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ORGANOBORON COMPOUNDS

CDVII *. REACTION OF 1-BORAADAMANTANE WITH PHOSPHORUS YLIDES: SYNTHESIS OF 4-ALKYL-3-BORAHOMOADAMANTANES

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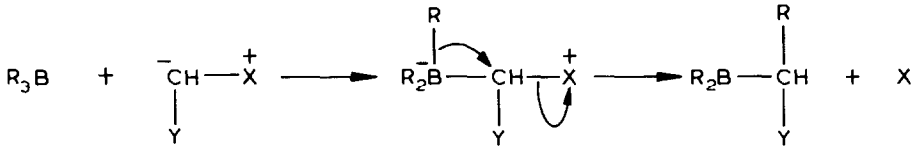
Summary

Alkylidenetriphenylphosphoranes react with the tetrahydrofuran complex of 1-boraadamantane to form stable adducts. The adducts rearrange to compounds of the 4-alkyl-3-borahomoadamantane series.

Introduction

Organoboranes react with ylides to give the products of insertion at a B–C bond. The reaction mechanism includes an initial coordination of the boron with the carbanion ylide fragment, followed by the migration of an alkyl group from boron to the adjacent carbon atom with the elimination of a leaving group [1,2]. A carbene type mechanism seems to be unlikely [1,2].



(X = Me_2SO, Me_2S, Me_3N, Ph_3P, Ph_3As;
Y = H, COPh, COOEt, $CONEt_2$)

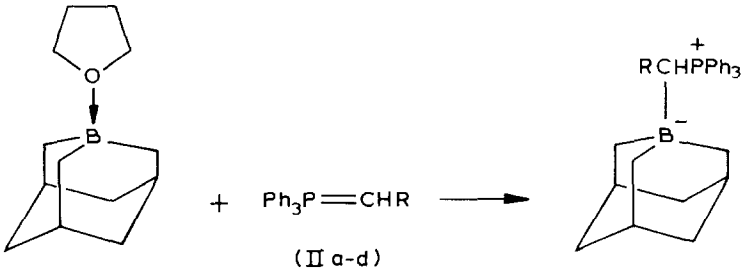
This reaction was first observed for the interaction between trialkylboranes and dimethylsulfoxonium methylide [1]. The oxidation resulted in the formation of a

* For Part CDVI see ref. 16.

mixture of products of one and two insertion processes. The reaction of triphenyl- and trialkylboranes with dimethylsulfonium methylide proceeds more smoothly, producing, after oxidation of the reaction mixture, alcohols containing one carbon atom more than the starting compound [3]. Trialkylboranes react with trimethylammonium methylide in an analogous manner [4,5], with secondary alkyl groups migrating more easily than primary ones. The migration in the adduct of triphenylborane with methylenetriphenylphosphorane, takes place at the temperature of boiling chlorobenzene [6]. Triphenylarsonium benzylide reacts with tri-n-hexylborane to give, after hydrolysis, the products of single and double insertion [7]. Some functional derivatives of sulfur ylides have also been reacted with organoboranes [7,8]: here the reaction leads to vinyloxyboranes, which have been, without isolation, hydrolysed to form the carboxylic acids derivatives, RCH_2COX (X = Ph, OEt, NEt_2).

The reaction of triorganoboranes with ylides described above is of considerable theoretical interest, though it has very limited preparative significance. Thus, due to the fact that only one group on the boron atom takes part in the reaction, oxidation of an unsymmetrical borane, R_2BCH_2R, gives a mixture of homologues which is difficult to separate, even when the reaction mixture does not contain products of the double homologation. At the same time, the reaction with ylides proved to be a very valuable method with tricyclic boron compounds, because it makes it possible a selective expansion of one of the rings by one carbon atom, thereby progressing to new types of polyhedral boron compounds. 3-Borahomoadamantane complexes [9] were obtained using the reaction of trimethylammonium methylide with 1-boraadamantane.

