The Reactions of Copper(I) 1-Alkenyltrimethylborates with Allylic Bromides or 2-Propynyl Bromide

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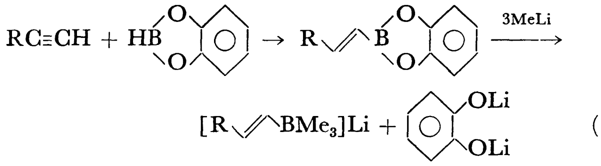
Synopsis. The reactions between copper(I) 1-alkenyltrimethylborates (readily obtainable from 2-(1-alkenyl)-1,3,2-benzodioxaboroles and methyllithium) and allylic bromides or 2-propynyl bromide were found to give corresponding coupling products. These reactions provide new synthetic routes to 1,4-alkadienes or 1,2,7-alkatrien-5-ynes.

In a series of our investigations of the chemistry of copper(I) organoborate complexes,[1-7] we have now discovered a novel cross-coupling reaction of 1-alkenyltrimethylborates with allylic bromides or 2-propynyl bromide. The reactions provide new synthetic procedures for 1,4-alkadienes or 1,2,7-alkatrien-5-ynes from alkynes *via* hydroboration, respectively.

Addition of a solution of lithium (*E*)-1-hexenyltrimethylborate (**1**) prepared from 2-(1-hexenyl)-1,3,2-benzodioxaborole and three equivalents of methyllithium to a suspension of copper(I) iodide in tetrahydrofuran at −30 °C resulted in the disappearance of copper(I) iodide, and a clear solution was obtained as shown in Eqs. 1 and 2. Although we have not undertaken a detailed study of this complex, copper(I) 1-hexenyltrimethylborate (**2**) is considered to be formed *via* metal exchange reaction. No reaction occurred between allyl bromide and lithium 1-hexenyltrimethylborate (**1**) at room temperature, whereas when corresponding copper(I) borate (**2**) was used, the reaction proceeded smoothly (Eq. 3). VPC analysis revealed the formation of 1,4-nonadiene in a 97% yield.

The reaction was then applied to representative alkenylborates and allylic bromides. The results are summarized in Table 1. The 1,4-dienes thus obtained were indicated to be a single isomer in each case by VPC analysis, presumably *E*-isomer, because of IR (955 cm⁻¹) and direct comparison with authentic samples.

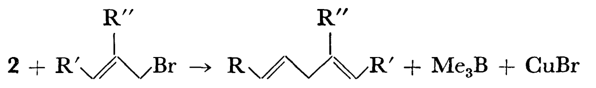


(1)

1

(2)

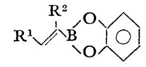
2



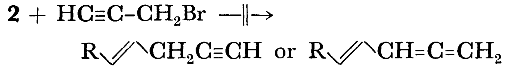
(3)

In the same way, copper(I) (*E*)-1-alkenyltrimethylborates react with 2-propynyl bromide (Eq. 5). At first, it was expected that the reaction of such copper(I) alkenylborates (**2**) with 2-propynyl bromide should give 4-alken-1-ynes (**3**) or 1,2,4-alkatrienes (**4**) as shown in Eq. 4. The reaction products actually obtained, however, were confirmed as 1,2,7-alkatrien-5-ynes (**5**).

TABLE 1. REACTION OF COPPER(I) ALKENYLTRIMETHYLBORATES WITH ALLYLIC BROMIDES AND 2-PROPYNYL BROMIDE

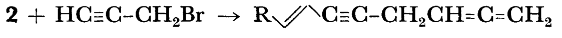
 R¹=	R²=	Allylic or 2-propynyl bromides[a)]	Product	Yield[b)] %
Butyl	H	$CH_2=CHCH_2Br$	1,4-Nonadiene	97
		$CH_2=C(CH_3)-CH_2Br$	2-Methyl-1,4-nonadiene	81
		$CH_3CH=CHCH_2Br$	2,5-Decadiene	46
			3-Methyl-1,4-nonadiene	52
Hexyl	H	$CH_2=CHCH_2Br$	1,4-Undecadiene	89
		2-Cyclohexenyl bromide	1-(2-Cyclohexenyl)-1-octene	42
Phenyl	H	$CH_2=CHCH_2Br$	1-Phenyl-1,4-pentadiene	92
Butyl	H	$HC\equiv CCH_2Br$	1,2,7-Dodecatrien-5-yne	54
Pentyl	H		1,2.7-Tridecatrien-5-yne	55
Hexyl	H		1,2,7-Tetradecatrien-5-yne	40
Ethyl	Ethyl		7-Ethyl-1,2,7-decatrien-5-yne	71

a) Allylic bromide/alkenylborane = 1.2. 2-Propynyl bromide/alkenylborane = 2.4.
b) Based on alkenylboranes employed.



