### ORGANOBORON COMPOUNDS.

# 358. REACTION OF LITHIUM ETHOXYETHYNYLTRIALKYLBORANATES

# WITH ELECTROPHILIC REAGENTS

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The reaction of 1-alkynyltrialkylboranates of alkali metals (I) with electrophilic reagents, which is a new method for the formation of a C-C bond, includes an attack of the electrophile on the  $\beta$  C atom of the triple bond, causing the migration of an alkyl radical from the B atom to the  $\alpha$  C atom [1, 2]:

 $\begin{array}{c} R_{3}\bar{B}-C\equiv C-R'+X-Y \rightarrow \\ (I)\\ R=Alk \end{array} \xrightarrow{\delta^{+}} C=C \xrightarrow{R'} X + Y^{\Theta}$ 

This scheme is of a general nature for various electrophilic reagents (HHal, RCOOH, RSHal, RCOHal, RHal,  $R_2SO_2$ , and  $R_3\overline{OX}$ ). At the same time, the application of water to boranates of type I results in the cleavage of the B-C<sub>SP</sub> bond and the formation of a 1-alkyne and trialkylborane [3]:

$$R_{3}\overline{B} - C \equiv CR'Li^{+} + H_{2}O \rightarrow R_{3}B + HC \equiv CR' + LiOH$$
(2)

The reaction of trimethylchlorosilane with I proceeds according to scheme (1) with 1,2 migration of an alkyl and according to scheme (2) [4].

We studied the lithium ethoxyethynyltrialkylboranates, which, as it turned out, have specific chemical features not characteristic of 1-alkynyltrialkylboranates of type I.

The lithium ethoxyethynyltrialkylboranates (II) were synthesized by reacting equimolar amounts of the trialkylborane and lithium ethoxyacetylide in an ether-THF mixture at 0°C. The formation of a compound of tetracoordinated B is indicated by a signal in the <sup>11</sup>B NMR spectrum with a chemical shift of 20 ppm relative to  $Et_20$ ·BF<sub>3</sub>:

$$R_{3}B + \text{LiC} \equiv \text{COEt} \rightarrow R_{3}\overline{B}C \equiv \text{COEtLi}^{+}$$

$$R = n - Pr, n - Bu, s - Bu, n - C_{5}H_{11}$$
(3)

When water is added, the boranates of type II, like the boranates of type I, undergo hydrolysis according to Eq. (4):

$$R_{2}\overline{B}C \equiv C - OEtLi^{+} + H_{2}O \rightarrow R_{3}B + HC \equiv C - OEt + LiOH$$
(4)

The reaction of lithium 1-alkynyltrialkylboranates with iodine is known to produce acetylene hydrocarbons with good yields [5, 6]:

$$R_{3}\overline{B}C \equiv CR'Li^{+} + I_{2} \rightarrow \underset{R}{\overset{R_{2}B}{\longrightarrow}} C = C \overset{\mathcal{A}R'}{\overset{I}{\longrightarrow}} + L_{II} \rightarrow R_{2}BI + RC \equiv CR'$$
(5)

We might have hoped to use this method to obtain alkylethoxyacetylenes, which have found great applications in organic synthesis [7], from boranates of type II. However, the execution of the reaction of compounds of type II with iodine under the conditions in [5] did not lead to positive results, although the formation of an alkylethoxyacetylene during the reaction was established from the IR spectra. The spectrum of boranates of type II

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(1)

R	R'Hal	R′C≡COEt	Yield,
n-Pr n-Bu n-C <sub>5</sub> H <sub>i1</sub> cyclo-C <sub>5</sub> H n-Pr	MeI CH <sub>2</sub> =CHCH <sub>2</sub> Br CH <sub>2</sub> =CHCH <sub>2</sub> I CH <sub>2</sub> =CHCH <sub>2</sub> Br Me CH <sub>2</sub> Br	$MeC=COEt$ $CH_2=CHCH_2C=COEt$ $CH_2=CHCH_2C=COEt$ $CH_2=CHCH_2C=COEt$ $Me$ $CH_2C=COEt$ $Me$ $Me$	35 * 33 37 60 30

TABLE 1. Acetylene Compounds R'C $\equiv$ COEt Obtained by Reacting R<sub>3</sub> $\overline{B}C\equiv$ COC<sub>2</sub>H<sub>5</sub>Li<sup>+</sup> with R'Hal

