

CONCLUSIONS

5-(Hydroxymethyl)-2,2,5-triphenyl-1,3,2,5-dioxaborataphosphoniarinane reacts with diphenylamine and o-aminobenzoic acid with the formation of 5-(aminomethyl)-2,2,5-triphenyl-1,3,2,5-dioxaborataphosphoniarinanes, whereas 1,5,3,7-diammoniadiphosphacyclooctanes are formed with m- and p-aminobenzoic acids. With o-aminobenzoic acid, hydroxymethylphosphines and hydroxymethylphosphonium salts give the corresponding aminomethylphosphines and aminomethylphosphonium salts.

LITERATURE CITED

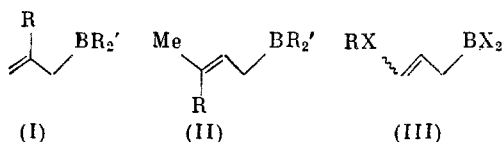
1. B. A. Arbuzov, O. A. Erastov, and G. N. Nikonov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 4, 952 (1980).
2. B. A. Arbuzov, O. A. Erastov, and G. N. Nikonov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 9, 2129 (1980).
3. B. A. Arbuzov, O. A. Erastov, G. N. Nikonov, et al., *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 8, 1845 (1983).
4. B. A. Arbuzov, O. A. Erastov, and G. N. Nikonov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 12, 2771 (1979).
5. B. A. Arbuzov, O. A. Erastov, G. N. Nikonov, et al., *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 7, 1545 (1981).

ISOPRENYLATION OF CARBONYL COMPOUNDS, ESTERS, AND ALKOXYACETYLENES WITH 2-DIPROPYLBORYLMETHYL-1,3-BUTADIENE AND THE SYNTHESIS OF IPSENOL AND IPSDIENOL

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Allyl derivatives of boron are used extensively for obtaining, modifying, and functionalizing different classes of organic compounds [1]. In their properties, chemical activity, and uses, these compounds differ significantly from other organoboranes; this is due to their ability to react with allyl rearrangement [1]. The properties of allyl (I, R = H), methallyl (I, R = Me), crotyl (II, R = H), and prenyl (II, R = Me) organoboranes [1, 2], as well as several 3-substituted organoboranes (III) (RX = RO, RS, R₃Si) [3], have been studied in detail.

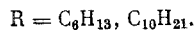
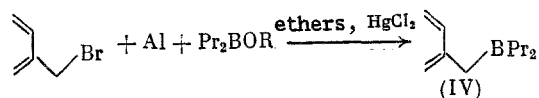


The present communication presents the synthesis of the first representative of a new type of allylborane - 2-dipropylborylmethyl-1,3-butadiene (IV) - and its use in the isoprenylation of carbonyl compounds, esters, and alkoxyacetylenes.*

Reagent (IV) was obtained in a yield of 75-80% by the reaction of 2-bromomethyl-1,3-butadiene, alkoxydipropylborane, and aluminum activated with mercuric chloride in a small amount of ether.

*For previous communication, see [4].

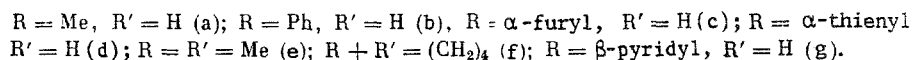
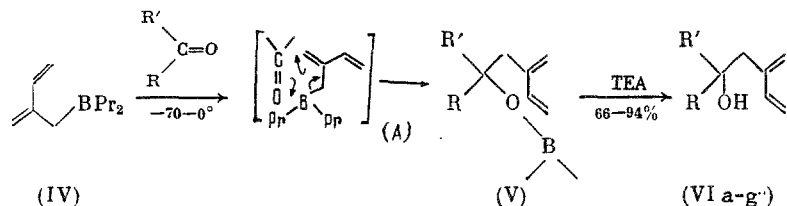
N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 6, pp. 1343-1351, June, 1989. Original article submitted August 6, 1987.



