ORGANOBORON COMPOUNDS.

398. CONDENSATION OF TRIALLYLBORON WITH ALKENYLACETYLENES

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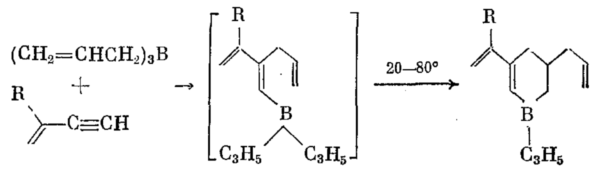
The reactions of allyl derivatives of boron with acetylenic compounds are used to prepare various classes of organic compounds [1-3]. We found that allylboron-acetylenic condensation of triallylborane (TAB) with vinyl- and isopropenylacetylene proceeds by the usual scheme [1-3] in three successive stages with the formation of cyclic or bicyclic boron derivatives with conjugated bonds.

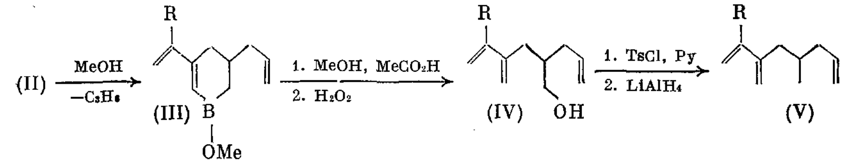
The condensation of TAB with alkenylacetylenes [4-6] begins at ~ 20°C with vigorous evolution of heat. At 20-80°C, 3-alkenyl-1,5-diallyl-1-bora-2-cyclohexene (II) is obtained. The products of allylboronation (I) cannot be isolated because of the high rate of the second stage of the reaction, i.e., the transformation of (I) into (II). A similar phenomenon has already been observed in the study of the condensation of TAB with acetylene, phenyl- and cyclohexenylacetylene, and also of trimethallylborane with alkylacetylenes [1-3].

Monocyclic boranes (II) are thermally stable up to 80°C, and can be isolated by distillation in a yield of ~85%.



R = H (a), Me (b).

In the action of methanol on (IIa) (an exothermal reaction), 1 mole of propylene is liberated and (IIIa) is obtained in a yield of 91%. This compound, and also (IIIb), is conveniently prepared without isolation of (II), by alcoholysis of the raw product of the reaction between TAB and alkenylacetylene (20-80°C); the yield of (IIIa, b) is > 80%, based on the initial TAB



R = H (a), Me (b).

1-Boracyclohexene compounds (II) and (III) polymerize by the action of O_2 to form a colorless porous compound. As in the case of 3-alkyl compounds [7], the $B-C_{sp^2}$ bond in the monocyclic compounds (III) is cleaved by heating with a mixture of MeOH and AcOH. The subsequent oxidation of the organoboranes formed leads to trienic alcohols (IVa, b). Tosylates of alcohols (IV) are converted by the action of $LiAlH_4$ into the corresponding previously unknown trienic hydrocarbons (Va, b). If this protolytic cleavage of boranes (III) is carried out by heating with higher organic acids, the trienes (V) obtained contain ~ 20% of an admixture of isomeric compounds (GLC)

$$\text{(IIIa)} \xrightarrow[150-200^\circ]{C_{17}H_{35}COOH} 80\%\ \text{(Va)} + 20\%\ \text{of isomers of (Va)}$$

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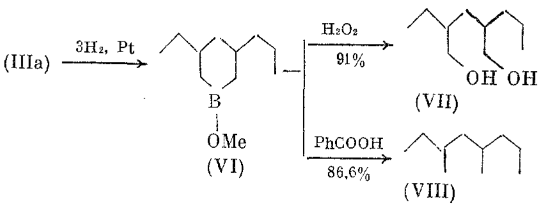
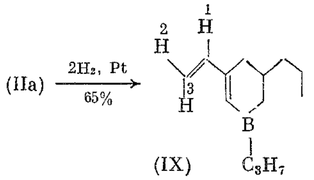
The methoxy derivative (IIIa) is readily hydrogenated over technical Pt black into a 1-boracyclohexane compound (VI), which on oxidation gives the diol (VII), and on acidolysis, the already described [8] 3,5-dimethyloctane (VIII)



