SYNTHESIS OF 3,5-DIMETHYLENECYCLOHEXENE DERIVATIVES BY THE DEHYDROBORYLATION OF 3-BORABICYCLO[3.3.1]NON-6-ENE COMPOUNDS

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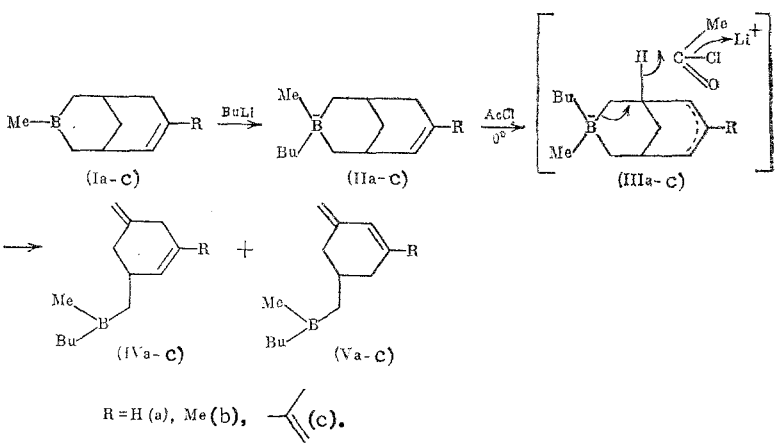
UDC 542.91:547.595.2:542.945.5:547.1'127

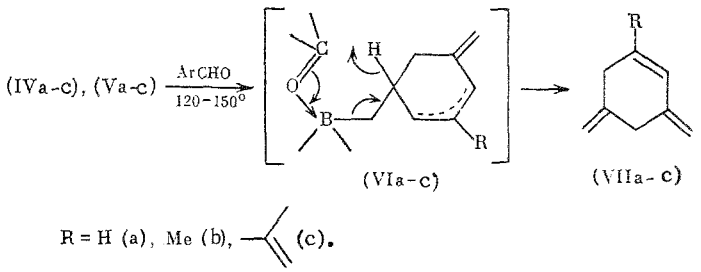
The hydroborylation of unsaturated compounds is a standard reaction in organic synthesis [1]. On the other hand, the reverse process, namely dehydroborylation, is often required, i.e., an olefin or diene must be obtained from the corresponding organoborane. The transalkylation of trialkylboranes by higher olefins or aromatic aldehydes may be used for this purpose [1]. The reactions of the corresponding borate complexes with an acyl chloride are used for the deborylation of bicyclic compounds [2, 3]. Although these reactions differ in mechanism, they all proceed with the removal of a hydride ion from the β-carbon atom.

In the present work, we describe the use of two types of β-hydride elimination for the synthesis of new 3,5-dimethylenecyclohexene derivatives from 3-borabicyclo[3.3.1]non-6-ene compounds (I) obtained by the allylboron–acetylene condensation [1].

Borate (IIa) prepared by the action of butyllithium on 3-methyl-3-borabicyclo[3.3.1]-non-6-ene (Ia) reacts with acetyl chloride to form a mixture of isomeric dienes (IVa) and (Va) in 68% yield.



Subsequent heating of the mixture of (IVa) and (Va) with an aromatic aldehyde [3] led to 3,5-dimethylenecyclohexene (in 64% yield); the overall yield of triene (VIIa) from bicyclic nonene (Ia) was 44%.



The conversion of (IVa) and (Va) to (VII) also proceeds by the elimination of a β-hydride hydrogen through the reductive action of trialkylboranes. There is evidence to suggest that

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2625-2627, November, 1987. Original article submitted March 27, 1987.

0568-5230/87/3611-2439$12.50

the reaction of organoboranes with an aromatic aldehyde is accomplished through cyclic transition state (VI) and is a synchronous process [4].

We should note that displacement of the double bonds to the ring does not occur under the reaction conditions and during the separation of (VIIa)-(VIIc).

EXPERIMENTAL

All the operations with the organoboron compounds were carried out in a dry argon atmosphere. The PMR spectra were taken on Bruker WM-250 and Tesla BS-467 spectrometers at 60 MHz. The ^{11}B NMR spectra were taken on a Bruker SXP/4-100 spectrometer. The IR spectra were taken on a UR-20 spectrometer.

