g (70%) of di-tert-butyl 1-butene-1-boronate, b.p. 46° (0.3 mm). The analytical sample was redistilled, b.p. 117–120° (35 mm), n_D^{27} 1.4164, λ_{max}^{film} 6.18 (C=C), 7–8 (B–O) 11.10 (*trans*-C=C) μ. (Found: C, 68.04; H, 11.96; B, 5.26. $C_{12}H_{25}BO_2$ calcd.: C, 67.92; H, 11.88; B, 5.10%.)

Allylic bromination of 1-butene-1-boronic esters

In a typical experiment bromine vapor, 2.64 g (0.16 mole), was slowly carried by a stream of dry nitrogen into a refluxing solution of 3.5 g (0.016 mole) of di-tert-butyl 1-butene-1-boronate and 0.1 g of benzoyl peroxide in 50 cc of carbon tetrachloride. Addition of the vapor was completed in 45 min and evolution of hydrogen bromide was noted during this period. After refluxing an additional 30 min, the mixture was distilled to yield 1.27 g of brominated product, b.p. 66–71° (0.4 mm). The IR spectra showed a strong alkene absorption at 6.19 μ. An analytical sample was redistilled, b.p. 59–62° (0.3 mm). (Found: C, 45.94; H, 7.74; B, 3.27; Br, 30.84. $C_{12}H_{24}BBrO_2$ calcd.: C, 49.52; H, 8.31; B, 3.71; Br, 27.46%.)

Attempted bromination with *N*-bromosuccinimide yield similar results with the exception that the product was more difficult to purify. Attempted dehydrohalogenation of these brominated products with pyridine and tert-butylamine yielded butyl borate as the only identifiable product, plus tars.

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