Borane (IV) is stable in an inert gas atmosphere, is not polymerized, and can be stored for long periods of time; it is easily oxidized and hydrolyzed in air.

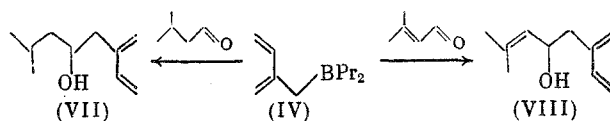
As might be expected, compound (IV) exhibits an enhanced chemical activity, which is characteristic for allyl derivatives of boron [1]. In the presence of water and alcohols, the bond between boron and the isoprenyl group is readily cleaved, affording isoprene and Pr_2BOR .

Borane (IV) reacts with aldehydes and ketones at -70 to 0°C by addition of the carbonyl group to form boron esters (V), whose reesterification with higher alcohols - for example, triethanolamine (TEA) - affords the corresponding dienyl alcohols (VIa-f) in a yield of 66-94%.



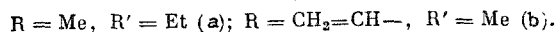
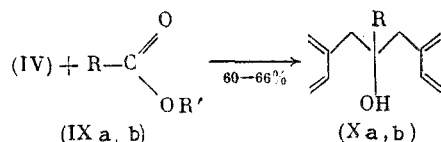
The reaction can be carried out without solvent by adding a carbonyl compound to (IV) in the ratio 1:1. If necessary, any inert solvent can be used: ether, THF, hexane, benzene, CCl_4 , etc.

We used the given isoprenylation method to synthesize ipsenol and ipsdienol [4], mono-terpenyl alcohols that are the basic components of the aggregational sex pheromone of bark beetles (*Ips* and *Pityokteines*) [5]. (\pm)-Ipsenol (VII) was obtained in a yield of 94% by the reaction of compound (IV) with isovaleric aldehyde, and (\pm)-ipsdienol (VIII) was synthesized in a yield of 96% by the isoprenylation of 3,3-dimethylacrolein.*



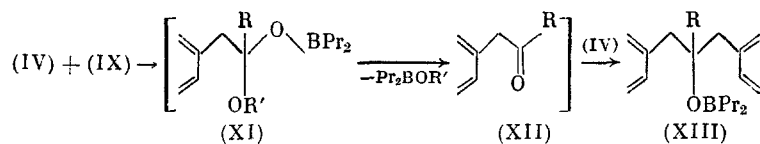
In the synthesis of 3-methylene-1-(β -pyridyl)pent-4-en-1-ol (VIg) from nicotinic aldehyde and compound (IV), 2 moles of (IV) per mole of carbonyl compound were used. The first mole of borane (IV) coordinates with the nitrogen atom of the pyridine ring to form a stable complex, which then undergoes isoprenylation by a second mole of (IV) to give the diboron compound.

When esters (IXa, b) react with compound (IV), they undergo diisoprenylation. However, these reactions are very slow. At room temperature and a (IV):(IX) ratio of 2:1, the reaction does not reach completion even after one week. When the reaction mixture was treated with TEA, tetraenyl (Xa) and pentaenyl (Xb) alcohols were obtained in a yield of over 60%.



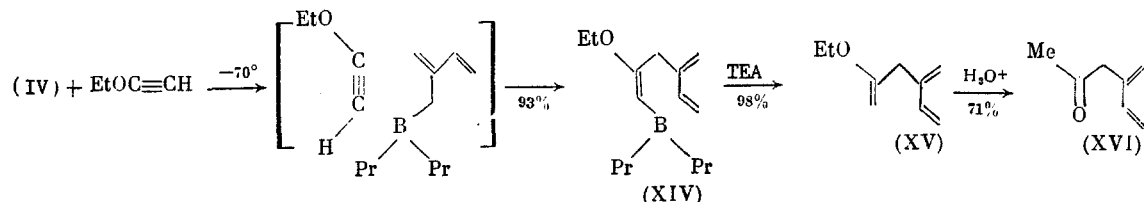
The isoprenylation of esters takes place according to the following proposed scheme:

*For the asymmetric synthesis of compounds (VII) and (VIII), see [6].