\*According to GLC data.

in solution is characterized by an intense band at 2165 cm<sup>-1</sup> (C=C). Immediately after the addition of the iodine solution this absorption disappears, and a band appears at 2270 cm<sup>-1</sup>, which is characteristic of alkylethoxyacetylenes [7]. The intensity of this band decreases sharply with time. The corresponding decrease in the relative concentration of the 1-ethoxy-alkylacetylenes is clearly attributable to their sensitivity to the action of the electrophiles [7], i.e., to I<sub>2</sub> and R<sub>2</sub>BI, which were present in the reaction mixture, in the case investigated. The indicated difficulty in obtaining 1-ethoxyalkylacetylenes by this method could be overcome by carrying out the reaction at  $-78^{\circ}$ C in the presence of quinoline. Under these conditions the expected acetylene compounds of type III were isolated in the individual state with yields ranging from 30 to 60% [8]:

$$R_{3}\overline{B}C \equiv COEt + I_{2} \xrightarrow{C_{3}H_{7}N} RC \equiv COEt$$
(III)
$$R = n-Bu, s-Bu, cyclopentyl$$
(6)

It should be stressed that the reaction is of preparative significance for the introduction of secondary alkyl groups, since the direct alkylation of lithium ethoxyacetylide has been described only for primary alkyl halides [7, 9, 10].

Boranates of type II react under mild conditions with MeI and  $CH_2$ =CHCH<sub>2</sub>Hal according to a reaction of the Wurtz type, yielding methyl- and allylethoxyacetylene, respectively (Table 1):

$$R_{3}\overline{B}C \equiv COEtLi^{+} + R'Hal \rightarrow R_{3}B + R'C \equiv COEt + LiHal$$
(IV)
$$R' = Me, CH_{2} = CHCH_{2}$$
(7)

As we have already noted, the latter type of conversion is not characteristic of the reactions of lithium 1-alkynyltrialkylboranates with electrophiles and is observed only in the case of the reaction of I with water [3] and partially with Me<sub>3</sub>SiCl [4]. The 1-ethoxy-4-alken-1-ynes obtained according to reaction (7) (see Table 1) do not contain admixtures of allenes. This is of practical interest, since the reaction of allyl halides with lithium ethoxyacetylide is accompanied by isomerization of a considerable portion of the acetylene compounds to allenes [10].

The decreased yields of the ethoxyacetylene compounds (see Table 1) were evidence of some secondary reactions, apparently intramolecular alkylation according to scheme [8], which is characteristic of 1-alkynyltrialkylboranates and results in the formation of compounds of type V:

$$R_{3}\overline{B}C \equiv COEtLi^{+} + R'Hal \rightarrow \underset{R_{2}B'}{\overset{R}{\longrightarrow}} C = C \overset{rOEt}{\overset{R}{\longrightarrow}} + LiHal$$
(8)

TABLE 2. Acetylene Compounds Obtained by Reacting  $H_2O$  or  $I_2$  with the Products of the Reaction of  $R_3\overline{B}C\equiv$ COEtLi<sup>+</sup> with  $R_3B$  [11]

	Yield,	6
R	RC≕CH	RG==CR
n-Pr n-Bu n-C <sub>5</sub> H <sub>11</sub> C <sub>3</sub> H <sub>5</sub> **	84 84 58 59	87 63 50 *

\*Isolated preparatively. +The reaction was carried out at -78°C.

However, in the experiments with geranyl bromide and lithium ethoxyethynyltripropylboranate among the reaction products we expected to find both geranylethoxyacetylene, which forms according to scheme (7), and an organoboron compound, which has, as the spectral and chemical data indicated, structure VI



The PMR spectrum of VI has signals of the geranyl radical at 1.60 (MeC=C), 1.92 (C= $CCH_2CH_2C=C$ ), 2.68 (C= $CCH_2C=C$ ), and 4.99 ppm (HC=C), as well as signals of propyl protons at 0.75-1.45 ppm. At the same time, the spectrum contains only traces of the methylene protons of the ethoxy group at 3.7 ppm, which should be present in compound V. The protolysis product of borane VI produces a mass spectrum containing a molecular ion with m/e 248, which corresponds to the replacement of the dipropylboryl group in VI by a hydrogen atom.

