

290. Dephenylation Reactions of Phenylboron Acids and Esters.

By E. W. ABEL, W. GERRARD, and M. F. LAPPERT.

Dephenylation (B-C cleavage), at high temperatures, of diphenylboronous acid and esters, $\text{Ph}_2\text{B}\cdot\text{Y}$ (Y = OH or OR), and of phenylboronic acid and esters, $\text{Ph}\cdot\text{BY}_2$, are described.

CONTINUING the study of reactions of phenylboron acids,¹⁻⁵ we now show that at temperatures approaching 200° phenylboronic acid affords benzene and metaboric acid, whereas diphenylboronous acid accordingly gives benzene and phenylboronic anhydride. As the latter anhydride readily gives the acid with water, complete dephenylation of boron occurred when diphenylboronous acid was heated with water. Analogously, when an alkyl diphenylboronite, $\text{Ph}_2\text{B}\cdot\text{OR}$, was heated with the corresponding alcohol, the ester of phenylboronic acid or of boric acid was formed according to the proportion of alcohol. When R in the alcohol was different, a mixture of the two alkyl borates, instead of the desired mixed borate, was obtained. Experiments with optically active 1-methylheptyl compounds show that there is no C-O fission.

At 200° the esters of diphenylboronous acid themselves were much more stable and slowly disproportionated rather than undergoing dephenylation by the elimination of olefin. In one example triphenylboron was isolated. Dimethyl phenylboronate slowly disproportionated to trimethyl borate and methyl diphenylboronite. The amount of tri-*n*-butyl borate was slowly reduced when this ester was heated (200°) with *n*-butyl diphenylboronite, and di-*n*-butyl phenylboronate was isolated.

Pyrolysis of *n*-octyl diphenylboronite at 340° gave phenylboronic anhydride (presumably from the production of the acid on treatment with water), benzene, and octene (apparently a mixture of oct-2- and -3-ene as judged from the absence of vinyl absorption in the infrared spectrum, a similar rearrangement having been postulated for the dehydration of octan-1-ol by phosphoric acid⁶).

These results are of fundamental interest in the search for "boron polymers" stable to high temperatures. The dephenylation reactions have correlation with the dephenylation (desilylation) of certain phenylsilanes.⁷

EXPERIMENTAL

Preparations and Procedures.—Phenylboronic acid was prepared by Bean and Johnson's method,⁸ diphenylboronous acid by that of Abel *et al.*⁹ Dimethyl phenylboronate was obtained by Dandegaonker, Gerrard, and Lappert's procedure,⁴ the alkyl diphenylboronites by a method described by us previously,² and tri-*n*-butyl borate according to Johnson and Tompkins.¹⁰ Analytical techniques have been described previously.^{2,3} Rotatory powers are recorded for *l* = 10 cm. Unless otherwise stated, reactions were carried out in sealed tubes.

Pyrolysis of Phenylboronic Acid.—The acid (6.89 g.) was heated at 200° for 25 hr. Subsequently, benzene (4.30 g., 98%), b. p. 80°, n_D^{20} 1.4992, was removed at 20°/15 mm. and trapped at -80°. Metaboric acid (2.60 g., 100%) (Found: B, 23.8. Calc. for HO_2B : B, 24.5%) remained as a pale grey glass.

¹ Lappert, *Chem. Rev.*, 1956, **56**, 959.

² Abel, Gerrard, and Lappert, *J.*, 1957, 112.

³ *Idem*, *J.*, 1957, 3833.

⁴ Dandegaonker, Gerrard, and Lappert, *J.*, 1957, 5051.

⁵ Ainley and Challenger, *J.*, 1930, 2171; Challenger and Richards, *J.*, 1934, 405; Letsinger and Remes, *J. Amer. Chem. Soc.*, 1955, **77**, 2489.

⁶ Whitmore and Herndon, *ibid.*, 1933, **55**, 3428; Waterman and Te Nuyt, *Rec. Trav. chim.*, 1932, **51**, 533; Abel, Gerrard, and Lappert, *Chem. and Ind.*, 1958, 158.

⁷ Eaborn, *J.*, 1953, 3148, and subsequent papers.

⁸ Bean and Johnson, *J. Amer. Chem. Soc.*, 1932, **54**, 4415.