The first step consists of addition across the C=O bond, leading to the boron ketal (XI). This compound is unstable and decomposes (β -elimination) to the dipropylboric acid ester and ketone (XII). The latter is more reactive than ester (IX) and reacts immediately with a second molecule of (IV), affording ester (XIII). A similar pattern was observed earlier in the allylborylation of esters by triallyl-, diallyl(alkyl)-, or allyl(dialkyl)-boranes [7, 8]. It should be noted that allylborylation of carbonic acid esters, in contrast to the isoprenylation described in this work, is very rapid.

Compound (IV), like other allylboranes [1, 2], is readily added to ethoxyacetylene. The reaction takes place at -70 to 0°C and affords 1-dipropylboryl-E-2-ethoxy-4-methylene-1,5-hexadiene (XIV) in a yield of 93%.



This reaction is the first example of the isoprenylation of acetylene compounds.

When adduct (XIV) is treated with alcohols, the B-C bond is readily cleaved to give 2-ethoxy-4-methylene-1,5-hexadiene (XV). Compound (XV) can be conveniently obtained in a single flask without isolation of borane (XIV).

The hydrolysis of triene (XV) with 1% hydrochloric acid affords 2-vinyl-1-penten-4-one (XVI). In contrast to carbinols (VIa-g), (VII), (VIII), and (Xa, b), triene (XV), ketone (XVI), and borane (XIV) are not hydrolyzed at 0 - 20°C and may be stored for a long time at this temperature in an inert gas atmosphere.

Thus, 2-dipropylborylmethyl-1,3-butadiene (IV) is a convenient C-5 syntone and may be used successfully to insert an isoprene fragment into different organic compounds.

Several reagents for inserting an isoprene fragment into organic compounds are known at present. Thus, the Lewis acid- or Bu_4NF -initiated isoprenylation of carbonyl compounds by means of 2-trimethylsilylmethyl-1,3-butadiene [9], its tin analogs [10], and isoprene (ene reaction) [11] have been described. The zinc analog of 2-bromomethyl-1,3-butadiene has been shown to be a good isoprenylation reagent [12, 13] (attempts to obtain the analogous magnesium derivative and use it in synthesis have proven unsuccessful [12]).

It should be emphasized that the use of borane (IV) as an isoprenylation agent has many advantages compared with analogous derivatives, such as silicon and tin: the reactions take place under mild conditions, do not require catalysts, and are not complicated by side reactions. Moreover, borane (IV) can be used for the isoprenylation of acetylene compounds, which was not possible earlier. The structure of compounds (VI)-(XVI) was confirmed by IR and NMR spectroscopy.

The IR spectra of carbinols (VI), (VII), (VIII), and (X), boron esters (V), trienes (XIV) and (XV), and ketone (XVI) contain characteristic strong bands in the region 1595 - 1597 and 3090 cm^{-1} ; they contain bands of medium intensity at 1635 and 3010 cm^{-1} . The spectra of alcohols (VI), (VII), (VIII), and (X) have a broad band at 3300 - 3400 cm^{-1} (OH), with a shoulder at 3580 cm^{-1} (free hydroxyl). In the spectrum of borane (XIV) a very strong band at 1590 cm^{-1} (B-CH=C) is superposed over the band at 1595 cm^{-1} . Triene (XV) also has absorption bands at

1659 and 3120 cm^{-1} $\left(\begin{array}{c} \text{OEt} \\ | \\ \text{CH}_2=\text{C} \\ | \\ \text{C} \end{array} \right)$, and ketone (XIV) has a band at 1716 cm^{-1} $\left(\begin{array}{c} \text{C}=\text{O} \end{array} \right)$.