Unexpectedly, only the allylic double bonds in 3-vinyl-1,5-diallyl-1-bora-2-cyclohexene (IIa) become hydrogenated under these conditions, and the conjugated system is not affected. Compound (IX) is obtained



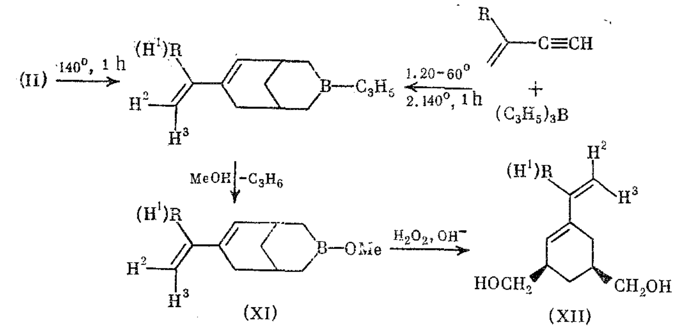
The reason for this difference in the behavior of (IIa) and (IIIa) remains unclear.

In the PMR spectrum of (IX), a multiplet of aliphatic protons is observed in the 0.7-2.8 ppm region, a singlet at 6.12 (BCH=C), and also three groups of signals (doublets of doublets) at 6.47 (H^1) and 5.17 (H^2) and 5.42 ppm (H^3) ($J_{H^1H^3}$ = 17.5, $J_{H^1H^2}$ = 10, $J_{H^2H^3}$ = 1.6 Hz), which indicates the presence of a 1,3-dienic system.

At 120-140°C, compounds (II) transform into 7-vinyl- (Xa) or 7-isopropenyl-3-allyl-3-borabicyclo[3.3.1]-non-6-ene (Xb). This transformation can easily be followed by IR spectra: a decrease, and then disappearance of an intense band at 1570 cm^{-1}, and the appearance of a band at 1610 cm^{-1} are observed. For complete transformation of (II) → (X), it is sufficient to heat the compound for 1 h at 135-140°C.

The bicyclic compounds (X) can be obtained by adding vinylacetylene or isopropenylacetylene to TAB heated to 120°C. Because of the heat of reaction, the temperature is spontaneously maintained at 120-140°C.

From the preparative point of view, the stagewise method is most convenient: At first the reaction is carried out at 20-60°C, and then the reaction mixture is heated for 1 h at 140°C. The yield of the bicyclic compounds (X), which are readily isolated by distillation, reaches 85%.



R = H (a), Me (b).

By the action of methanol on (X), 1 mole of propylene is liberated, and methoxy derivatives (XI) are obtained, which on oxidation yield cis-diols (XII) with a system of conjugated double bonds. The PMR spectra of the diols (XII) (broadened singlet of the vinyl cyclic proton, and not a doublet as in the bicyclic derivatives) indicates a pseudoequatorial orientation of the hydroxymethyl groups. Examination of the Dreiding models shows that the dihedral angle ($H^2C^2C^3H^3$) is close to 90°.

Our investigation demonstrates the high preparative importance of the allylboron-acetylenic condensation in the preparation of hydrocarbons, alcohols, and diols with a system of conjugated double bonds.

EXPERIMENTAL

All the operations with the organoboron compounds were carried out in a dry argon atmosphere. The IR spectra were measured on an UR-20 spectrometer; the PMR spectra, on the Varian DA-60-IL apparatus, using TMS as the inner standard.

