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ORGANOBORON COMPOUNDS

CDXI *. SYNTHESIS OF 2-SUBSTITUTED 1-IODO-4-HYDROXYMETHYL-1,6-HEPTADIENES FROM 1-BORA-2-CYCLOHEXENE COMPOUNDS

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Summary

3-Substituted 1-methoxy-5-allyl-1-boracyclohex-2-enes, obtained by the condensation of triallylborane with acetylenic compounds with sequential methanolysis, react with I_2 and MeONa to form dimethyl esters of iodine-containing boronic acids (IV). Oxidation of the latter compounds with hydrogen peroxide in alkaline medium gives rise to 2-substituted 1-iodo-4-hydroxymethyl-1,6-heptadienes (V), which may be used in the prostaniod synthesis.

Results and discussion

As found by Zweifel and coworkers [1], the reaction of iodine with alkenyldialkylboranes in the presence of NaOH produces olefins, which are formed as a result of the migration of an alkyl group from the boron atom to adjacent carbon. The following mechanism of the reaction of vinylboranes iodination has been supposed, which includes the addition of iodine at the double bond with the formation of a bridging iodonium ion, the migration of a hydrocarbon radical with an inversion at the migration centre, and subsequent *trans*-elimination of a boron-containing group and iodine [1,2].

Esters of dialkenylborinic acids also undergo similar conversions [3].

It was of interest to study this reaction for the example of 3-substituted 1-methoxy-5-allyl-1-boracyclohex-2-enes (I), which are obtained by the condensation of acetylenic compounds with triallylborane followed by methanolysis [4]. Compounds I are the esters of cyclic borinic acids, containing both saturated and olefinic

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* For part CDX see ref. 9.

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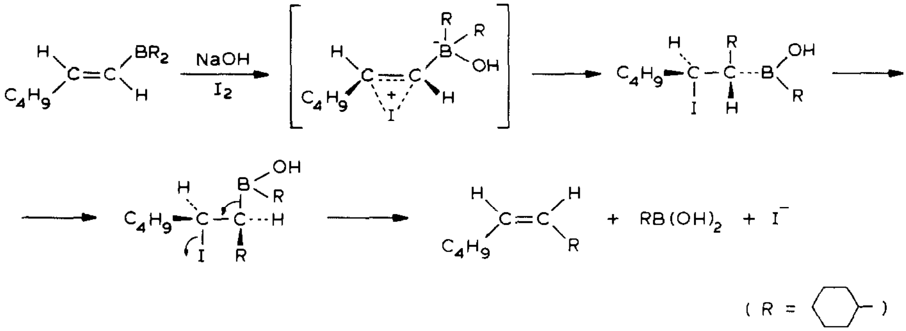
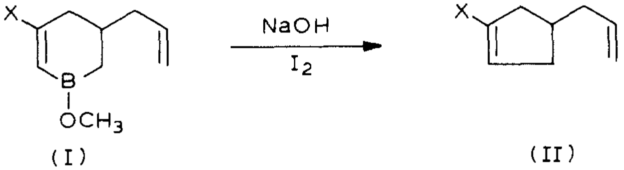
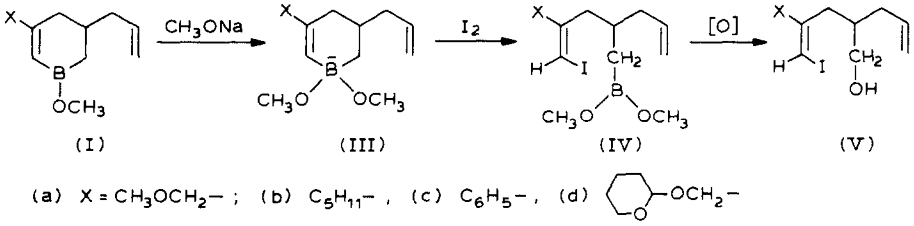


group at the boron atom. Hence, it could be expected that, on treatment of I with iodine and an alkali, compounds II would be formed as a result of the migration of the aliphatic group to the alkenyl one.



It turned out, however, that the reaction of I with iodine and NaOH proceeds through the cleavage of a boron–alkenyl bond with the formation of 4-substituted dihydroxy-(5-iodo-2-allylpent-4-enyl)boranes. Further oxidation of the latter with hydrogen peroxide in alkaline medium leads to 2-substituted 1-iodo-4-hydroxymethyl-1,6-heptadienes (V), containing ~ 10–15% of impurities (GLC).