We have investigated the reaction of the tetrahydrofuran complex of 1-boraadamantane with phosphorus ylides. The reaction of equimolar quantities of the phosphoranes IIa–d with the tetrahydrofuran complex (I) of 1-boraadamantane at 20°C is accompanied by decolouration and heat evolution in giving the stable intermediate adducts IIIa-d.



(I) (III a-d)

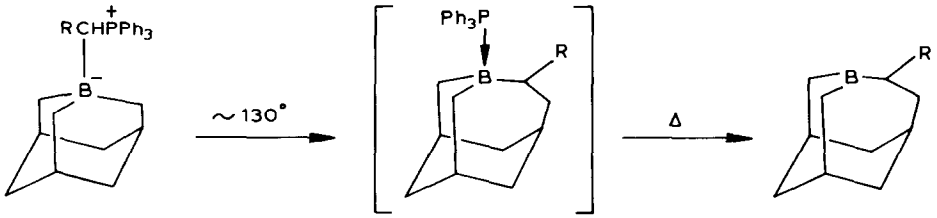
(R = H(a), Me(b), Et(c), n-Pr(d))

Alkylidenetriphenylphosphoranes are known to form stable complexes with boron compounds possessing higher complexing ability (i.e. $BHal_3$, B_2H_6) [10,11]: of the triorganoboranes, only triphenylborane has been shown to form a stable complex with a phosphorane [6,10].

Adducts IIIa–d are colourless, crystalline substances which are stable at room

temperature but which decompose above 100°C. The ^{11}B NMR spectra of IIIa–d in THF are characterized by signals in the region of −15 to −17 ppm which are similar to those of lithium methyl-1-boraadamantanate (−20.3 ppm) [12].

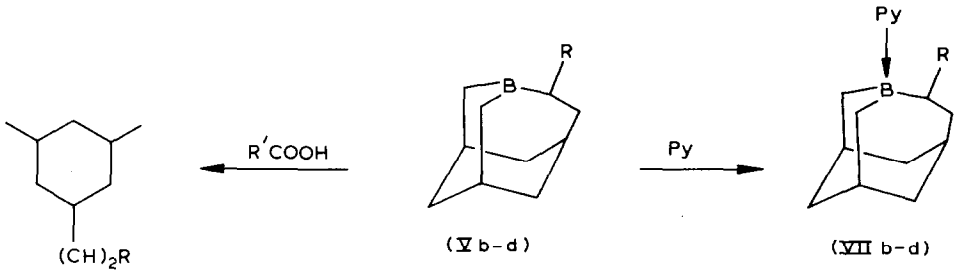
The adducts IIIb–d rearrange, on heating, to compounds of the 4-alkyl-3-borahomoadamantane series (IVb–d).



(III b-d) (IV b-d) (V b-d)

(R = Me(b), Et(c), n-Pr(d))

The reactions were carried out in boiling chlorobenzene (b.p. 132°C). After the reaction was complete, the solvent was distilled off and the 4-alkyl-3-borahomoadamantanes (Vb–d) were isolated as colourless, readily oxidizible liquids, by distilling the residue in vacuum. Besides the main products (Vb–d), decomposition of the betaines also gives small amounts of the double insertion products, which can be isolated by distillation. As noted above, the products of di-homologation were earlier observed in reactions of trialkylboranes with ylides [1,7]. Compound IIIa reacts only at the temperatures above 180°C, as a result of which free 3-borahomoadamantane was not isolated by this method. Structures of compounds Vb–d were confirmed by elemental analysis, physico-chemical methods, and by acidolysis. The acidolysis of Vb–d with stearic acid gives 1-alkyl-*cis*-3,*cis*-5-dimethylcyclohexanes (VIb–d). The hydrocarbons do not contain 1,*cis*-3,*cis*-5-trimethylcyclohexane (GLC), hence the 4-alkyl-3-borahomoadamantanes obtained (Vb–d) do not contain starting 1-boraadamantane. 1-Boraadamantane is always present as an impurity in the synthesis of 3-borahomoadamantane complexes by the use of trimethylammonium methylide [9].



