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ORGANOBORON COMPOUNDS

CDXII *. THE SYNTHESIS OF 2-SUBSTITUTED 1-IODO-1,4-PENTADIENES BY IODINATION OF 1,4-PENTADIENYLBORON DERIVATIVES

B.M. MIKHAILOV* and L.I. LAVRINOVICH

N.D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, Leninskii Prospect 47, Moscow (U.S.S.R.)

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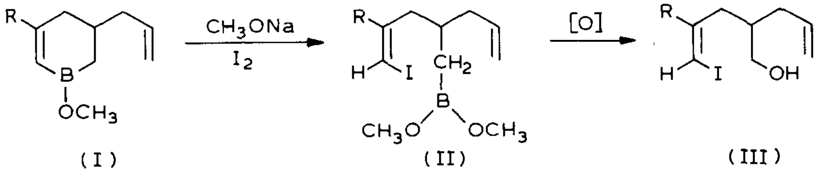
Summary

2-Substituted dimethoxy(1,4-pentadienyl)boranes, which are obtained by the condensation of triallylborane with acetylenic compounds followed by methanolysis, react with iodine in the presence of NaOH to form 2-substituted 1-iodo-1,4-pentadienes.

In a previous paper [1], we reported the iodination of 3-substituted 1-methoxy-5-allyl-1-boracyclohex-2-enes (I) and showed that the process occurs with rupturing of the boron–alkenyl bond to produce 4-substituted dimethoxy(5-iodo-2-allyl-4-pentenyl)boranes (II). The latter compounds were further oxidized to 2-substituted 1-iodo-4-hydroxymethylhepta-1,6-dienes (III).



(1)

Compounds of type I are prepared by the interaction of triallylborane with monosubstituted acetylenes followed by methanolysis, they are the products of the second stage of allylboron-acetylene condensation [2]. The first stage of the process involves the formation of 2-substituted diallyl(1,4-pentadienyl)boranes (IV), which convert gradually at room temperature to 3-substituted 1,5-diallyl-1-boracyclohex-2-enes (V).

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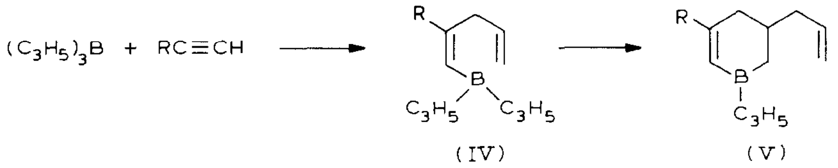
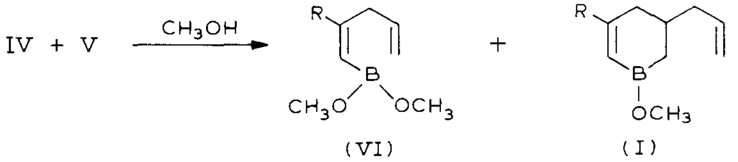
* For part CDXI see ref. 1.



(2)

The allylboration reaction of acetylenes may be stopped at any time by treating the reaction mixture with methanol, thus obtaining a mixture of 2-substituted dimethoxy(1,4-pentadienyl)boranes (VI) and I, and also (in the case where the reaction is not carried out to completion) of dimethoxyallylborane.



(3)

The aim of the present work was to discover the optimal conditions for the preparation of compounds of type VI and also to investigate the iodination that occurred.

The rate of formation of IV and the rate of further cyclization of IV to V (reaction 2) depend on the nature of the acetylenic component, the temperature and the ratio of the reagents. In order to obtain an optimum quantity of IV in the reaction mixture, it was necessary to select the corresponding conditions for the reaction to be conducted. With this goal in mind, we studied the reaction of triallylborane with phenylacetylene with the aid of ^1H NMR spectroscopy with different ratios of reagents and reaction times. It turned out that the optimum quantity of compound IV is formed at a temperature of 3–5°C during 7 h. In this case, the rate of formation of IV increases considerably with an increase in the $All_3B/PhC{\equiv}CH$ ratio (see Table 1).