⁹ Abel, Dandegaonker, Gerrard, and Lappert, *J.*, 1956, 4697.

¹⁰ Johnson and Tompkins, *Org. Synth.*, 1933, **13**, 16.

Pyrolysis of Diphenylboronous Acid.—The acid (6.86 g.) was heated at 175° for 8 hr. Benzene (2.79 g., 96%), n_D^{20} 1.5033 (m. p. of dinitrobenzene 90°), was removed and trapped at -80°. The residue of phenylboronic anhydride (3.79 g., 97%) (Found: B, 10.5. Calc. for C_6H_5OB : B, 10.4%) recrystallized as phenylboronic acid from hot water; subsequent dehydration produced a pure sample of the anhydride, m. p. 216°.

Interaction of Diphenylboronous Acid and Water.—The acid (5.50 g.) and water (1.09 g.) were heated at 175° for 20 hr. Removal of benzene (4.61 g., 98%), n_D^{20} 1.5029 (m. p. of dinitrobenzene 89°) was effected at 20°/10 mm., to leave boric acid (1.90 g., 100%) (Found: B, 17.2. Calc. for H_3O_3B : B, 17.4%) as a fine white powder.

Interaction of 1-Methylheptyl Diphenylboronite and 1-Methylheptyl Alcohol.—The ester (4.47 g.), α_D^{20} -3.71° (from ROH, α_D^{20} +6.22°), and alcohol (1.98 g.), α_D^{20} +6.22°, were heated at 200° for 12 hr. Distillation gave a forerun (0.54 g.), b. p. 25—130°/0.05 mm., and di-(+)-1-methylheptyl phenylboronate (4.71 g., 90%), b. p. 130°/0.05 mm., n_D^{20} 1.4680, α_D^{20} +11.50° (Found: B, 3.11. Calc. for $C_{22}H_{39}O_2B$: B, 3.13%). Benzene (1.14 g., 95%), n_D^{20} 1.4993, b. p. 80°, was trapped at -80° during the distillation.

Interaction of Alkyl Diphenylboronite and Alcohols.—(a) The methyl ester (6.19 g.) and methanol were heated at 200° for 50 hr. Vapour-phase chromatography of the product revealed methyl borate and benzene only. A quantitative infrared analysis of the mixture revealed 59% of benzene by volume, corresponding closely to a mixture of methyl borate (1 mol.) and benzene (2 mols).

(b) The *n*-butyl ester (6.35 g.) and butan-1-ol were heated at 200° for 50 hr. Distillation gave tri-*n*-butyl borate (5.72 g., 94%), b. p. 106°/8 mm., n_D^{20} 1.4097 (Found: B, 4.8. Calc. for $C_{12}H_{27}O_3B$: B, 4.7%). Benzene (4.16 g., 100%), b. p. 80°, n_D^{20} 1.4990, was trapped at -80° during the distillation, and there was a solid residue (0.17 g.).

(c) (-)-1-Methylheptyl diphenylboronite (5.84 g.), α_D^{20} -3.71° (from ROH, α_D^{20} +6.22°), and (+)-octan-2-ol (5.18 g.), α_D^{20} 6.22°, were heated at 200° for 100 hr. Distillation gave a fore-run (1.33 g.), b. p. 25—140°/0.05 mm., and (+)-1-methylheptyl borate (6.33 g., 80%), b. p. 140°/0.05 mm., n_D^{20} 1.4297, α_D^{20} +19.86° (Found: B, 2.8. Calc. for $C_{24}H_{51}O_3B$: B, 2.7%). During the distillation benzene (2.93 g., 95%), b. p. 80°, n_D^{20} 1.4999 (m. p. of dinitrobenzene, 90°), was trapped at -80°.

Rates of Dephenylation of Alkyl Diphenylboronites.—Samples (ca. 0.2 g.) of the ester (1 mol.) and the alcohol (2 mols.) were sealed and heated at 200°. The rate of dephenylation was followed by infrared analysis (for benzene) after stated times; the results are shown in Tables 1 and 2.

TABLE 1. Buⁿ ester.

Time (hr.)	1	2	4	8	20	25	30	40	45
Reaction (%)	11	16	32	51	71	79	86	97	100

TABLE 2. *n*-C₆H₁₃·CHMe ester.