(VI b-d) (V b-d) (VII b-d)

(R = Me(b), Et(c), n-Pr(d))

It is obvious that the 3-borahomoadamantane structure (Vb–d) is essentially less

TABLE 1

^{11}B NMR CHEMICAL SHIFTS OF SOME 4-METHYL-3-BORAHOMOADAMANTANE COMPOUNDS

Compound	Chemical shift (ppm)
Vb [a]	+79.5
Vb·Et_2O [b]	+79.5
Vb·THF [b]	+22.4
Vb·Ph_3P [c]	+10.3
Vb·Py [c]	0.0

[a] Neat. [b] With an excess ligand. [c] A solution in $CDCl_3$.

strained than the 1-boraadamantane structure; however, 4-alkyl-3-borahomoadamantane compounds (Vb–d) have a higher complexing capacity than trialkylboranes in forming complexes with a number of ligands (Table 1).

The complexes of Vb–d with pyridine (VIIb–d) are fairly stable, e.g. the liquid pyridinate VIId may be purified by distilling in vacuum.

It should be noted that a homologue of 3-borahomoadamantane, namely 4,4-dimethyl-3-borahomoadamantane, was first prepared by a fourstage synthesis from 1-boraadamantane in an overall yield of 48% [13].

Experimental

All operations with organoboron compounds were performed in an atmosphere of dry argon. Tetrahydrofuran-1-boraadamantane (I) was synthesized as previously reported [14]. ^1H NMR spectra were recorded on a TESLA BS-497 instrument (100 MHz), and ^{13}C NMR spectra were obtained on a BRUKER WM-250 spectrometer (68.69 MHz for carbon). The assignment of spectral lines was carried out with the aid of off-resonance methods. For compounds VIb–d, the β, γ and δ CH_2 groups in the side chain were assigned on the basis of an additional scheme supposed in [15].

Mass spectra were measured on a VARIAN CH-6 spectrometer, and GLC analyses were conducted on a CHROM-4 apparatus, using a 2.4 m column of stainless steel and polyethyleneglycol as the stationary phase.

1-(Methylenetriphenylphosphorane)-1-boraadamantane (IIIa)

A mixture of 34.2 g (95.7 mmol) of methyltriphenylphosphonium bromide and 4.8 g (122.6 mmol) of sodium amide in 180 ml of THF was refluxed with stirring for 3 h and then cooled to 20°C. The precipitate was filtered off, and to the filtrate was added 20.0 g (97.0 mmol) of I in 80 ml of THF. Decolouration and warming-up of the solution were observed. The solvent was distilled off, the residue was washed with hexane (3 × 40 ml) and then with acetone (2 × 10 ml) to leave 34.2 g (87%) of IIIa as a white powder, m.p. 185–188°C. Found: C, 82.12; H, 7.92; B, 2.52; P, 7.22. $C_{28}H_{32}BP$ calcd.: C, 81.94; H, 7.86; B, 2.63; P, 7.56%.

1-(Ethylidenetriphenylphosphorane)-1-boraadamantane (IIIb)

To a solution of the ylide IIb, prepared from 48.76 g (131.5 mmol) of $EtPPh_3Br$ and 6.1 g (156 mmol) of $NaNH_2$ in 240 ml of THF, was added, with stirring, 27.5 g (133.5 mmol) of I in 100 ml of THF (in this process the reaction mixture underwent

decolouration and an increase in temperature). The precipitate was filtered off, the solvent was distilled off and the residue was washed with hexane (3 × 40 ml) and then with acetone (2 × 15 ml) and dried in vacuum to give 52.2 g (94%) of IIIb, m.p. 131–132°C (dec). Found: C, 81.89; H, 8.20; B, 2.47; P, 7.09. $C_{29}H_{34}BP$ calcd.: C, 82.07; H, 8.07; B, 2.55; P, 7.31%.