Thus, with a starting reagent ratio of 1/1, 67% of phenylacetylene reacted to form compounds IV (45%) and V (22%) during a period of 7 h. After the same time and with a ratio of 2/1, the overall yield was 85% (70% of IV and 15% of V).

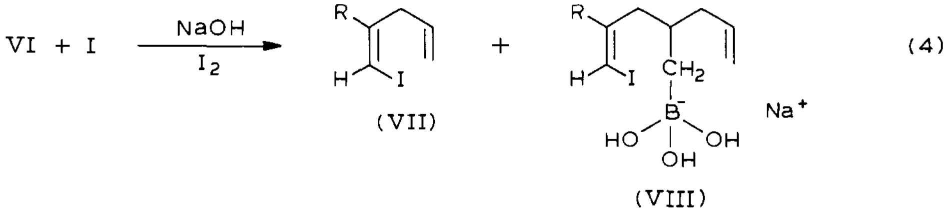
Unfortunately, determination of the quantitative content of the products of the condensation of triallylborane with the other acetylenes used, by ^1H NMR spectroscopy was unsuccessful owing to superposition of the signals. Therefore, the optimal conditions of the reaction (temperature and time) were selected by running a series of experiments for each case.

TABLE 1

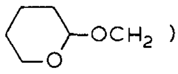
Ratio of $All_3B/PhC{\equiv}CH$	Quantity of $PhC{\equiv}CH$ reacted at 3–5°C during 7 h (%)	Quantities of compounds formed (%)		Ratio of IV/V
		IV	V	
1/1	67	45	22	2
1.5/1	76	56	20	2.8
2/1	85	70	15	4.66

Triallylborane was treated with 1-hexyne, 1-heptyne and propargyl methyl ether at 13–18°C for 7–10 h and then the reaction mixture was kept at 3–5°C for 17 h. The reaction with tetrahydropyranyl ether required a longer time. In all cases, 2 equivalents of triallylborane were used.

The methoxylation of the mixture of compounds IV and V (reaction 3) was performed under cooling. After removal of the volatile substances, the mixture of I and VI was dissolved in THF and iodinated in the presence of NaOH at −10°C. The 2-substituted 1-iodo-1,4-pentadienes that formed (VII) (reaction 4) were then separated from the borates (VIII).



(Ia, VIa, VIIa R = Ph, Ib, VIb, VIIb R = n-C_5H_{11},
Ic, VIc*, VIIc R = n-Bu; Id, VId, VIId R = $MeOCH_2$,
Ie, VIe, VIIe R =)



The yields of VIIa–VIIe obtained were equal to 55, 40, 43, 25 and 34%, respectively.

Zweifel and Whitney [4] synthesized (*E*)-1-iodo-1-hexene by hydroalumination of 1-hexyne followed by treatment with iodine. The 1-alkenylboronic acids show analogous behaviour with respect to iodine [5].

The compounds of type VII are colourless or slightly yellow oil-like liquids which can be distilled in a vacuum with no decomposition. Their structures were confirmed by IR and ^1H NMR spectral data as well as by elemental analyses. The IR spectra contain characteristic absorption bands in the region of 1595–1620 (>C=CI), 915, 995, 1640, 3060 and 3080 cm^{-1} ($CH_2CH{=}CH_2$). The ^1H NMR spectral data are presented in the Experimental section.

The 2-substituted 1-iodo-1,4-pentadienes can be used as starting substances for the synthesis of prostanoids.

Experimental

Reactions of the organoboron compounds were carried out in a dry argon atmosphere.

^1H NMR spectra were recorded on a Tesla BS-467 spectrometer (60 MHz, solutions in CCl_4, relative to TMS). IR spectra were obtained on a UR-20 instrument.