It was discovered that conducting the iodination of I in the presence of MeONa is more expedient. Under these conditions, the boronates III are formed, iodination of which furnishes 4-substituted dimethoxy(5-iodo-2-allylpent-4-enyl)boranes (IV). The latter are oxidized to analytically pure V in 80–90% yield.

The reaction of I with I_2 and MeONa proceeds at room temperature in a solution of THF. The dimethoxyboranes (IV), formed in 55–80% yield, are liquids, which can be distilled in vacuum with no decomposition. Their structures were confirmed by IR and ^1H NMR spectral data. In IR spectra, characteristic bands are in the region of 1595–1620 (C=CI), 1640 and 3080 ($CH=CH_2$), and 1320–1370 cm^{-1} (B–O).

Compounds Va–Vd are liquids, Va is mobile, while the remainder are viscous liquids. Compounds Va and Vb are distilled in vacuum without a decomposition, whilst Vc and Vd are destroyed. IR spectra of Va–Vd reveal absorption bands at 1600–1615 (C=CI), 1640 and 3080 ($CH=CH_2$), together with a broad band at

3200–3500 cm^{-1} (OH). ^{1}H NMR spectra also substantiate the structures of the compounds. Compounds V can be used for the synthesis of various prostanoids.

It is noteworthy that the formation of an alkenyl iodide in 15–22% yield takes place on iodination of a boronate, obtained from *E*-1-lithium-3-tert-butyldimethylsiloxy-1-octene and dimethoxy(*trans*-2-ethylcyclopentyl)borane [5].

Experimental

All operations with organoboron compounds were carried out under dry argon. Starting 3-substituted 1-methoxy-5-allyl-1-boracyclohex-2-enes were obtained by known methods: 3-methoxymethyl (Ia) [6], 3-phenyl (Ic) [7], 3-tetrahydropyranyloxymethyl (Id) [8]. The synthesis of 1-methoxy-5-allyl-3-pentyl-1-boracyclohex-2-ene (Ib) is described below.

^{1}H NMR spectra were recorded on a Tesla BS-467 spectrometer (60 MHz, relative to TMS). IR spectra were obtained on a UR-20 instrument.

1-Methoxy-5-allyl-3-pentyl-1-boracyclohex-2-ene (Ib)

To 14.8 g (0.11 mol) of stirred triallylborane were slowly added (dropwise) 10.6 g (0.11 mol) of 1-heptyne. The mixture was allowed to stand for 5 days until the reaction was completed (monitoring by the vanishing of a band at 3318 cm^{-1} in the IR spectrum), then it was treated with 9 ml of MeOH. 2.46 l of propylene was evolved. Distillation gave 12.2 g (50%) of Ib, b.p. 82–84°C (1 mmHg), n_D^{21} 1.4740. Found: C, 76.11; H, 11,35; B, 4.76. $C_{14}H_{25}BO$ calcd.: C, 76.37; H, 11.45; B, 4.91%. ^{1}H NMR spectrum (δ, ppm): 5.40–5.87 m (2 H, -CH=C$<$ and $>$C=CH-B$<$), 4.65–5.10 m (2H, $>$C=CH$_2$), 3.62 s (3H, OCH$_3$), 0.10–2.29 m (remaining 18H). IR spectrum (cm^{-1}): 1615 ($>$C=C–B), 1640 and 3080 (CH=CH$_2$), 1320–1380 (B–O).

Dimethoxy(5-iodo-4-methoxymethyl-2-allylpent-4-enyl)borane (IVa)