The structures of the synthesized compounds are also confirmed by ^1H and ^{13}C NMR spectra. Diene system protons have chemical shifts at 6.20 - 6.50 ppm for >C=CH and at 4.50 -

4.80 ppm for $\text{CH}_2=\text{C}$. The spin-spin interaction constants (SSIC) for protons in the trans position ($J_{\text{AX}}^{\text{trans}}$) range from 16.80 to 18.40 Hz, and those for protons in the cis position ($J_{\text{BX}}^{\text{cis}}$) range from 10.30 to 11.50 Hz, depending on the substituents.

The PMR spectra (250 MHz) of carbinols (VIa-g), (VII), and (VIII) exhibit a geminal nonequivalence of the CH_2 group at the asymmetric carbon atom at 0.05-0.15 ppm; the SSIC have the following values: $J^{\text{gem}} = 14.00 \pm 0.20$ Hz, $J^{\text{vic}} = 8.60 \pm 0.20$ and 4.20-5.20 Hz.

The chemical nonequivalence (0.01 ppm) of the CH_2 group in compound (Xb) is due to restrained rotation around the σ bond. Among other characteristics of the PMR spectra, the small values of the geminal and allyl SSIC of the diene system protons are to be noted; these are smaller than the resolution of the instrument (0.02 Hz) and do not appear in the spectra, which greatly simplifies their analysis. The very conservative nature of the chemical shifts and SSIC of the diene protons with respect to the effect of substituents should also be noted.

The ^{13}C spectra of the synthesized compounds contain all of the carbon atom signals. The isoprene fragment has signals at 42, 114, 119, 139, and 143 ppm.

EXPERIMENTAL

All operations with organoboron compounds were carried out in a dry argon atmosphere.

IR spectra were recorded on a UR-20 instrument. PMR spectra were recorded on Bruker-250 and Bruker-B-467 (60) instruments. ^{11}B and ^{13}C NMR spectra were recorded on a Bruker AM-300 instrument. Chemical shifts are shown on the δ scale relative to TMS.

2-Bromomethyl-1,3-butadiene [bp 63-65°C (82 mm)] was synthesized from isoprene according to [14].

Dipropylboric Acid Decyl Ester. A 41.4-g portion of decanol was added, after 40 min, to 36.6 g tripropylborane and 1 ml pivalic acid at 75-80°C. The reaction proceeded with evolution of heat and was accompanied by the release of propane. The mixture was heated for 1 h at 75-80°C; 46.6 g of product was isolated by distillation. Yield, 71%; bp 109-112°C (1.5 mm); n_D^{20} 1.4330. Found, %: C 75.69; H 13.82; B 3.85. $\text{C}_{16}\text{H}_{35}\text{BO}$. Calculated, %: C 75.58; H 13.38; B 4.26.

Dipropylboric acid hexyl ester was obtained analogously from tripropylborane and hexanol in a yield of 79%; bp 90-92°C (10 mm) (cf. [15]).

2-Dipropylborylmethyl-1,3-butadiene (IV). A 7-g portion of aluminum shavings, 0.1 g mercuric chloride, and 40 ml ether were placed in a three-necked bottle equipped with a mixer, dropping funnel, and a reflux condenser. The mixture was stirred for 10 min to activate the aluminum, 3 ml of 2-bromomethyl-1,3-butadiene were then added, and the mixture was heated to start the reaction (spontaneous boiling of ether). Then 28.0 g (0.19 mole) of 2-bromomethyl-1,3-butadiene and 37.7 g (0.19 mole) of dipropylboric acid hexyl ester were added dropwise. The reaction mass was boiled, with mixing, for another 2 h and cooled; ether was removed in a vacuum. The reaction mass was then heated carefully (70-110°C) to distill the fraction with a bp of 30-60°C (1.5 mm). A second distillation afforded 23.1 g (74%) of borane (IV); bp 39-40°C (1.5 mm), n_D^{20} 1.4569. Found, %: C 80.21; H 13.01; B 6.46. $\text{C}_{11}\text{H}_{21}\text{B}$. Calculated, %: C 80.51; H 12.90; B 6.59. The PMR spectrum (250 MHz, CDCl_3) is shown in Table 1. IR spectrum (without solvent): 1590, 1635, 3090 cm^{-1} .