1-(Propylidenetriphenylphosphorane)-1-boraadamantane (IIIc)

A mixture of 22.7 g (59 mmol) of propyltriphenylphosphonium bromide and 3.0 g (77 mmol) of sodium amide was refluxed for 1 h while being stirred in 150 ml of THF, then it was treated with 12.4 g (60 mmol) of I in 30 ml of THF. After decolouration of the dark-red solution, the precipitate was filtered off, the filtrate was evaporated, and the residue was washed with hexane (3 × 30 ml) and then acetone (2 × 10 ml) to leave 18 g (70%) of IIIc, m.p. 120–123°C (dec). Found: C, 81.80; H, 8.32; B, 2.34; P, 6.70. $C_{30}H_{36}BP$ calcd.: C, 82.12; H, 8.27; B, 2.47; P, 7.07%.

1-(Butylidenetriphenylphosphorane)-1-boraadamantane (IIId)

The ylide IId, obtained from 37.9 g (92 mmol) of Ph_3PBuBr and 4.5 g (118 mmol) of $NaNH_2$ in 150 ml of THF, was treated with 19.5 g (94.5 mmol) of I in 70 ml of THF. The precipitate was removed by filtration and the solvent by distillation, and the residue was washed with hexane (5 × 40 ml) and then with acetone (2 × 15 ml) to give 40.48 g (97%) of IIId, m.p. 97–100°C (dec). Found: C, 81.89; H, 8.49; B, 2.37; P, 6.79. $C_{31}H_{38}BP$ calcd.: C, 82.24; H, 8.47; B, 2.39; P, 6.85%.

4-Methyl-3-borahomoadamantane (Vb)

23.3 g (55 mmol) of the betaine IIIb was heated in 200 ml of boiling chlorobenzene for 1 h and then cooled to 20°C. After removal of the main volume of the solvent, the residue was vacuum distilled to give two fractions: (1) 6.2 g, b.p. 50–90°C (1.5 mmHg); and (2) 11.0 g (77%), Ph_3P, b.p. 180–190°C (1.5 mmHg), m.p. 77–79°C (from methanol).

Distillation of the first fraction afforded two portions: (1) 4.9 g (55%) of Vb, b.p. 54–55°C (1.5 mmHg), n_D^{20} 1.5132. Found: C, 81.29; H, 11.82; B, 6.64. $C_{11}H_{19}B$ calcd.: C, 81.46; H, 11.81; B, 6.67%. Mass spectrum (*m/e*): 162 [M^+]. ^1H NMR spectrum (δ, ppm, $CHCl_3$): 1.12 d(3H, CH_3); and (2) 1.0 g, b.p. 57–90°C (1.5 mmHg), n_D^{20} 1.5146. According to the mass spectrum (M^+) this fraction is a mixture of Vb and a product of dihomologation, with the latter predominating.

4-Ethyl-3-borahomoadamantane (Vc)

11.4 g (26.2 mmol) of IIIc was refluxed in 110 ml of PhCl during 1 h, the solvent was removed and the residue was distilled in vacuum, two fraction having been collected: (1) 2.98 g, b.p. 55–80°C (1.5 mmHg), n_D^{20} 1.5060; and (2) 5.68 g (82%), Ph_3P, b.p. 180–190°C (1.5 mmHg).

Repeated distillation of the first fraction gave: (1) 2.24 g (47%) of Vc, b.p. 58–60°C (1.5 mmHg), n_D^{20} 1.5058. Found: C, 81.45; H, 11.99; B, 6.05. $C_{12}H_{21}B$ calcd.: C, 81.83; H, 12.02; B, 6.14%. Mass spectrum (*m/e*): 174 [M^+]; and (2) 0.33 g of the dihomologation product, as colourless liquid, b.p. 58–80°C (1.5 mmHg), n_D^{20} 1.5095 (with Vc as an impurity).

4-n-Propyl-3-borahomoadamantane (Vd)

20.3 g (44.8 mmol) of the betaine IIId was refluxed in 160 ml of chlorobenzene for 45 min. After removal of the solvent, the first distillation gave: (1) 6.55 g of a colourless liquid, b.p. 80–120°C (2.5 mmHg); and (2) 9.88 g (87%) of Ph_3P, b.p. 195–205°C (2.5 mmHg).