In a 100 ml three-neck flask, fitted with a magnetic stirrer, thermometer, dropping funnel and a valve for introduction of argon, was placed 12.2 g (0.063 mol) of Ia in 20 ml of THF. To the solution were added at room temperature 19 ml of a methanolic solution of MeONa and 25 ml of a solution of 16.8 g (0.066 mol) of iodine in THF. The mixture was left to stand for twenty-four hours, whereupon THF and excess MeOH were distilled off. To the residue were added 50 ml of hexane, and an excess of iodine was decomposed with crystalline sodium thiosulfate. Subsequent filtration, evaporation, and distillation gave 15.3 g (69%) of IVa, b.p. 104–106°C (1 mmHg), n_D^{20} 1.5065. Found: C, 41.27; H, 6.41; B, 3.17; I, 36.36. $C_{12}H_{22}BIO_3$ calcd: C, 40.94; H, 6.30; B, 3.07; I, 36.04%. ^{1}H NMR spectrum (δ, ppm): 6.17–6.28 m (1H, $>$C=CHI), 5.38–6.0 m (1H, -CH=C$<$), 4.70–5.15 m (2H, $>$C=CH$_2$), 3.78–3.92 m (2H, OCH$_2$), 3.45 s (6H, B(OCH$_3$)$_2$), 1.77–2.33 m (5H, $\text{-CH}_2\text{-}\overset{|}{\text{C}}\text{H-CH}_2\text{-}$), 0.56–0.88 m (2H, B–CH$_2$).

Dimethoxy(5-iodo-2-allyl-4-pentylpent-4-enyl)borane (IVb)

As described for compound IVa, to 12.2 g (0.0554 mol) of Ib in 20 ml of THF were added 24 ml of a methanolic solution of MeONa and 25 ml of a solution of 14.7 g (0.058 mol) of iodine in THF. After twenty-four hours, THF and MeOH were removed, and to the residue were added 50 ml of hexane with subsequent treatment with sodium thiosulfate. After filtration, evaporation, and distillation, 17 g (81.6%)

of IVb was obtained, b.p. 115–118°C (1 mmHg), n_D^{20} 1.4989. Found: C, 47.88; H, 7.49; B, 2.89, I, 33.63. $C_{15}H_{28}BIO_2$ calcd.: C, 47.65; H, 7.47; B, 2.86; I, 33.56%. ^1H NMR spectrum (δ, ppm): 5.85–5.98 m (1H, >C=CHI), 5.38–5.77 m (1H,-CH=C<), 4.62–5.15 m (2H, >C=CH_2), 3.47 s (6H, 2 OCH_3), 0.47–2.37 m (remaining 18H).

Dimethoxy(5-iodo-2-allyl-4-phenylpent-4-enyl)borane (IVc)

In an analogous manner, from 13.1 g (0.0579 mol) of Ic, 18 ml of a methanolic solution of MeONa and 15.4 g (0.608 mol) of iodine were obtained 16 g (72%) of IVc, b.p. 135–138°C (1 mmHg), n_D^{20} 1.5637. Found: C, 50.30; H, 5.85; B, 2.91; I, 33.65. $C_{16}H_{22}BIO_2$ calcd.: C, 50.04; H, 5.77; B, 2.82, I; 33.04%. ^1H NMR spectrum (δ, ppm): 7.18 s (5H, C_6H_5), 6.33 s (1H, >C=CHI), 5.23–5.96 m (1H, -CH=C<), 4.63–5.06 m (2H, >C=CH_2), 3.34 s (6H, 2 OCH_3), 1.47–2.78 two broad signals (5H, -CH_2-CH-CH_2-), 0.50–0.78 broad signal (2H, B-CH_2).

Dimethoxy(5-iodo-4-tetrahydropyranyloxymethyl-2-allylpent-4-enyl)borane (IVd)

Starting from 13.9 g (0.0526 mol) of Id, 18 ml of a methanolic solution of MeONa and 14 g (0.0552) of iodine, 12.3 g (55%) of IVd were prepared, b.p. 155–160°C (1 mmHg), n_D^{20} 1.5129. Found: C, 45.70; H, 6.67; B, 2.70; I, 30.80. $C_{16}H_{28}BIO_4$ calcd.: C, 45.53; H, 6.69; B, 2.56; I, 30.06%. ^1H NMR spectrum (δ, ppm): 6.22–6.35 m (1H, >C=CHI), 5.40–5.98 m (1H, -CH=C<), 4.73–5.25 m (2H, C=CH_2), 4.52 broad s (1H, O-CH-O), 3.22–4.35 m with a singlet at 3.46 (10 H, 2 OCH_2 and 2 OCH_3), 1.30–2.33 two broad signals (10H, 5CH_2; 1H, B-C-CH-), 0.60–0.83 broad signal (2H, B-CH_2).