3-Vinyl-1,5-diallyl-1-bora-2-cyclohexene (IIa). A 45.3 g portion of TAB was placed in a flask with a thermometer, magnetic stirrer, "cold finger" condenser (CO_2 + acetone) and a stopcock for admitting gas, and then over 1 h 25.9 g of vinlyacetylene were introduced from an ampul. An evolution of heat was observed. The mixture was cooled, while the temperature was maintained at 30-50°C, and then heated for 1.5 h at 50-60°C. By distillation, 51 g (83.5%) of (IIa), bp 71-72°C (2.5 mm), n_D^{20} 1.5220, were obtained. Found: C 83.84; H 10.50; B 6.04%. $C_{13}H_{19}B$. Calculated: C 83.90; H 10.29; B 5.81%. IR spectrum (ν, cm^{-1}): 1570, 1640, 3090 ($CH_2=CHC=CHB$), 1640 and 3080 ($CH_2=CH$). PMR spectrum (50% solution in CCl_4, δ, ppm): 0.58-2.75 m (aliphatic protons), 4.45-5.60 m ($CH_2=C$), 5.30-6.25 m ($CH=C$), 6.12 s ($BCH=C$), 6.42 d.d (H^1) ($J_{H^1H^3}$ = 17.5, $J_{H^1H^2}$ = 10.5 Hz). Compound (IIa) is soluble in organic solvents, spontaneously ignites in air, and polymerizes under the influence of traces of O_2.

1-Methoxy-5-allyl-3-vinyl-1-bora-2-cyclohexene (IIIa). a) A 10 ml portion of MeOH was cautiously added to 25.2 g of (IIa). With spontaneous evolution of heat, 3.05 liter of propylene were liberated. By distillation, 21.6 g (91%) of (IIIa), bp 60-61°C (3 mm), n_D^{20} 1.5103, were isolated. Found: C 75.22; H 9.60; B 6.09%. $C_{11}H_{17}BO$. Calculated: C 75.03; H 9.73; B 6.14%. IR spectrum: (ν, cm^{-1}): 890, 922, 1000, 1580, 1640, 1648, 3082, 3096. PMR spectrum (50% solution in CCl_4, δ, ppm): 0.6-2.7 m (aliphatic protons), 3.68 s (MeOB), 4.7-5.5 m ($CH_2=C$), 6.48 d.d (H^1) $J_{H^1H^3}$ = 17.5, $J_{H^1H^2}$ = 11 Hz). In the presence of traces of air, (IIIa) is transformed into a colorless porous polymer.

b) A 15.3 g portion of vinylacetylene was added at 50-60°C to 39.5 of TAB. The mixture was heated for 1 h at 55°C, and then 20 ml of MeOH were added. With evolution of heat, 6.8 liter (0.3 mole) of propylene were liberated. By distillation, 40.8 g (81%) of (IIIa), bp 78-80°C (4 mm), n_D^{20} 1.5101, were isolated.

1-Methoxy-3-isopropenyl-5-allyl-1-bora-2-cyclohexene (IIIb). An 11 ml portion of isopropenylacetylene was added in the course of 1 h, with stirring, to 15.7 g of TAB at such a rate that the temperature of the exothermal reaction did not exceed 60°C. The mixture was heated for 1 h at 60°C, and then 25 ml of methanol were added at 0-20°C (propylene is liberated). By distillation of the residue, 18.2 g of (IIIb) (82%), bp 67-68°C (1.5 mm), n_D^{20} 1.5107, were isolated. Found: C 76.13; H 9.85; B 5.56%. $C_{12}H_{19}BO$. Calculated: C 75.81; H 10.07; B 5.69%. IR spectrum (ν, cm^{-1}): 885, 915, 1000, 1016, 1575, 1640, 3075, 3092. PMR spectrum (40% solution in CCl_4, δ, ppm): 0.6-2.7 m (aliphatic protons), 1.88 s ($MeC=C$), 3.60 s (MeOB), 4.7-5.25 m ($CH_2=C$), 5.4-6.2 m ($CH=C$), 5.78 ($BCH=C$). Compound (IIb) becomes oxidized and polymerizes in air, and is soluble in organic solvents.