(E)-1-Iodo-2-phenyl-1,4-pentadiene (VIIa)

In a 100 ml three-necked flask fitted with a magnetic stirrer, a thermometer, a dropping funnel and a valve was placed 10 g (0.075 mol) of triallylborane. To the

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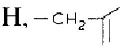
* VIc has previously been isolated in a pure state [3].

latter was added dropwise, on cooling (3–5°C), 3.9 g (0.038 mol) of phenylacetylene. After keeping the reaction mixture at 3–5°C for 7 h, 13 ml of MeOH was added slowly so that the temperature in the flask did not exceed 5°C. The propylene that evolved was collected in a trap (−70°C). Stirring was continued until gas evolution stopped (3 h). The removal of volatile substances in a vacuum afforded 6.45 g of a liquid mixture of dimethoxy(2-phenyl-1,4-pentadienyl)borane (VIa) and 1-methoxy-5-allyl-3-phenyl-1-boracyclohex-2-ene (Ia). To this mixture was added 20 ml of THF, and on stirring and cooling (−10°C), 17 ml of a 6 *N* solution of NaOH and 15 ml of a solution of 7.65 g of iodine in THF were carefully added. After being left to stand overnight, the solution had completely decolourized and separated into layers. The organic layer was separated, and THF was removed in a vacuum. To the residue, 30 ml of benzene was added, and the remaining water was removed by azeotropic distillation. Distillation of the residue gave 5.7 g (55%, calculated with respect to the initial phenylacetylene) of VIIa as a yellowish oil, b.p. 85–86°C (1 mmHg), n_D^{23} 1.6210. Found: C, 49.25; H, 4.17; I, 46.56. Calculated for $C_{11}H_{11}I$: C, 48.91; H, 4.11; I, 46.98%. ^{1}H NMR spectrum (δ, ppm): 7.07 s (5H, C_6H_5), 6.34 s (1H, $>C=CHI$), 5.25–5.99 m (1H, $-CH=C<$), 4.73–5.16 m (2H, $>C=CH_2$), 3.25 d (2H, $-\underset{\|}{C}-CH_2-\underset{\|}{C}-$).

(Z)-1-Iodo-2-n-pentyl-1,4-pentadiene (VIIb)

In the apparatus described above, 3.8 g (0.04 mol) of 1-heptyne was added to 10.6 g (0.08 mol) of triallylborane at 15–18°C. The mixture was kept at this temperature for 7 h and then at 3–5°C for 17 h. 13 ml of MeOH was slowly added dropwise on cooling (0–6°C), with subsequent stirring at room temperature for 4 h until propylene evolution had stopped. After the removal of volatile substances in a vacuum, to the resulting mixture of ethers Ib and VIb obtained (5.7 g) were added 15 ml of THF and then, at −10°C, 15 ml of a 6 *N* solution of NaOH and 15 ml of a solution of 7.2 g of iodine in THF. Further treatment was performed as described above. Distillation gave 4.2 g (40%, calculated with respect to 1-heptyne) of VIIb, b.p. 78–79°C (1 mmHg), $n_D^{20.5}$ 1.5133. Found: C, 45.74; H, 6.59; I, 47.90. Calculated for $C_{10}H_{17}I$: C, 45.47; H, 6.49; I, 48.04%. ^{1}H NMR spectrum (δ, ppm): 5.33–6.10 m (1H, –CH=C) with a multiplet at 5.92 (1H, $>C=CHI$), 4.85–5.28 m (2H, $>C=CH_2$), 2.93 d (2H, $-\underset{\|}{C}-CH_2-\underset{\|}{C}-$), 1.97–2.37 m (2H, ), 0.63–1.72 m (remaining 9H).