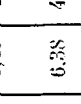
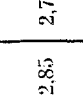
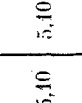
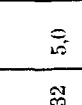

Analogously, 8.0 g of aluminum, 0.1 g mercuric chloride, 20.5 g (0.14 mole) 2-bromomethyl-1,3-butadiene, and 35.5 g (0.14 mole) dipropylboric acid decyl ester afforded 18.0 g (79%) of borane (IV).

Isoprenylation of Aldehydes. Synthesis of Ipsenol (VII). A 2.7-g portion of isovaleric aldehyde was added dropwise at -30°C to 5.2 g of borane (IV) in a distillation apparatus. The mixture was kept at 20°C for 30 min, then 6 ml of triethanolamine (TEA) was added. After distillation, 4.5 g (94%) of ipsenol (VII) was isolated; bp 94-96°C (19 mm), n_D^{20} 1.4654 (cf. [13]).

Carbinols (VIa), (VIe), (VIf), and ipsdienol (VIII) were obtained in an analogous manner (Table 2).

3-Methylene-1-phenyl-4-penten-1-ol (VIb). A 1.0-g portion of benzaldehyde was added at -70°C to 1.6 g of compound (IV) in 2 ml pentane. The mixture was kept for 30 min at 20°C, pentane was distilled off in a vacuum, and 2.5 ml TEA was added. A 1.5-g fraction (90%) of

TABLE 1. Chemical Shifts (δ , ppm) and SSIC (J, Hz) and SSIC (J, Hz) in the PMR Spectra of Compounds

$R_{i,j}$	δ_A	δ_B	δ_C	δ_D	δ_E	δ_F	J_X	δ_Y	J_{AX}	J_{BX}	J_{EP}	J_{EY}	J_{FY}	Remarks
CH_3- (VIa)	5.24	5.09	5.05	5.20	2.40	2.32	6.38	3.95	18.4	11.5	13.8	5.2	8.4	$\delta_{\text{CH}_3} = 1.22 \text{ d}$, $J = 6.8$, 7.30 m (5H); $\delta_{\text{OH}} = 2.12$
C_6H_5- (VIb)	5.32	5.13	5.08	5.15	2.70	2.58	6.40	4.82	17.2	10.5	13.7	4.2	8.5	
 (VIc)	5.27	5.11	5.08	5.14	2.81	2.68	6.38	4.85	17.4	10.4	14.2	5.2	8.8	$\delta_{\alpha} = 7.37$; $\delta_{\beta} = 6.52$; $\delta_{\gamma} = 6.25$; $\delta_{\text{OH}} = 2.50$
 (VI d)	5.33	5.18	5.13	5.20	2.85	2.72	6.44	5.10	17.5	10.5	14.0	14.8	8.8	$\delta_{\alpha} = 7.28$; $\delta_{\beta} = 7.0$; $\delta_{\gamma} = 7.4$; $\delta_{\text{OH}} = 2.35$
 (VIg)	5.25	4.80	5.10	5.10	2.65	2.65	6.42	5.10	17.8	10.5	-	-	7.0	$\delta_{\alpha} = \delta_{\beta} = 8.40$; $\delta_{\gamma} = 7.75$; $\delta_{\delta} =$ $= 7.25$; $\delta_{\text{OH}} = 5.10$ (60 MHz)
 (VIe)	5.32	5.0	4.85	5.32	2.30	-	6.25	-	17.8	10.5	-	-	-	$\delta_{\text{CH}_3} = 1.08 \text{ c}$; $\delta_{\text{OH}} = 1.60$ (60 MHz)
 (VI f)	5.34	5.12	5.08	5.22	2.55	-	6.43	-	16.8	10.3	-	-	-	$\delta_{\alpha}^{\text{equ}} = 1.80 \text{ m}$; $\delta_{\alpha}^{\text{ax}}$ and $\delta_{\beta} =$ $= 1.60 \text{ m}$