4-Methylene-2-allyl-5-hexene-1-ol (IVa). A mixture of 21.6 g of (IIIa), 34 ml of AcOH and 34 ml of MeOH was heated for 2 h at 95°C. After low-boiling compounds were removed in vacuo (2 mm), 65 ml of 10% NaOH were added to the residue, and then, at 0-5°C, 15 ml of 30% H_2O_2, and the mixture was left to stand overnight at 20°C. On the following day, it was extracted with ether (3 × 50 ml), and the ether extract was dried over Na_2SO_4. After distillation of the solvent, 14.9 g (81%) of (IVa), bp 85-85.5°C (4 mm), n_D^{20} 1.4895, were isolated. Found: C 78.60; H 10.62%. $C_{10}H_{16}O$. Calculated: C 78.85; H 10.59%. IR spectrum (ν, cm^{-1}): 900, 950, 1000, 1035, 1080, 1598, 1642, 3082, 3100, 3350. PMR spectrum (30% solution in CCl_4, δ, ppm): 1.48-2.55 m (aliphatic protons), 3.42 d (CH_2O, J = 5 Hz), 4.15 s (OH), 4.70-5.38 m ($CH_2=C$), 5.38-6.02 m ($CH=C$), 6.28 d.d (H^1) ($J_{H^1H^3}$ = 17.5, $J_{H^1H^2}$ = 11 Hz).

4-Methylene-2-allyl-5-methyl-5-hexen-1-ol (IVb). A 25 ml portion of AcOH was added to 11.8 g of (IIIb); the mixture became heated to 70°C. Then, 25 ml of MeOH were added, the mixture was boiled for 2 h (80°C), and the low-boiling compounds were distilled in vacuo (2 mm). To the residue, 38 ml of 10% NaOH were added, and then, at 0-5°C, 8 ml of 30% H_2O_2, and the mixture was left to stand overnight. On the following day, it was extracted with ether (4 × 50 ml). The ether extract, containing a small amount of a solid polymer, was filtered, and the filtrate dried over Na_2SO. After distillation of the solvent, 8.1 g (79%) of (IVb), bp 75-75.5°C (2 mm), n_D^{20} 1.4914, were isolated. Found: C 79.31; H 11.10%. $C_{11}H_{18}O$. Calculated: C 79.46; H 10.91%. IR spectrum (ν, cm^{-1}): 900, 950, 1000, 1035, 1600, 1640, 1642, 3075, 3098, 3360. PMR spectrum (30% solution in CCl_4, δ, ppm): 1.43-2.57 m (aliphatic protons), 1.87 s ($MeC=$), 3.40 d (CH_2O, J = 5 Hz), 3.60 s (OH), 4.70-5.20 m ($CH_2=C$), 5.37-6.10 m ($CH=C$).

3-Methylene-5-methyl-1,7-octadiene (Va). A solution of 22.6 g of p-toluenesulfonyl chloride in 37 ml of pyridine was added at 10-15°C to a solution of 17.7 g of (IVa) in 37 ml of pyridine. The mixture was stirred for 3 h at 20°C, then poured onto 170 g of ice, extracted with benzene, and the extract was dried over Na_2SO_4. After the benzene was removed in vacuo, a tosylate of alcohol (IVa) was obtained in the form of a viscous liquid, which was dissolved in a mixture of 60 ml of benzene and 200 ml of ether. To the solution obtained, a solution of 4.4 g of $LiAlH_4$ in 200 ml of ether was cautiously added at −70°C. The mixture was boiled for 4 h, and then 50 ml of water were added dropwise. The mixture was filtered, and the precipitate washed with ether. The organic layer was separated and dried over Na_2SO_4. By distillation, 12.8 g (82.5%) of hydrocarbon (Va), bp 62-62.5°C (29 mm), n_D^{20} 1.4588, were isolated. Found: C 88.03; H 11.84%. $C_{10}H_{16}$. Calculated: C 88.16; H 11.84%. IR spectrum (ν, cm^{-1}): 895, 918, 1000, 1600, 1640, 3082. PMR spectrum (50% solution in CCl_4, δ, ppm): 0.86 d (Me, J = 5 Hz), 1.50-2.00 m (aliphatic protons), 4.65-5.40 m ($CH_2{=}C$), 5.40-6.00 m ($CH{=}C$), 6.32 d.d (H^1) ($J_{H^1H^3} = 17.5$, $J_{H^1H^2} = 10.5$ Hz).