Subsequent distillation of the first fraction afforded: (1) 4.30 g (51%) of Vd, b.p. 86–87°C (2.5 mm Hg), n_D^{20} 1.5054. Found: C, 81.83; H, 12.12; B, 5.49. $C_{13}H_{23}B$ calcd.: C, 82.16; H, 12.20; B, 5.69%; and (2) 1.26 g of the double homologation product mixed with Vd, b.p. 88–104°C (2.5 mmHg), n_D^{20} 1.5112.

1-n-Propyl-cis-3,cis-5-dimethylcyclohexane (VIb)

A mixture of 26.0 g (90 mmol) of stearic acid and 3.24 g (20 mmol) of Vb was heated under reduced pressure (120 mmHg) to 250°C for 2 h. Crude VIb was distilled off, washed with 3 ml of a 20% solution of NaOH, extracted with ether, and distilled, to yield 1.95 g (63%) of VIb, which contained no impurities (GLC), b.p. 62°C (8 mmHg), n_D^{20} 1.4369. ^{13}C NMR spectrum (δ, ppm): 37.65 (C(1)), 42.25 (C(2)), 44.75 (C(4)), 32.8 (C(5)), 22.9 (C(1′)), 40.2 (C(1″)), 20.3 (C(2″)), 14.5 (C(3″)). Mass spectrum (m/e): 154 [M^+]. Found: C, 85.70; H, 14.28. $C_{11}H_{22}$ calcd.: C, 85.67; H, 14.33%.

1-n-Butyl-cis-3,cis-5-dimethylcyclohexane (VIc)

In an analogous manner, heating a mixture of 1.63 g (9.35 mmol) of Vc and 15.7 g (55 mmol) of stearic acid to 250°C at 110 mmHg pressure for 2 h gave 0.81 g (52%) of pure (GLC) VIc, b.p. 73°C (6 mmHg), n_D^{20} 1.4411. Found: C, 85.68; H, 14.29. $C_{12}H_{24}$ calcd.: C, 85.63; H, 14.37%. ^{13}C NMR spectrum (δ, ppm): 37.9 (C(1)), 42.4 (C(2)), 44.8 (C(4)), 32.8 (C(5)), 22.95 (C(1′)), 37.6 (C(1″)), 29.6 (C(2″)), 23.3 (C(3″)), 14.2 (C(4″)). Mass spectrum (m/e): 168 [M^+].

1-n-Pentyl-cis-3,cis-5-dimethylcyclohexane (VId)

Similarly, starting with 2.98 g (15.7 mmol) of Vd and 21.48 g (76 mmol) of stearic acid, heating the mixture to 250°C at 90 mmHg for 2 h, produced 2.23 g (78%) of pure (GLC) VId, b.p. 82–84°C (7 mmHg), n_D^{20} 1.4432. Found: C, 85.76; H, 14.35. $C_{13}H_{26}$ calcd.: C, 85.63; H, 14.37%. ^{13}C NMR spectrum (δ, ppm): 37.9 (C(1)), 42.3 (C(2)), 44.7 (C(4)), 32.75 (C(5)), 22.9 (C(1′)), 37.8 (C(1″)), 26.9 (C(2″)), 32.6 (C(3″)), 22.9 (C(4″)), 14.1 (C(5″)). Mass spectrum (m/e): 182 [M^+].

Pyridine-4-methyl-3-borahomoadamantane (VIIb)

To 0.35 g (2.15 mmol) of Vb, dissolved in 8 ml of hexane, was added with heat evolution 0.18 g (2.28 mmol) of pyridine. The solvent was distilled off and the residue was recrystallised from methanol, to yield 0.51 g (98%) of VIIb, m.p. 103–106°C. Found: C, 79.27; H, 10.07; B, 4.51. $C_{16}H_{24}BN$ calcd.: C, 79.67; H, 10.03; B, 4.48%. ^1H NMR spectrum (δ, ppm, CH_2Cl_2): 0.18 d (3H, CH_3), pyridine protons 7.45 t (2H, β), 7.83 t (1H, γ), 8.39 d (2H, α). Mass spectrum (m/e): 241 [M^+].