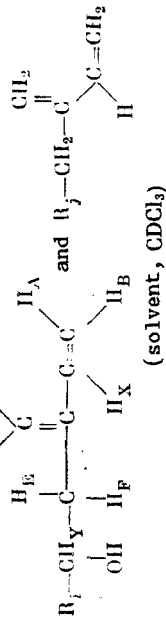
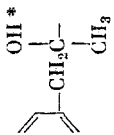
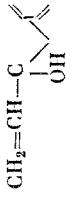
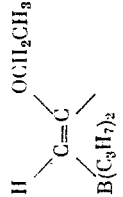
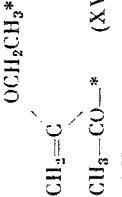


TABLE 1 (continued)

R_i, j	δ_A	δ_B	δ_C	δ_D	δ_E	δ_F	δ_X	δ_Y	J_{AX}	J_{BX}	J_{EF}	J_{EY}	J_{FY}	Remarks
$(CH_2)_2CHCH_2^{**}$ (VII)	5,15	4,95	4,95	4,95	2,22	2,15	6,27	3,75	19,0	11,2	-	-	-	1.85 sept ($\underline{CH(CH_3)_2}$), 0.9 d ($-CH_3$)
$(CH_2)_2C=CH^{**}$ * (VIII)	5,30	4,85	5,05	5,10	2,30	2,17	6,25	4,30	16,9	10,8	-	-	-	1.62 s and 1.53 s ($-CH_3$); $\delta_{OH} = 2.60$ (60 MHz)
 (Xa)	5,30	5,15	5,0	5,20	2,37		6,40	-	17,4	11,2	-	-	-	$\delta_{CH_3} = 1.04$ s; $\delta_{OH} = 1.50$ (60 MHz)
 (Xb)	5,30	5,10	5,07	5,25	2,54	2,53	6,40	-	18,0	10,8	15,5	-	-	$\delta_{OH} = 1.95$; 5.85 d,d ($J = 16,7$ and 10.5) ($CH=C$), 5.47 d ($J = 16.7$), 5.03 d ($J = 10.5$, $CH_2=C$)
 (XIV)	5,25	5,05	4,95	5,15	3,28		6,50	-	18,0	11,0	-	-	-	5.25 s ($\triangle B-CH=$), 3.88 q (OCH_2 , $J = 7.0$), 1.30 m ($-CH_2-$), 0.93 t (CH_3)
 (XV)	5,15	4,90	5,0	5,0	2,85		6,25	-	17,5	11,0	-	-	-	3.76 s ($CH_2=C$), 3.62 q ($-OCH_2-$), 1.18 t (CH_3- , $J = 7.0$) (60 MHz)
$CH_2=CO^{**}$ (XVI)	5,25	4,90	5,2	5,2	3,16		6,33	-	17,6	10,9	-	-	-	2.02 s (CH_3CO-) (60 MHz)
$(C_6H_7)_2^{**}$ (IV)	4,83	5,0	4,88	5,05	2,28		6,47	-	17,0	10,6	-	-	-	1.47 tr.q ($C-CH_2-C$, $J = 7$ and 7.2), 1.24 t ($\triangle B-CH_2$, $J =$ $7.7 = 7.6$), 0.95t ($-CH_3$)

*Solvent, CCl_4 .**Solvent, C_6D_6 .