3-Methylene-2,5-dimethyl-1,7-octadiene (Vb). Similarly, from 6.1 g of carbinol (IVb) and 8 g of p-toluenesulfonyl chloride in 24 ml of pyridine, a tosylate was obtained in the form of a viscous liquid, which was reduced by 1.4 g of $LiAlH_4$ in 140 ml of ether. Yield, 4.1 g (74.5%) of (Vb), bp 67.5-68°C (21 mm), n_D^{20} 1.4641. Found: C 87.68; H 12.06%. $C_{11}H_{18}$. Calculated: C 87.92; H 12.07%. IR spectrum (ν, cm^{-1}): 895, 915, 1000, 1600, 1640, 1642, 3080, 3098. PMR spectrum (40% solution in CCl_4, δ, ppm): 0.82 d (Me, J = 6 Hz), 1.38-2.58 m (aliphatic protons), 1.85 ($MeC{=}$), 4.68-5.15 m (6H, $CH_2{=}C$), 5.35-6.05 m (1H, $CH{=}C$).

1-Methoxy-5-n-propyl-3-ethyl-1-boracyclohexane (VI). When 15.8 g of (IIIa), 0.1 g of technical Pt and 30 ml of hexane were shaken for 3 h in a hydrogenation flask, 6.05 liter of H_2 were absorbed. After filtration, 15.2 (93%) of (VI), bp 49-50°C (2.5 mm), n_D^{20} 1.4461, were isolated by distillation. Found: C 72.32; H 12.90; B 5.98%. $C_{11}H_{23}BO$. Calculated: C 72.54; H 12.72; B 5.94%. In the IR spectrum there is an intense band at 1370 cm^{-1} (BO). Compound (VI) is oxidized and hydrolyzed in air, and dissolves in organic solvents.

2-n-Propyl-4-ethyl-1,5-pentanediol (VII). A 24 ml portion of 30% H_2O_2 was added with stirring and cooling (0-5°C) to a mixture of 13 g of (VI) in 40 ml of 20% NaOH. On the following day, the mixture was extracted with ether, and the organic layer was dried over Na_2SO_4. By distillation, 11.4 (91%) of (VII), bp 132-134°C (3 mm), n_D^{20} 1.4604, were isolated. Found: C 68.93; H 12.50%. $C_{10}H_{22}O_2$. Calculated: C 68.92; H 12.72%. IR spectrum (ν, cm^{-1}): 1045, 1120, 1382, 1468, 2874, 2928, 2958 and a broad band at 3330.

3,5-Dimethyloctane (VIII). A mixture of 30 g of benzoic acid and 8.8 g of (VI) was heated in a Faworski flask for 30 min at 200-210°C in a vacuum of 155 mm; then 6.8 g of hydrocarbon (VIII), bp 105-107°C (155 mm) was distilled into the receiver. The compound was washed three times with a 3 N solution of alkali and H_2O, and then distilled over Na. Yield, 5.8 g (86.6%) of hydrocarbon (VIII), bp 158-159°C (754 mm) (comp. [7]). According to GLC data, the purity of (VIII) was > 99%.

1,5-Di-n-propyl-3-vinyl-1-bora-2-cyclohexane (IX). A 6.45 g portion of vinylacetylene was added in the course of 1 h at 30-45°C to 16.6 g of TAB. The mixture was heated for 1 h at 50-60°C, dissolved in 25 ml of hexane and hydrogenated in a hydrogenation flask over 0.1 g of technical Pt. After 5 h, 5.5 liter of H_2 were absorbed. After filtration and distillation, 15.5 g (65%) of (IX), bp 58-60°C (2 mm), n_D^{21} 1.4904, were isolated. Found: C 81.91; H 12.42; B 5.82%. $C_{13}H_{23}B$. Calculated: C 82.12; H 12.19; B 5.69%.