The investigation of the reaction of lithium ethoxyethynyltripropylboranate with MeI conclusively cleared up the situation with respect to the structure of the compounds formed when alkyl halides are reacted with compounds of type II. This reaction results in the formation of both 1-ethoxy-1-propyne (see Table 1) and the alkenyldipropylborane (VII):



The IR spectrum of VII has an absorption band at 1628  $\text{cm}^{-1}$  (B-C=C), but in the PMR spectrum there are only signals of aliphatic protons. Protolysis of borane VII by triethanolamine resulted in the formation of a mixture of the E and Z isomers of 4-methyl-4-octene.

The question of the path for the formation of borane VII arises. The following conversions may be postulated. The trialkylborane is obtained at first according to scheme (7) and is then added at the triple bond of the original boranate of type II to form the alkenyltrialkylboranate (VIII) [Eq. (9)], which is converted with the elimination of  $R_2BOEt$  into the 1-alkynyltrialkylboranate (IX) [Eq. (10)]. The latter then reacts with MeI to form VII [Eq. (11)]:

 $R_{3}\overline{B}C \equiv COEt + R_{3}B \rightarrow C = C$ (9)
(II)  $R_{2}B (VIII)$ 

$$\begin{array}{c} R_{3}\overline{B} & OEt \\ C=C & \rightarrow R_{3}\overline{B}C\equiv CR + R_{2}BOEt \\ R_{2}B & R & (IX) \end{array}$$

$$(10)$$

$$R_{3}\overline{B}C \equiv CR + MeI \rightarrow (VII)$$
(11)

This hypothesis is based on the discovery of significant amounts of the ethyl dialkylborate, which was detected in the <sup>11</sup>B NMR spectra ( $\delta$  -50 ppm relative to Et<sub>2</sub>0·BF<sub>3</sub>), in the reaction mixture. In addition, in one case, ethyl diamylborate was isolated from the reaction mixture and characterized by elemental analysis and its PMR spectrum. Evidence in support of the postulated paths for the formation of alkenylborane VII would be provided by the ability of compounds of type II to react with trialkylboranes according to Eqs. (9) and (10). It was found that such a reaction does, in fact, take place. The addition of a trialkylborane to a solution of a compound of type II in an ether-THF mixture is accompanied by an increase in the temperature of the mixture, the course of the reaction being monitored according to the changes in the IR and <sup>11</sup>B NMR spectra. The IR spectrum shows a sharp decrease in the absorption at 2165 cm<sup>-1</sup> (compound of type II, C=CO), and a weak band appears at 2150 cm<sup>-1</sup> (compound of type IX). The <sup>11</sup>B NMR spectrum contains the following signals: at 20 ppm, which is characteristic of boranates of type I, and at -50 ppm, which is caused by the dialkylborate.

Further support for schemes (9) and (10) was obtained by chemical methods. The decomposition of the reaction products by water yields terminal acetylenes [Eq. (2)], while the action of iodine [Eq. (5)] produces symmetrical dialkylacetylenes (both reactions are unequivocal evidence of the formation of boranate IX):

$$R_{3}\overline{B}C\equiv CR - | \xrightarrow{H_{2}O} RC\equiv CH \\ I_{2} RC\equiv CR$$

The results of the experiments are presented in Table 2.

Thus, reactions (9) and (10) represent the transition from the ethoxyacetylene to the terminal alkyl- and symmetrical dialkylacetylenes. It is noteworthy that only primary trialkylboranes undergo reactions (9) and (10). When a boranate and a trialkylborane with different alkyls are used, a mixture of all the possible alkynes in the particular case forms:

$$(n-C_{5}H_{11})_{3}\overline{BC} \equiv COEt + (n-Pr)_{3}B - \begin{vmatrix} H_{12}O \\ 34\% \\ I_{2} \\ m-PrC \equiv CPr-n + n-C_{5}H_{11}C \equiv CC_{5}H_{11}-n \\ I_{2} \\ 25\% \\ 20\% \\ 20\% \\ 20\% \\ 24\% \end{vmatrix}$$

The latter finding is clearly due to the rapidly established equilibrium in the boranatetrialkylborane system:

$$R_{3}\overline{B}C \equiv COEt + R_{3}'B \gtrsim R_{3}'BC \equiv COEt + R_{3}B$$

### EXPERIMENTAL

All the operations with the organoboron compounds were carried out in an atmosphere of dry nitrogen. The PMR spectra were recorded on a Varian DA-60IL instrument, the internal reference was HMDS, and the chemical shifts are given relative to TMS.