TABLE 2. Characteristics of the Synthesized Compounds

Compound	Yield, %	Bp, °C mm (p, mmHg)	n_D^{20}	Found Calculated, %	
				C	H
(VIa)	86	67-68(19)	1.4680	<u>75.10</u> 74.95	<u>10.64</u> 10.78
(VIb)	90	76-77(2)	1.5500	<u>82.62</u> 82.72	<u>8.08</u> 8.10
(VIc)	73	77-80(2)	1.5180	<u>73.03</u> 73.14	<u>7.42</u> 7.37
(VIId)*	66	**	1.5633	<u>66.31</u> 66.63	<u>6.75</u> 6.71
(VIg)	64	**	1.5550	<u>75.68</u> 75.39	<u>7.48</u> 7.48
(VIe)	96	55-56(15)	1.4605	<u>76.26</u> 76.14	<u>11.06</u> 11.18
(VIf)	60	89-90(10)	1.5019	<u>78.65</u> 78.89	<u>10.62</u> 10.62
(VII)	94	94-96(19) **	1.4654		
(VIII)	96	48-50(1) ***	1.4879		
(Xa)	61	70-72(2)	1.5084	<u>80.94</u> 80.85	<u>10.14</u> 10.18
(Xb)	66	78-80(2)	1.5113	<u>81.25</u> 82.05	<u>9.41</u> 9.54
(XIV) ****	93	75-78(1,5)		<u>76.67</u> 76.93	<u>11.55</u> 11.55
(XV)	98	56-57(19)	1.4613	<u>77.91</u> 78.21	<u>10.07</u> 10.21
(XVI)	71	74-76(58)	1.4661	<u>76.09</u> 76.32	<u>8.87</u> 9.15

*Found, %: S 17.60. Calculated, %: S 17.79.

**The material was purified on a column and was not distilled.

***Cf. [13].

****Found, %: B 4.71. Calculated, %: B 4.62.

carbinol (VIb) was distilled from the reaction mixture; bp 98-104°C (3 mm). This fraction was further purified on an SiO₂ column (160/100 μ ; eluent, hexane-ether, 7:1; R_f 0.56 (Silufol, pentane:ether = 5:1) and distilled; bp 76-77°C (2 mm).

Alcohols (VIc, d) were synthesized in an analogous manner (see Table 2).

3-Methylene-(β -pyridyl)pent-4-en-1-ol (VIg). A 1.0-g portion of 3-pyridine aldehyde in 1 ml benzene was added after 20 min to 1.5 g borane (IV) in 2 ml benzene at 0-5°C. The mixture was colored bright yellow due to complex formation. An additional 1.5 g of compound (IV) was then added, and the mixture was kept for 1 h at ~20°C. The completion of the reaction was monitored by the disappearance of the band at 1735 cm⁻¹ (>C=O) in the IR spectrum. Benzene was removed in a vacuum, the residue was dissolved in ether, and 4.0 ml of H₂O, 4.1 ml of 6 N NaOH, and 8.3 ml of 30% H₂O₂ were added, with mixing (-10 to 0°C). The mixture was stirred for 3 h at 20°C, the ether layer was removed, and the aqueous layer was extracted with ether (2 \times 10 ml). The extracts were cooled and dried with Na₂SO₄. After removal (in a vacuum) of ether and propanol, formed as a result of the oxidation of the Pr-B< fragment, 1.9 g of a brownish oil was obtained. Chromatography on 60 g SiO₂ (eluent, hexane: ether = 1:6) afforded 1 g (64%) of carbinol (VIg); n_D^{20} 1.555, R_f 0.30 (Silufol, hexane: ether = 1:3).

3,7-Dimethylene-5-methylnona-1,8-dien-5-ol (VIIIa). A 0.6-g portion of ethyl acetate was added at 0°C to 2.2 g of compound (IV). The mixture was kept for 1 week at 20°C. Unreacted ethyl acetate was distilled in a vacuum, and 4.5 ml TEA was added to the residue. Pure carbinol (VIIIa) was isolated from the distilled fraction (bp 70-80°C at 2 mm) by chromatography on SiO₂; R_f 0.67 (Silufol, pentane:ether = 5:1); bp 70-72°C (2 mm); yield, 0.8 g (61%); n_D^{20} 1.5084.

3,7-Dimethylene-5-vinylnona-1,8-dien-5-ol (VIIIb) was obtained in an analogous manner; R_f 0.50 (Silufol, pentane:ether = 10:1) (see Table 2).