7-Vinyl-3-allyl-3-borabicyclo[3.3.1]non-6-ene (Xa). a) In a flask fitted with a "cold finger" condenser (CO_2 + acetone), thermometer, inlet for gas and magnetic stirrer, 31.5 g of TAB were placed, and 12.5 g of vinylacetylene were introduced from an ampul at such a rate that the temperature of the mixture was spontaneously maintained at 35-45°C (exothermal reaction). The mixture was left to stand for 1.5 h at 50-60°C, and then heated to 120°C; the temperature rose spontaneously to 140°C. The mixture was heated for 40 min at 135-140°C. By distillation, 32.2 g (74%) of (Xa), bp 72-73°C (2 mm), n_D^{20} 1.5210, were isolated. Found: C 83.70; H 10.38; B 5.92%. $C_{13}H_{19}B$. Calculated: C 83.90; H 10.29; B 5.91%. IR spectrum (ν, cm^{-1}): 1610, 1640, 3080, 3092 (double bonds). PMR spectrum (40% solution in CCl_4, δ, ppm): 0.78-2.75 (aliphatic protons), 4.71 d.d (H^2), 4.91 d.d (H^3), 6.18 d.d (H^1) ($J_{H^1H^3} = 17.5$, $J_{H^2H^3} = 1.6$ Hz), 5.65 br. d (ring $CH{=}C$, J = 5.5 Hz).

b) A 15.2 g portion of (IIa) was heated for 1 h at 120-140°C. In the IR spectrum, the band at 1570 cm^{-1} disappeared, and a band at 1610 cm^{-1} appeared. By distillation, 11.8 g (78%) of (Xa), bp 70-72°C (2.5 mm), were isolated.

7-Isopropenyl-3-allyl-3-borabicyclo[3.3.1]non-6-ene (Xb). A 6.7 g portion of isopropenylacetylene was added 12.4 g of TAB. The reaction proceeds with evolution of heat. The mixture was heated for 1 h at 50-60°C, and for 40 min at 120-140°C. By distillation, 15.6 g (85.1%) of (Xb), bp 76-77°C (2 mm), n_D^{20} 1.5223, were isolated. Found: C 83.74; H 10.77; B 5.80%. $C_{14}H_{21}B$. Calculated: C 84.01; H 10.53; B 5.41%. PMR spectrum (30% solution in CCl_4, δ, ppm): 0.80-2.78 (aliphatic protons), 1.75 ($MeC{=}C$), 4.42-4.95 ($CH_2{=}C$), 5.37-6.12 ($CH{=}C$ of the allylic radical), 5.75 br. d (ring $C{=}CH$, J = 5 Hz).

3-Methoxy-7-vinyl-3-borabicyclo[3.3.1]non-6-ene (XIa). A reaction mixture obtained by the above method from 15.7 g of TAB and 6.1 g of vinylacetylene, was heated for 1 h at 120-140°C. Then, at 0-20°C, 10 ml of MeOH were added to the mixture, which was heated to 70°C; 2.82 liter of propylene were liberated (in the qualitative formation of the bicyclic compound, 2.64 liter of the gas should be liberated). By distillation of the residue, 15.6 g (76.1%) of (XIa), bp 65-67°C (2 mm), n_D^{21} 1.5192, were isolated. Found: C 75.21; H 9.67; B 6.08. $C_{11}H_{17}BO$. Calculated: C 75.03; H 9.73; B 6.14%. PMR spectrum (50% solution in CCl_4, δ, ppm): 0.92 m (CH_2B), 1.58-2.75 m (aliphatic protons), 3.50 s (MeOB), 5.67 br.d (J = 5 Hz, ring CH=C), 6.22 d.d (H^1), 4.77 d.d (H^2), and 4.93 d.d (H^3) ($J_{H^1H^3} = 17.5$, $J_{H^1H^2} = 10$, $J_{H^2H^3} = 1.6$ Hz).