The chromatographic analysis of the alkynes was carried out on a Khrom-2 instrument, the column was 50 m  $\times$  0.25 mm, and the stationary phase was triethylene glycol dibutyrate. An internal reference (toluene) was used for the quantitative analysis. The column temperature was 50-80°C. The determination of 6-dodecyne was carried out on a Khrom-4 instrument, the column contained polyethylene glycol on Chezasorb, its length was 1.2 m, the temperature was 80°C, a flame-ionization detector was used, and the internal reference was toluene.

<u>Preparation of Solutions of Lithium Ethoxyethynyltrialkylboranates.</u> A 3.5-g portion (0.05 mole) of ethoxyacetylene was added over the course of 10 min at 20°C to an ethereal solution (1.5 N) containing 0.05 mole of MeLi, the mixture was stirred for 10 min and then cooled to 0°C, 150 ml of THF were added, and finally 0.05 mole of the trialkylborane was added dropwise. In the case of a solid R<sub>3</sub>B, a solution of the latter in THF was added. The reaction was weakly exothermic, and a homogeneous solution formed at the end of the additions.

<u>Hydrolysis of Lithium Ethoxyethynyltripropylboranate</u>. A weighed portion of cyclohexane (an internal reference) was added to a solution of lithium ethoxyethynyltripropylboranate obtained according to the foregoing procedure, 10 ml of the solution were collected, and the compound was hydrolyzed by 20 ml of  $H_2O$  at 0°C. The aqueous layer was saturated with NaCl, and the organic layer was analyzed by GLC. For the quantitative analysis a correction factor for ethoxyacetylene relative to cyclohexane was determined preliminarily. According to the GLC data, 75% of the ethoxyacetylene was regenerated.

<u>1-Ethoxy-2-cyclopentylacetylene.</u> A solution of lithium ethoxyethynyltricyclopentylboranate, which was obtained from 0.085 mole of ethoxyethynyllithium and 18.6 g (0.085 mole) of tricyclopentylborane was cooled to  $-78^{\circ}$ C, 20 ml of quinoline were added to it, and then a solution of 2.16 g of I<sub>2</sub> in 50 ml of THF was added. The mixture was stirred for 2 h at  $-78^{\circ}$ C. After heating to  $\sim 20^{\circ}$ C, the solvents were quickly distilled off at 40 torr, and then the reaction product was collected in a trap cooled to  $-78^{\circ}$ C at 1 torr. The product was redistilled over powdered KOH. This yielded 6.3 g (54%) of 1-ethoxy-2-cyclopentylacetylene, bp 66-67°C (9 mm), np<sup>2°</sup> 1.4605. Found: C 77.76; H 10.25%. Calculated for C<sub>9</sub>H<sub>14</sub>O: C 78.21; H 10.21%. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1240 (s, C-O), 2270 (s, C=C). PMR spectrum ( $\delta$ , ppm): 1.25 (t, 3 H, Me, J=7 Hz), 1.56 [m, 8 H, (CH<sub>2</sub>)<sub>4</sub>], 2.49 (m, 1 H, HCC=C), 3.90 (q, 2 H, C=COCH<sub>2</sub>, J=7 Hz).

<u>1-Ethoxy-3-methylpentyne</u>. In analogy to the preceding method, 7.2 g (58%) of 1-ethoxy-3-methylpentyne with bp 64-65°C (45 mm) and  $n_D^{2^\circ}$  1.4227 were obtained from 18 g (0.1 mole) of (s-Bu)<sub>3</sub>B. Found: C 76.12; H 11.15%. Calculated for C<sub>8</sub>H<sub>14</sub>O: C 76.14; H 11.18%. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1230 (s, C-O), 2270 (s, C=C). PMR spectrum ( $\delta$ , ppm): 0.89-1.43 (superimposed multiplets of CH<sub>3</sub> and CH<sub>2</sub> groups with a triplet of the ethoxy methyl group at 1.30 ppm, total of 11 H), 2.20 (m, 1 H, HCC=C), 3.92 (q, 2 H, CH<sub>2</sub>-O, J=7 Hz).