(E)-1-Iodo-2-methoxymethyl-4-hydroxymethyl-1,6-heptadiene (Va)

In a three-necked flask, fitted with a thermometer, condenser, dropping funnel and a magnetic stirrer, were placed consequently at room temperature 9.4 g (0.0267 mol) of IVa in 20 ml of ether and 5.3 ml of a 20% solution of NaOH. After cooling to 0°C 12 ml of 30% H_2O_2 was added dropwise, and the mixture was allowed to stand overnight. The ethereal layer was washed with water to neutral reaction and dried over Na_2SO_4. Evaporation of ether and distillation of the residue afforded 6 g (76%) of Va as a colourless liquid, b.p. 109–110°C (1 mmHg), n_D^{20} 1.5372. Found: C, 40.89; H, 5.86; I, 42.48. $C_{10}H_{17}IO_2$ calcd.: C, 40.55; H, 5.79; I, 42.85%. ^1H NMR spectrum (δ, ppm): 6.28 s (1H, >C=CHI), 5.57–6.03 m (1H, -CH=C<), 4.87–5.23 m (2H, >C=CH_2), 3.87 s (2H, OCH_2), 2.77–3.63 m with a singlet at 3.26 (6H, CH_2OH, OCH_3), 1.67–2.41 m (5H, CH_2-CH-CH_2).

(Z)-1-Iodo-4-hydroxymethyl-2-pentyl-1,6-heptadiene (Vb)

As described above, to 17 g (0.045 mol) of IVb in 30 ml of ether were added 9 ml of a 20% solution of NaOH and then, dropwise on cooling, 7 ml of 30% H_2O_2. After standing overnight, the ethereal layer was separated, washed with water to neutral reaction, and dried over Na_2SO_4. Removal of ether and distillation of the residue yielded 12.2 g (84%) of Vb, b.p. 131–132°C (1 mmHg), n_D^{20} 1.5242. Found: C, 48.72; H, 7.22; I, 39.70. $C_{13}H_{23}IO$ calcd.: C, 48.46; H, 7.19; I, 39.38%. ^1H NMR spectrum (δ, ppm): 5.93 s (1H, >C=CHI), 5.53–6.08 m (1H, -CH=C<), 4.85–5.19 m (2H, >C=CH_2), 3.44 d (2H, OCH_2), 0.75–2.55 (remaining 17H).

(E)-1-Iodo-2-phenyl-4-hydroxymethyl-1,6-heptadiene (Vc)

To 10.8 g (0.028 mol) of IVc in 20 ml of ether was added 5.6 ml of a 20% solution of NaOH. The mixture was cooled to 0°C, whereupon to it were added dropwise 5 ml of 30% H_2O_2. After standing overnight, the ethereal solution was separated, washed with water, and dried over Na_2SO_4. After removing ether, to the residue, which was a yellowish viscous liquid with a small admixture of flocks, were added 5 ml of MeOH. Filtration and distilling off the methanol gave 8.15 g (88%) of Vc. Found: C, 51.44; H, 5.29; I, 39.05. $C_{14}H_{17}IO$ calcd.: C, 51.23; H, 5.22; I, 38.67%. ^1H NMR (δ, ppm): 7.24 s (5H, C_6H_5), 6.41 s (1H, $>$C=CHI), 5.34–5.90 m (1H, -CH=C$<$), 4.78–5.16 m (2H, $>$C=CH_2), 3.35 d (2H, OCH_2), 1.33–2.90 m (remaining 6H).

(E)-1-Iodo-2-tetrahydropyranyloxymethyl-4-hydroxymethyl-1,6-heptadiene (Vd)

To 11.7 g (0.0277 mol) of IVd in 20 ml of ether were added 5.5 ml of a 20% solution of NaOH. After cooling to 0°C, to the mixture were added dropwise (slowly) 4 ml of 30% H_2O_2. After standing overnight, further treatment was performed as described above to give 9.4 g (93%) of Vd as a colourless, viscous liquid. Found: C, 46.14; H, 6.45; I, 35.06. $C_{14}H_{23}IO_3$ calcd.: C, 45.92; H, 6.33; I, 34.65%. ^1H NMR spectrum (δ, ppm): 6.28 s (1H, $>$C=CHI), 5.45–6.08 m (1H, -CH=C$<$), 4.78–5.25 m (2H, $>$C=CH_2), 4.57 broad s (1H, O–CH–O), 3.22–4.38 m (6H, 3 OCH_2), 2.77 broad s (1H, OH), 1.29–2.43 m (remaining 11 H).

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