Pyridine-4-ethyl-3-borahomoadamantane (VIIc)

0.39 g (2.2 mmol) of Vc in 8 ml of hexane was treated with 0.17 g (2.2 mmol) of pyridine. The solvent was distilled off and the residue was recrystallized from

methanol to give 0.54 g (98%) of VIIc, m.p. 78–80°C. Found: C, 79.47; H, 10.20; B, 4.51. $C_{17}H_{26}BN$ calcd.: C, 79.80; H, 10.27; B, 4.21%. ^1H NMR spectrum (δ, ppm, CH_2Cl_2): proton signals of Vc: 0.21–2.13, pyridine protons signals: 7.43 t (2H, β), 7.81 t (1H, γ), 8.41 d (2H, α). Mass spectrum (m/e): 255 [M^+].

Pyridine-4-n-propyl-3-borahomoadamantane (VIId)

To a solution of 0.82 g (4.3 mmol) of Vd in 12 ml of hexane was added 0.38 g (4.8 mmol) of pyridine. The solvent was distilled off, and then vacuum distillation of the residue gave 1.11 g (98%) of VIId, as a viscous transparent liquid, b.p. 136–138°C (1.5 mmHg), n_D^{20} 1.5620. Found: C, 80.35; H, 10.53; B, 4.15. $C_{18}H_{28}BN$ calcd.: C, 80.29; H, 10.49; B, 4.03%. ^1H NMR spectrum (δ, ppm, CH_2Cl_2): proton signals of Vd: 0.4–2.2, pyridine protons signals: 7.40 t (2H, β), 7.88 t (1H, γ), 8.44 d (2H, α). Mass spectrum (m/e): 269 [M^+].

References

1 J.J. Tufariello, L.T.C. Lee, J. Am. Chem. Soc.,. 88 (1966) 4757.
2 F. Bickelhaupt and J.W.F.K. Barnick, Rec. Trav. Chim. Pays Bas, 87 (1968) 188.
3 J.T. Tufariello, P.W. Wojtkovski and L.T.C. Lee, J. Chem. Soc., Chem. Commun., (1967) 505.
4 W.K. Musker and R.R. Stevens, Tetrahedron Lett., (1967) 995.
5 W.K. Musker and R.R. Stevens, Inorg. Chem., 8 (1969) 255.
6 R. Köster and B. Rickborn, J. Am. Chem. Soc., 89 (1967) 2782.
7 J.J. Tufariello, L.T.C. Lee and P.W. Wojtkovski, J. Am. Chem. Soc., 89 (1967) 6804.
8 D.J. Pasto and P.W. Wojtkovski, Tetrahedron Lett., (1970) 215.
9 B.M. Mikhailov, N.N. Govorov, Ya.A. Angelyuk, V.G. Kiselev and M.I. Struchkova, Izv. Akad. Nauk SSSR, Ser. Khim., (1980) 1621.
10 D. Seyferth and S.O. Grim, J. Am. Chem. Soc., 83 (1961) 1613.
11 M.F. Hawthorne, J. Am. Chem. Soc., 83 (1961) 367.
12 M.E. Gurskii, D.G. Pershin and B.M. Mikhailov, J. Organomet. Chem., 246 (1983) 19.
13 L.S. Vasilyev, V.V. Veselovskii, M.I. Struchkova and B.M. Mikhailov, J. Organomet. Chem., 225 (1982) 115.
14 B.M. Mikhailov and T.K. Baryshnikova, Dokl. Akad. Nauk SSSR, 243 (1978) 929.
15 L.P. Lindeman and J.Q. Anams, Anal. Chem., 43 (1971) 1245.
16 B.M. Mikhailov and E.A. Shagova, J. Organomet. Chem., 258 (1983) 131.