 $np^{20}$  <u>1-Ethoxyhexyne.</u> A 0.9-g yield (30%) of 1-ethoxyhexyne with bp 49-50°C (10 mm) and  $np^{20}$  1.4277 (compare [7]) was obtained according to the procedure just described from 4.54 g (0.025 mole) of  $(n-Bu)_{3}B$  and 1.75 g (0.025 mole) of ethoxyacetylene.

<u>1-Ethoxy-4-penten-1-yne</u>. a. A solution of 6.6 g of allyl bromide in 10 ml of ether was added to a solution of lithium 1-ethoxyethynyltributylboranate, which had been obtained from 0.054 mole of lithium ethoxyacetylide and 9.84 g (0.54 mole) of  $(n-Bu)_{3}B$ , at0°C, and the mixture was stirred for 2 h at  $\sim 20$ °C, after which the solvent and the low-boiling products were distilled off at 2 torr into a trap cooled to -78°C. The solvent was removed at atmospheric pressure, and the residue was redistilled. This yielded 2 g (34%) of 1-ethoxy-4-penten-1-yne, bp 60-61°C (40 mm),  $n_D^{2^\circ}$  1.4430 (compare [8]). IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1005 ( $\delta$ , CH<sub>2</sub>=CH), 1230 (s, C-O), 1641 (C=C), 2275 (s, C=C), 3062 and 3089 (=CH<sub>2</sub>). PMR spectrum ( $\delta$ , ppm): 1.28 (t, 3 H, Me, J=7 Hz), 2.77 (d t, 2 H, C=CCH<sub>2</sub>C=C), 3.96 (q, 2 H, CH<sub>2</sub>O, J=7 Hz), 4.81-5.38 (m, 2 H, CH<sub>2</sub>=C), 5.45-6.09 (m, 1 H, CH=C).

b. With the use of allyl iodide, 3.7 g (37%) of 1-ethoxy-4-penten-1-yne with  $n_D^{20}$ 1.4398 were obtained from 0.091 mole of 1ithium ethoxyethynyltriamylboranate. Redistillation of the residue yielded 3.6 g of ethoxydiamylborane (18%), bp 70-71°C (2 mm). Found: C 72.89; H 13.51; B 4.88%. Calculated for C<sub>12</sub>H<sub>27</sub>BO: C 72.73; H 13.73; B 5.46%. PMR spectrum ( $\delta$ , ppm): 3.85 (q, 2 H, OCH<sub>2</sub>, J = 7 Hz), 1.4-0.5 (signals of aliphatic protons, 25 H). <sup>11</sup>B NMR spectrum: -54 ppm (relative to Et<sub>2</sub>0·BF<sub>3</sub>).

c. A 2.1-g yield (60%) of 1-ethoxy-4-penten-1-yne with np<sup>20</sup> 1.4415 was obtained according to method a from 0.32 mole of lithium ethoxyacetylide, 7 g (0.032 mole) of tricyclopentylborane, and 6 g (0.05 mole) of allyl bromide.

<u>E,E-1-Ethoxy-5,9-dimethyl-4,8-decadien-1-yne (Geranylethoxyacetylene).</u> A 21-g portion of geranyl bromide was added dropwise at 0°C to a solution containing 0.097 mole of lithium ethoxyethynyltripropylboranate, and the mixture was stirred for 3 h at 0°C. After the removal of the solvent in the vacuum of a water-jet pump, the residue was extracted twice with isopentane (100-ml portions). The solvent was removed, and the residue was distilled. The following fractions were collected: 1) bp 74-94°C (0.02 mm) and 2) bp 120-140°C (0.02 mm). Repeated distillation of the first fraction yielded 6.2 g (31%) of geranylethoxyacetylene, bp 79-83°C (0.02 mm),  $n_D^{2^\circ}$  1.4782. Found: C 80.77; H 10.87%. Calculated for C<sub>14</sub>H<sub>20</sub>O: C 81.50; H 10.75%. IR spectrum (v, cm<sup>-1</sup>): 1230 s (C-O), 1620 w, and 1670 w (C=C), 2285 s (C=C). PMR spectrum ( $\delta$ , ppm): 1.26 (t, 3 H, Me, J=7 Hz), two superimposed signals with a center at 1.57 (9 H, Me-C=C), 2.00 (br s, 4 H, CH<sub>2</sub>C=C), 2.71 (d, 2 H, C=CCH<sub>2</sub>C=C, J=7 Hz), 3.89 (q, 2 H, CH<sub>2</sub>O, J=7 Hz), 5.05 (m, 2 H, CH=C).