(Z)-1-Iodo-2-n-butyl-1,4-pentadiene (VIIc)

A mixture of 10.6 g (0.08 mol) of triallylborane and 3.3 g (0.04 mol) of 1-hexyne was kept for 8 h at 15–17°C and at 3–5°C for 17 h followed by treatment with 13 ml of MeOH at 0–6°C. The removal of volatile substances yielded 5.1 g of a colourless liquid, which was dissolved in 10 ml of THF. To the solution was added 14 ml of a 6 *N* solution of NaOH at −10°C and then 15 ml of a solution of 6.9 g of iodine in THF. Distillation furnished 4.3 g (43%, calculated with respect to 1-hexyne) of VIIc, b.p. 70–71°C (1 mmHg), n_D^{18} 1.5190. Found: C, 43.52; H, 6.16; I, 50.98. Calculated for $C_9H_{15}I$: C, 43.22; H, 6.04; I, 50.74%. ^{1}H NMR spectrum (δ, ppm): 5.37–6.22 m (1H, $-CH=C<$) with a multiplet at 5.90 (1H, $>C=CHI$), 4.83–5.27 m (2H, $>C=CH_2$), 2.93 d (2H, $-\underset{\|}{C}-CH_2-\underset{\|}{C}-$), 1.87–2.46 m (2H, ), 0.72–1.87 m (remaining 7 H).

(E)-1-Iodo-2-methoxymethyl-1,4-pentadiene (VIId)

A mixture of 10.6 g (0.08 mol) of triallylborane and 2.8 g (0.04 mol) of propargyl methyl ether was kept for 10 h at 13–15°C and for 17 h at 3–5°C followed by treatment with 13 ml of NaOH at 0–6°C. The removal of volatile substances afforded 5.16 g of a liquid to which was added, at -10°C, 15 ml of a 6 *N* solution of NaOH and 15 ml of a solution of 7.5 g of iodine in THF. Distillation gave 2.4 g (25.3%) of VIId, b.p. 60–61°C (1 mmHg), n_D^{20} 1.5280. Found: C, 35.87; H, 4.73; I, 52.95. Calculated for $C_7H_{11}IO$: C, 35.32; H, 4.66; I, 53.30%. ^1H NMR spectrum (δ, ppm): 6.27 m (1H,$>C{=}CHI$), 5.40–6.08 m (1H, $-CH{=}C<$), 4.86–5.28 m (2H,$>C{=}CH_2$), 3.83 d (2H,$-OCH_2-$), 3.25 s (3H, OCH_3), 2.93 d (2H,$-\underset{\|}{C}-CH_2-\underset{\|}{C}-$).

(E)-1-Iodo-2-tetrahydropyranyloxymethyl-1,4-pentadiene (VIIe)

A mixture of 10.6 g (0.08 mol) of triallylborane and 5.6 g (0.04 mol) of propargyl tetrahydropyranyl ether was kept for 16.5 h at 15–18°C and for 40 h at 3–5°C followed by treatment with 13 ml of MeOH at 5–10°C. Volatile substances were distilled off, and to the remaining mixture of ethers Ie and VIe were added dropwise, at -10°C, 21 ml of a 6 *N* solution of NaOH and 20 ml of a solution of 10 g of iodine in THF. Distillation gave 4.18 g (34%) of VIIe, b.p. 132–133°C (1 mmHg), n_D^{21} 1.5307. Found: C, 43.37; H, 5.58; I, 40.97. Calculated for $C_{11}H_{17}IO_2$: C, 42.87; H, 5.57; I, 41.18%. ^1H NMR spectrum (δ, ppm): 6.28 m (1H,$>C{=}CHI$), 5.38–6.08 m (1H,$-CH{=}C<$), 4.83–5.28 m (2H,$>C{=}CH_2$), 4.52 broad s (1H, $-O-\underset{|}{C}H-O-$), 3.20–4.30 m (4H, 2 OCH_2), 2.95 d (2H, $-\underset{\|}{C}-CH_2-\underset{\|}{C}-$), 1.22–2.13 m (6H, 3 CH_2 of the tetrahydropyranyl ring).

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