3-Methyl-3-borabicyclo[3.3.1]non-6-ene (Ia). A sample of 28.7 g 3-methoxy-3-borabicyclo[3.3.1]non-6-ene [5] was added over 2 h to a solution of MeMgI obtained from 6.5 g Mg and 15 ml MeI in 100 ml ether. The mixture was heated at reflux for 1 h. The ethereal layer was separated and the residue was extracted with four 50-ml portions of hexane. Distillation gave 19 g (74.2%) (Ia), bp 55-56°C (13 mm), n_D^{18} 1.4885. Found, %: C 80.65, H 11.35, B 7.73. $C_9H_{15}B$. Calculated, %: C 80.65, H 11.28, B 8.07. IR spectrum (ν, cm^{-1}): 1645, 3018, and 3060 (C=CH). PMR spectrum in CCl_4 (δ, ppm): 0.65 s (CH_3), 1.2-1.26 m (10 H), 5.5 m (CH=C).

3,7-Dimethyl-3-borabicyclo[3.3.1]non-6-ene (Ib) was obtained by analogy from 31.3 g 3-methoxy-7-methyl-3-borabicyclo[3.3.1]non-6-ene [5] and MeMgI (from 5 g Mg and 13.5 ml MeI in 100 ml ether). The product yield was 22.17 g (78.6%), bp 49-50°C (6 mm), n_D^{22} 1.4819. Found, %: C 80.65, H 11.72, B 7.42. $C_{10}H_{17}B$. Calculated, %: C 81.12, H 11.57, B 7.30. PMR spectrum in $CDCl_3$ (δ, ppm): 0.65 s (3H, B–CH_3), 1.57 s (3H, CH_3–C=C), 5.42 m (1H, CH=C).

7-Isopropenyl-3-methyl-3-borabicyclo[3.3.1]non-6-ene (Ic) was obtained by analogy from 26 g 3-methoxy-7-isopropenyl-3-borabicyclo[3.3.1]non-6-ene [6] and MeMgI (from 3.16 g Mg and 8.2 ml MeI). The product yield was 17.4 g (73%), bp 59-60°C (1 mm), n_D^{20}1.5155. Found, %: C 82.83, H 11.19, B 5.99. $C_{12}H_{19}B$. Calculated, %: C 82.79, H 11.00, B 6.21. PMR spectrum in $CDCl_3$ (δ, ppm): 0.63 s (3H, B–CH_3), 1.85 s (3H, CH_3–C=C), 4.89 and 4.91 s (2H, CH_2=C), 5.89 d (1H, CH=C).

(5-Methylene-3-methyl-2-cyclohexen-1-yl)- (IVb) and (5-Methylene-3-methyl-3-cyclohexen-1-ylmethyl)butyl(methyl)borane (Vb). A sample of 20.9 g 3,7-dimethyl-3-borabicyclo[3.3.1]-non-6-ene (Ib) in 50 ml ether was added to a 250-ml three-necked flask and 65 ml 2.25 N n-BuLi in hexane was added at from −70 to −60°C. The mixture was warmed to 20°C and stirred for 1 h. Then the temperature was lowered to 0°C and 11.5 g acetyl chloride was introduced using a syringe through a rubber septum. A white precipitate formed. The mixture was maintained for 1 h at 20°C and ether was distilled off in vacuum. The residue was washed with three 50-ml portions of pentane. Distillation of the solvent gave 15.7 g (55%) of a ~1:1 mixture of (IVb) and (Vb) as indicated by PMR spectroscopy, bp 68-70°C (1 mm), n_D^{20} 1.4789. Found, %: C 81.99, H 12.21, B 5.09. $C_{14}H_{25}B$. Calculated, %: C 82.36, H 12.34, B 5.30. IR spectrum (ν, cm^{-1}): 889, 1612, 1630 sh, 1643, 3030 sh, 3080. PMR spectrum (δ, ppm): 0.78 s (3H, B–CH_3), 1.76 s and 1.67 s (CH_3–C=C), 4.62, 4.67, 4.69, and 4.74 (2H, CH_2=C), 5.23 (CH=C), 5.93 (CH=C–C=C).