Repeated distillation of the second fraction yielded 4.4 g (10.5%) of VI, bp 132-134°C (0.02 mm). Found: C 81.75; H 12.64; B 2.61%. Calculated for  $C_{24}H_{45}B$ : C 83.71; H 13.14; B 3.14%. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1621 m (BC=C). PMR spectrum ( $\delta$ , ppm): 0.75-2, spectrum of aliphatic protons with pronounced signals at 1.60 (Me) and 1.99 (CH<sub>2</sub>C=C), 2.28 (d, C=CCH<sub>2</sub>-C=C, J=7 Hz), 4.99 (m, HC=C). The spectrum contains weak signals at 3.72 ppm (CH<sub>2</sub>O), which are evidence of the presence of impurities.

<u>Protolysis of (5-Propyl-8,12-dimethyl-4,7-ll-tridecatrien-4-yl)dipropylborane (VI).</u> A 4.4-g portion of VI was heated with 40 g of triethanolamine at 2 torr, the liquid with bp 105-120°C being distilled. Repeated distillation yielded 2.3 g (73%) of 9-propyl-2,6-dimethyl-2,6,9-tridecatriene, bp 109-112°C (2 mm),  $np^{2°}$  1.4731, molecular ion with m/e 248 (C18H32). IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1650 and 1668 (C=C). PMR spectrum ( $\delta$ , ppm): complicated spectrum of aliphatic protons at 0.75-2.15 with intense signals at 1.59 (CH<sub>3</sub>C=C) and 1.98 (C=CCH<sub>2</sub>C=C), 2.62 (C=CCH<sub>2</sub>C=C), 4.95 (m, CH=C).

Reaction of Lithium Ethoxyethynyltripropylboranate with MeI. A 23.4-g portion (0.165 mole) of MeI was added at 0°C to a solution of lithium ethoxyethynyltripropylboranate, which was obtained from 0.165 mole of lithium ethoxyacetylide and 23.2 g (0.165 mole) of tripropylborane. The mixture was heated to  $\sim 20^{\circ}$ C and left to stand overnight. The solvent and the low-boiling products were distilled at 15 torr into a trap cooled by a mixture of dry ice and acetone. The methylethoxyacetylene in the distillate was determined by GLC (35% yield).

The residue was washed with 100 ml of isopentane, and the residue of LiI was filtered. After the removal of the isopentane, the residue was redistilled twice. This yielded 7.35 g (25%) of (5-methyl-4-octen-4-yl)dipropylborane, bp 79-82°C (3 ml). Found: C 80.62; H 13.74; B 4.46%. Calculated for  $C_{15}H_{31}B$ : C 81.07; H 14.06; B 4.87%. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1625 m (BC=C). <sup>11</sup>B NMR spectrum: -85 ppm (relative to BF<sub>3</sub>·Et<sub>2</sub>0, 50°C).

<u>4-Methyl-4-octene</u>. A 6-g portion of (5-methyl-4-octen-4-yl)dipropylborane was heated with 40 g of triethanolamine. Distillation of the liquid yielded a fraction with bp 68-70°C (58 mm). Repeated distillation yielded 2.7 g of a mixture of the Z and E isomers of 4-methyl-4-octene, bp 67-70°C (58 mm),  $n_D^{2°}$  1.4242 (compare [12]). Molecular ion with m/e 126 (C<sub>9</sub>H<sub>18</sub>). IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1665 (C=C). PMR spectrum ( $\delta$ , ppm): 0.73-2.07 (spectrum of aliphatic protons, 17 H), 5.02 (t m, 1 H, CH=C, J=7 Hz). According to GLC data, Z:E=1.7:1.