1-Dipropylboryl-E-2-ethoxy-4-methylene-1,5-hexadiene (XIV). A 0.9-g portion of ethoxyacetylene was added at -70°C to 2.2 g of borane (IV) in 5 ml pentane. The mixture was kept for 30 min at $\sim 20^\circ\text{C}$, after which 2.4 g (93%) of borane (XIV) was isolated by distillation; bp $75-78^\circ\text{C}$ (1.5 mm).

2-Ethoxy-4-methylene-1,5-hexadiene (XV). A 4.3-g portion of ethoxyacetylene was added at -70°C to 10.0 g of borane (IV) in 5 ml pentane. The mixture was kept for 30 min at $\sim 20^\circ\text{C}$. The solvent was then distilled in a vacuum, and 8 ml of TEA was added. Distillation afforded 8.2 g (98%) of triene (XV), with a bp of $50-58^\circ\text{C}$ (19 mm). Repeat distillation afforded 7.7 g (89%) of triene (XV), with a bp of $56-57^\circ\text{C}$ (19 mm).

2-Vinyl-1-penten-4-one (XVI). A mixture of 5.7 g of triene (XV) and 5 ml of 1% hydrochloric acid were mixed for 1.5 h at $\sim 20^\circ\text{C}$. The organic layer was separated, and the aqueous layer was extracted with ether (2×5 ml). The extracts were pooled with the organic layer, washed with aqueous K_2CO_3 and water to a neutral reaction, and dried with Na_2SO_4 . A 3.2-g yield (71%) of ketone (XVI) was obtained; bp $74-76^\circ\text{C}$ (58 mm); n_D^{20} 1.4661.

CONCLUSIONS

1. 2-Dipropylborylmethyl-1,3-butadiene, the first example of allylboranes with a 1,3-diene system, was synthesized by the reaction of 2-bromomethyl-1,3-butadiene, aluminum, and alkoxy(dipropyl)borane.

2. A convenient method was developed for obtaining dienyl and polyenyl alcohols, ketone, and vinyl esters. The method is based on the isoprenylation of carbonyl compounds, esters, and ethoxyacetylene by means of 2-dipropylborylmethyl-1,3-butadiene.

LITERATURE CITED

1. B. M. Mikhailov and Yu. N. Bubnov, *Organoboron Compounds in Organic Synthesis*, Harwood Academic Publ., London-Paris-Utrecht-New York (1984).
2. Yu. N. Bubnov, M. Sh. Grigorian, A. V. Tsyban' (Tsyban), and B. M. Mikhailov, *Synthesis*, 902 (1980).
3. R. W. Hoffmann and R. Metternich, *Liebigs Ann. Chem.*, 2390 (1985).
4. Yu. N. Bubnov and M. Yu. Étinger, *Tetrahedron Lett.*, 26, 2797 (1985).
5. A. M. Moiseenkov, K. V. Lebedeva, and B. A. Cheskis, *Usp. Khim.*, 53, 1709 (1984).
6. Yu. N. Bubnov and M. Yu. Étinger, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1687 (1988).
7. B. M. Mikhailov, Yu. N. Bubnov, A. V. Tsyban' (Tsyban), and M. Sh. Grigorian, *J. Organomet. Chem.*, 154, 131 (1978).
8. B. M. Mikhailov, Yu. N. Bubnov, and A. V. Tsyban', *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1892 (1978).
9. A. Hosomi, Y. Araki, and H. Sakurai, *J. Org. Chem.*, 48, 3122 (1983).
10. A. Hosomi, H. Iguchi, M. Endo, and H. Sakurai, *Chem. Lett.*, 977 (1979).
11. B. B. Snider and D. J. Rodini, *Tetrahedron Lett.*, 21, 1815 (1980).
12. R. G. Riley, R. M. Silverstein, J. A. Katzenellenbogen, and R. S. Lenox, *J. Org. Chem.*, 39, 1957 (1974).
13. A. G. Martinez and J. L. M. Contelles, *Synthesis*, 742 (1982).
14. R. C. Krug and T. F. Yen, *J. Org. Chem.*, 21, 1082 (1956).
15. B. M. Mikhailov and L. S. Vasil'ev, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 682 (1962).