Analogously, (Ia) and (Ic) gave (IVa) and (Va) and (IVc) and (Vc) in 68 and 70% yields, respectively.

3,5-Dimethylene-1-methylcyclohexene (VIIb). A mixture of 14.4 g of the mixture of (IVb) and (Vb) and 14 g veratraldehyde was heated in vacuum in a distillation apparatus. A sample of 6 g of a product with bp 60-75°C (14 mm) was obtained over 40 min with bath temperature 115-135°C. This product was redistilled in vacuum and subjected to chromatography on silica gel with pentane as the eluent. The product was redistilled to give 3.7 g (43%) (VIIb), bp 67-67.5°C (31 mm), n_D^{20} 1.5129. IR spectrum (ν, cm^{-1}): 890 (δ), 1610, 1653, 3019, 3080. PMR spectrum in $CDCl_3$ (δ, ppm): 2.78, 2.98 (4H, CH_2), 4.7 m and 4.76 m (4H, CH_2=C), 5.97 (1H, CH=C). ^{13}C NMR spectrum in $CDCl_3$ (δ, ppm): 137.2 (C^1), 125.5 (C^2), 143.4 and 143.6 ($C^{3,5}$), 39.0 and 39.5 ($C^{4,6}$), 108.2 and 108.4 ($\underline{CH_2}$=C), 23.1 (CH_3). Found, %: C 89.75, H 10.22. C_9H_{12}. Calculated, %: C 89.93, H 10.07. Gas-liquid chromatography indicated greater than 97% purity.

3,5-Dimethylenecyclohexene (VIIa) was obtained by analogy in 64% yield from (IVa) and (Va), bp 62-64°C (62 mm), n_D^{20} 1.5075, bp 65.5°C (77 mm), n_D^{20} 1.5130 [7]. IR spectrum (ν,

cm^{-1}): 890 (δ), 1600, 1640, 1658, 3032, 3080. PMR spectrum in $CDCl_3$ (δ, ppm): 2.88 and 3.09 (4H, CH_2), 4.79 m (4H, CH_2=C), 5.8 d. m and 6.18 d. m (2H, CH=CH, J = 9 Hz). ^{13}C NMR spectrum in $CDCl_3$ (δ, ppm): 128.3 (C^1), 129.3 (C^2), 142.9 and 143.05 ($C^{3,5}$), 39.8 (C^4), 33.7 (C^6), 110.5 ($\underline{C}H_2$=C–C=C), 108.3 ($\underline{C}H_2$=C). Found, %: C 90.45, H 9.65. C_8H_{10}. Calculated, %: C 90.50, H 9.50.

1-Isopropenyl-3,5-dimethylenecyclohexene (VIIc) was synthesized by analogy in 43% yield from (IVc) and (Vc), bp 77-78°C (7 mm), n_D^{20} 1.5645. IR spectrum (ν, cm^{-1}): 880 (δ), 1618, 1656, 3020, 3080, 3095. PMR spectrum in $CDCl_3$ (δ, ppm): 1.96 s (3H, CH_3), 3.04 m (4H, CH_2), 4.81 m, 4.9 and 4.93, 5.02 and 5.12 (6H, CH_2=C). ^{13}C NMR spectrum in $CDCl_3$ (δ, ppm): 142.6, 143.5, 143.6 ($C^{1,3,5}$), 126.3 (C^2), 39.5 (C^4), 34.5 (C^6), 112.05 and 112.65 ($\underline{C}H_2$=C–C=C–C=CH_2), 108.7 ($\underline{C}H_2$=C), 20.5 (CH_3). Found, %: C 90.10, H 9.56. $C_{11}H_{14}$. Calculated, %: C 90.35, H 9.65.

CONCLUSIONS

Two consecutive β-hydride elimination reactions in borate complexes derived from 3-borabicyclo[3.3.1]non-6-ene gave derivatives of 3-methylenecyclohexene and 3,5-dimethylenecyclohexene.

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