Synthesis of Acetylene Hydrocarbons. A 0.05-mole portion of a trialkylborane was added dropwise at 0°C to an ether-THF solution containing 0.025 mole of lithium ethoxyacetylide. The mixture was heated to  $\sim 20$ °C and stirred for 30 min. Upon cooling, 5 ml of a solution were recovered and hydrolyzed by 15 ml of water. The aqueous layer was saturated with NaCl, the organic layer was separated, and the yields of the alkynes were determined by GLC. The reaction mixture remaining after the collection of the sample was cooled to -78°C, and a solution of 8.9 g of I<sub>2</sub> in 20 ml of THF was added. After being stirred at -78°C for 1 h, the mixture was heated to  $\sim 20$ °C, and 25 ml of a 20% HaON solution containing a small amount of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> were added. The aqueous layer was saturated with K<sub>2</sub>CO<sub>3</sub>. The yields of the dialkylacetylenes were determined by GLC analysis of the organic layer (see Table 2).

<u>6-Dodecyne.</u> A 3.5-g portion (0.05 mole) of ethoxyacetylene was added dropwise at 20°C to 32 ml of a 1.5 N solution of MeLi. Then the mixture was cooled to 0°C, and 120 ml of THF and 24 g (0.107 mole) of tri-n-amylborane were added in succession. The mixture was stirred for 1 h at  $\sim$ 20°C, cooled to -78°C, and given an addition of a solution of 12.7 g of I<sub>2</sub> in 20 ml of THF. After stirring for 1.5 h at -78°C, the mixture was heated to  $\sim$ 20°C and washed twice with 30 ml of 20% NaOH containing Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The aqueous layer was extracted with 50 ml of ether, and the combined organic layer was evaporated to half its volume in a vacuum. A solution of 5 g of NaOH in 25 ml of H<sub>2</sub>O was added to the residue, then 30 ml of 30% H<sub>2</sub>O<sub>2</sub> were added, and the mixture was stirred for 1 h and left to stand overnight. The organic layer was removed, and the aqueous layer was saturated with Na<sub>2</sub>SO<sub>4</sub>. After the removal of the solvent, 5.03 g (50%) of 6-dodecyne with bp 60-61°C (2 mm) and np<sup>2°</sup> 1.4402 (compare [13]) were obtained by distillation. According to the GLC data, the substance does not contain impurities.

#### CONCLUSIONS

1. Lithium ethoxyethynyltrialkylboranates, which can be obtained from trialkylboranes and lithium ethoxyacetylide, are converted into 1-ethoxyalkynes under the action of iodine.

2. The application of methyl iodide or an allyl halide to lithium ethoxyethynyltrialkylboranates results in the formation of ethoxymethylacetylene and ethoxyallylacetylenes, respectively, as well as the alkenyldialkylboranes.

3. Lithium ethynyltrialkylboranates are capable of reacting with primary trialkylboranes to form lithium 1-alkynyltrialkylboranates and ethoxydialkylboranes. The latter reaction represents the transition from ethoxyacetylene to terminal and symmetrical alkynes.

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### REACTION OF 0, 0-DIISOPROPYL DITHLOPHOSPHATE WITH

# NITRILES OF CARBOXYLIC ACIDS

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It is known [1, 2] that HCl reacts with a mixture of dithio acids of phosphorus and nitriles to form chlorothiophosphates and the corresponding thioamides. The main direction of the reaction of dialkylcyanamides with dithiophosphates is the formation of dialkylamides and dialkyl esters of isothiocyanatothiophosphoric acid [3]. The formation of unstable products of the addition of the dithio acids at the  $C\equiv N$  bond is possible in these reactions, although such an addition product has been successfully isolated in only one case [4]. The addition product of 0,0-diisopropyl dithiophosphate to benzonitrile was ascribed the structure of 0,0-diisopropyl S-benzimidoyl dithiophosphate [4]. However, as it has now been ascertained, the addition product undergoes isomerization with 1,3-S  $\rightarrow N$  migration of the thiophosphoryl group during the reaction.

In the present investigation we studied the reaction of 0,0-diisopropyl dithiophosphate (I) with benzonitrile (II), phenylacetonitrile (III), adipodinitrile (IV), and ethyl cyanoacetate (V). The reactions proceeded in the absence of catalysts in 10-15 days. Nitriles III and IV react more slowly (up to 4 months) and less completely, further conversions of

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