Time (hr.)	1	2	4	6	8	20	30	50
Reaction (%)	8	15	25	34	41	66	72	95

*Interaction of *n*-Octyl Diphenylboronite and Butan-1-ol.*—The ester (10.37 g.) and alcohol (5.22 g.) were heated at 200° for 50 hr. Distillation gave tri-*n*-butyl borate (5.16 g., 96%), b. p. 74°/0.01 mm., n_D^{20} 1.4097 (Found: B, 4.6%), and tri-*n*-octyl borate (4.21 g., 90%), b. p. 164°/0.01 mm., n_D^{20} 1.4361 (Found: B, 2.9%). Benzene (5.48 g., 100%), b. p. 80°, n_D^{20} 1.4970, was trapped at -80° during the distillation.

Pyrolysis of Ethyl Diphenylboronite.—The ester (7.04 g.) was heated at 200° for 100 hr. Distillation then gave diethyl phenylboronate (1.07 g.), b. p. 43°/0.05 mm., n_D^{20} 1.4800 (Found: B, 6.2. Calc. for $C_{10}H_{15}O_2B$: B, 6.1%), ethyl diphenylboronite (3.37 g.), b. p. 92°/0.05 mm., n_D^{20} 1.5540 (Found: B, 5.2. Calc. for $C_{14}H_{15}OB$: B, 5.2%), and triphenylboron (2.00 g.), b. p. 154°/0.05 mm. (Found: B, 4.70. Calc. for $C_{18}H_{15}B$: B, 4.56%). Trapped at -80° was a mixture (0.22 g.) of benzene and triethyl borate (detected by vapour-phase chromatography).

*Pyrolysis of *n*-Octyl Diphenylboronite.*—The ester (16.28 g.) was heated at 340°, under a reflux air-condenser (6"), and volatile matter was allowed to distil off. After 130 hr. no further change took place. Vapour-phase chromatography of the volatile matter revealed benzene and octene (by comparison with authentic samples), and a quantitative infrared analysis showed them to be present in equimolar proportions. The tar-like residue (5.98 g.) (Found: B,

10.2%) was extracted with boiling water, and the hot aqueous solution decolorized with charcoal. On cooling, phenylboronic acid crystallized, and after dehydration at 110° for 10 hr. phenylboronic anhydride (4.2 g.) (Found: B, 10.3%), m. p. 214°, was obtained.

Pyrolysis of Dimethyl Phenylboronate.—The ester (4.61 g.) was heated at 200° for 100 hr. Distillation afforded dimethyl phenylboronate (3.66 g.), n_D^{20} 1.4953 (Found: B, 7.2. Calc. for $C_8H_{11}O_2B$: B, 7.2%), and methyl diphenylboronite (0.49 g.), n_D^{20} 1.5691 (Found: B, 5.42. Calc. for $C_{13}H_{13}OB$: B, 5.53%) (authentic infrared spectrum). Trapped at -80° during the distillation was trimethyl borate (0.21 g.) (Found: B, 9.4. Calc. for $C_3H_9O_3B$: B, 9.9%). There was a residue (0.14 g.).

Interaction of n-Butyl Diphenylboronite and Tri-n-butyl Borate.—*n*-Butyl diphenylboronite (5.53 g.) and tri-*n*-butyl borate (5.36 g.) were heated at 200° for 100 hr. Distillation gave tri-*n*-butyl borate (3.71 g.), b. p. 110°/10 mm., n_D^{20} 1.4138 (Found: B, 4.8%), di-*n*-butyl phenylboronate (3.51 g.), b. p. 126°/10 mm., n_D^{20} 1.4773 (authentic infrared spectrum) (Found: B, 4.7. Calc. for $C_{14}H_{23}O_2B$: B, 4.6%), and *n*-butyl diphenylboronite (3.21 g.), b. p. 156°/9 mm., n_D^{20} 1.5374 (Found: B, 4.7. Calc. for $C_{14}H_{19}OB$: B, 4.54%). Benzene (0.09 g.) was trapped at -80° during the distillation and there was a residue (0.28 g.).

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THE NORTHERN POLYTECHNIC,
HOLLOWAY ROAD, LONDON, N.7.

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