3-Methoxy-7-isopropenyl-3-borabicyclo[3.3.1]non-6-ene (XIb). a) A 5 ml portion of MeOH was added dropwise to 5.1 g of (Xb). With evolution of heat, 0.57 liter of propylene was liberated. The mixture was boiled for 10 min. By distillation, 4.63 g (95.4%) of (XIb), bp 69-70°C (2 mm), n_D^{20} 1.5188, were isolated. Found: C 75.66; H 10.45; B 5.35%. $C_{12}H_{19}BO$. Calculated: C 75.81; H 10.07; B 5.69%. IR spectrum (ν, cm^{-1}): 1606, 1631 and 3090. PMR spectrum (30% solution in CCl_4, δ, ppm): 0.92 m (CH_2B), 1.55-2.70 (aliphatic protons), 1.83 (MeC=C), 3.50 s (MeOB), 4.75 and 4.85 two m (CH_2=C), 5.80 br.d (ring C=CH, J = 6 Hz).

b) A 13.5 ml portion of isopropenylacetylene was added in the course of 40 min to 19.2 g of TAB. The temperature of the reaction was spontaneously maintained in the range of 40-60°C. Then, the mixture was heated for 40 min at 120-140°C, cooled to 0°C, and 12 ml of MeOH were cautiously added, so that 3.5 liter of propylene were liberated at 0-60°C. By distillation, 21.6 g (79%) of (IXb), bp 68-70°C (2 mm), n_D^{21} 1.5184, were isolated.

1-Vinyl-3,5-cis-dihydroxymethyl-1-cyclohexane (XIIa). A 50 ml portion of 20% NaOH was added with stirring, in the course of 1 h, to 23.7 g of (Xa). The hydrolysis proceeded with vigorous evolution of heat and liberation of propylene (2.84 liter, 0.127 mole). Then, at 0-5°C, 33 ml of 30% H_2O_2 were added in the course of 30 min. On the following day, the mixture was extracted with ether, and the extract was dried over Na_2SO_4. After removal of the solvent in vacuo, the residue (20.2 g), in the form of a colorless substance, mp 80-84°C, was crystallized from water. Yield, 16.6 g (76.5%) of (XIIa), mp 86-88°C. Found: C 70.89; H 9.36%. $C_{10}H_{16}O_2$. Calculated: C 71.39; H 9.58%. IR spectrum (ν, cm^{-1}): 1612, 1647, 3098 (CH=CCH=CH_2), 3330 and 3400 (OH). PMR spectrum (30% solution in CD_3OD), δ, ppm): 0.65-2.45 m (aliphatic protons), 3.40-3.60 m (CH_2O), 4.81 s (OH), 5.68 br.s (ring CG=C), 4.83 d (H^2) and 6.37 d.d (H^1) ($J_{H^1H^3} = 17.5$, $J_{H^1H^2} = 10$, $J_{H^2H^3} = 1.6$ Hz).

1-Isopropenyl-3,5-cis-dihydroxymethyl-1-cyclohexene (XIIb). A 20 ml portion of 20% NaOH was added to 3.5 g of (IXb), and then, at 0-5°C, (XIb), 5 ml 30% H_2O_2. On the following day, the organic layer was extracted with ether (3 ×40 ml). After the removal of ether, 3.2 g of a raw diol remained, which was crystallized from water. Yield, 2.68 g (82%) of (XIb), mp 95-97°C. Found: C 71.93; H 9.92%. $C_{11}H_{18}O_2$. Calculated: C 72.42; H 9.95%. IR spectrum (ν, cm^{-1}): 1611, 1635, 3095 (CH_2=C−C=CH), 3220, 3315 (OH). PMR spectrum (30% solution in CD_3OD, δ, ppm): 0.42-2.75 (aliphatic portions), 1.88 s (Me), 3.35-3.55 m (CH_2O), 4.72 s (OH), 4.82 and 4.95 (CH_2=C), 5.82 br. s (ring CH=C).

CONCLUSIONS

Condensation of triallylborane with vinyl- and isopropenylacetylene yields, depending on the temperature, the corresponding substituted derivatives of 2-borinene (20-80°C) or 3-borabicyclo[3.3.1]non-6-ene (120-140°C) with a system of conjugated double bonds. These compounds were used for the preparation of different derivatives of 1,3-butadiene, isoprene or vinylcyclohexene (hydrocarbons, alcohols or diols).

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HYDROSILYLATION OF DIALLYL SULFIDE WITH TRICHLOROSILANE

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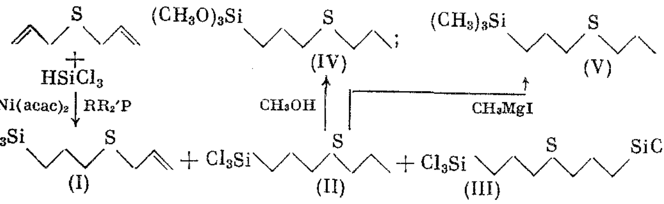
The hydrosilylation of unsaturated sulfides in the presence of metallocomplex catalysts proceeds in a much more complex way than in the case of their oxygen analogs, and is accompanied by several side processes [1-4]. In the presence of $H_2PtCl_6 \cdot 6H_2O$ and $(Ph_3P)_3RhCl$, triethyl-, triethoxy-, and diethylsilanes form monoadducts with dialkenyl sulfides [1, 2], and dialkylfluorosilanes also form bis-adducts [5]. The complex $(PhCN)_2PdCl_2 \cdot Ph_3P$, which is effective in the hydrosilylation of olefins, in the reaction with unsaturated sulfides cleaves the S−C bond in them [6]. The aim of the present work was to clarify the possible hydrosilylation of dialkenyl sulfides by readily accessible halohydrosilanes on the already described Ni−catalytic systems [7-9].

The data on the hydrosilylation of diallyl sulfide by trichlorosilane are given in Table 1. Depending on the experimental conditions, the molar ratio between the olefin and the silane, the phosphine and the solvent used, the process can be shifted in the direction of formation of one of the following reaction products (I)-(III):



The equimolar ratio between the reagents is optimal for the preparation of 7-trichlorosilyl-4-thiohept-1-ene (I), and the presence of a halophosphine increases its yield to 40%. With a twofold molar excess of $HSiCl_3$, 1-trichlorosilyl-4-thioheptane (II) is formed together with the bis-adduct (III). In mixtures containing products (I)-(III), the ratio between (I) and (II) was determined by GLC and PMR spectra. If the reaction is carried out under more rigid conditions (120°C, 3 h), (I) is not formed and products (II) and (III) are readily separated because of the great difference between their melting points. However, increase in temperature and duration of the process causes side processes already described [1, 2], i.e., disproportionation, polymerization and cleavage of the S−C bond. As a result, there is an increase in the formation of the polymeric residue and several low-boiling products, including $SiCl_4$ and $CH_3CH_2CH_2SiCl_3$, which were isolated in the form of methoxy derivatives. By treatment with methanol, the trichlorosilyl substituted sulfide (II) was converted into 1-trimethoxysilyl-4-thioheptane (IV).

Compound (II) was methylated without distillation of the low-boiling admixtures, since the trimethylsilyl derivatives of the decomposition products formed as the result of a reaction with a Grignard reagent are readily separated from 1-trimethylsilyl-1-thioheptane (V).

The side processes are suppressed when the hydrosilylation reaction is carried out in a solvent, for example, in chloroform the disproportionation of trichlorosilane is completely suppressed.

It should be noted that, in contrast to the Pt- and Rh catalysts [1, 2], with the nickel−phosphine system studied, unsaturated sulfides can be hydrolyzed by nearly one order of magnitude more rapidly and at a temperature lower by 20-40°C, which favors a decrease in side reactions.

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