(4)

3 **4**



(5)

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For example, 2-(1-hexenyl)-1,3,2-benzodioxaborole gave 1,2,7-dodecatrien-5-yne, the elemental analysis and mass spectrum ($m/e = 160$, M^+) of which coincided with $C_{12}H_{16}$. The IR spectrum bands at 1955, 855 cm⁻¹ due to $-CH=C=CH_2$, 955 cm⁻¹ for *trans*-CH=CH–, and 2180 cm⁻¹ for $-C\equiv C-$ structure were observed. The NMR spectrum indicated the presence of two vinylic hydrogens ($-CH_2CH^{\alpha}=CH^{\beta}-$), because H^{α} centered at 4.00 splits into doublet-triplet ($J = 16$ and 6 Hz) and H^{β} at 4.62 splits into a doublet ($J = 16$ Hz), and three allenic protones ($-CH_2-CH^{\gamma}=C=CH^{\delta}_2$),[5)] H^{γ} centered at 4.93 splits into triplet-triplet ($J = 6$ and 7 Hz) and two H^{δ} at 5.25 split into doublet-triplet ($J = 7$ and 3 Hz). All of these data are in good agreement with the 1,2,7-alkatrien-5-yne structure.

Stereoselective formation of alkenylboranes *via* hydroboration of alkynes followed by transfer of stereodefined alkenyl groups to alkyl halides should provide one of the simplest method for the synthesis of stereodefined alkenes. Although it is evident that copper(I) alkenylborates[8)] have a considerably high utility for such a purpose, the applicability of the present new reagents to coupling and addition reactions is now under further investigation.

Experimental

Materials. Commercial allylic bromides, alkynes, and 2-propynyl bromide were used. The tetrahydrofuran was purified by distillation from $LiAlH_4$ before use. 1-Alkenylbenzodioxaboroles are prepared by Brown's method[9] from 1,3,2-benzodioxaborole and alkynes.

The IR and NMR spectra were taken on a Hitachi-Perkin Elmer Model 125 spectrophotometer and a Hitachi R-22 spectrometer at 90 MHz using tetramethylsilane as an internal standard, respectively.

General Procedure. The following procedures for the preparation of 1,4-nonadiene and 1,2,7-dodecatrien-5-yne are representative.

A dry 50 ml flask equipped with a septum inlet and a magnetic stirring bar was flushed with dry nitrogen. The flask was charged with 2-(1-hexenyl)-1,3,2-benzodioxaborole[9] (2.30 g, 10 mmol) and 10 ml of dry tetrahydrofuran. To this mixture was added methyllithium (22 ml of 1.26 M solution, 30 mmol) in ether at 0 °C and stirred for an additional 2 h to form lithium 1-hexenyltrimethylborate. Copper(I) iodide (3.8 g, 20 mmol) and 50 ml of dry THF were placed into a separate 200 ml-flask and cooled to −30 °C. The resultant lithium 1-hexenyltrimethylborate solution was gradually added under vigorous stirring. After 1 h, precipitated copper(I) iodide was completely disolved and a clear solution was obtained. To this solution was added allyl bromide (1.45 g, 12 mmol). The reaction mixture was allowed to warm up to room temperature and stirred for an additional 2 h. After the reaction was complete, the residual organoborane was oxidized with 3 ml of aqueous 3M-NaOH and 3 ml of 30%-H_2O_2 at room temperature for 2 h. The product was extracted by ether. The combined extract was washed with saturated NaCl solution and dried over magnesium sulfate. VPC analysis revealed the formation of 1,4-nonadiene (9.7 mmol, 97%).

The procedure for the preparation of 1,2,7-decatrien-5-yne is as follows: To the solution of copper(I) 1-hexenyltrimethylborate described above was added 2-propynyl bromide (2.86 g, 24 mmol) at −30 °C, and then the mixture was allowed to warm up to room temperature. After 2 h, residual organoborane was oxidized by alkaline hydrogen peroxide. VPC analysis of the ether extract indicated the presence of 5.4 mmol (54%) of 1,2,7-dodecatrien-5-yne.

Identification of the Products. In all cases analytically pure samples were obtained by preparative VPC with Varian autoprep Model-2800 and characterized by NMR, IR, and mass spectra,and refractive indices, and elemental analyses. *1,4-Nonadiene* and *1-phenyl-1,4-pentadiene* were characterized by direct comparison with authentic samples prepared by the methods reported by Negishi[10] and Speziale,[11] respectively.

2-Methyl-1,4-nonadiene: $n_D^{22}=1.4389$. Found: C, 86.74; H, 13.02%. Calcd for $C_{10}H_{18}$: C, 86.88; H, 13.12%. Mass: *m/e*=138 (M^+). IR (CCl_4): 3080, 1650, 975, 895, 965 cm^{-1}. NMR (CCl_4): τ, 9.1 (3H, t, J=6 Hz), 8.5—8.8 (4H, m), 8.31 (3H, s), 7.9—8.15 (2H, m), 7.36 (2H, d, J=5 Hz), 5.35 (2H, s), 6.59 (2H, m).

2,5-Decadiene: $n_D^{22}=1.4410$. Found: C, 86.65; H, 13.20%. Calcd for $C_{10}H_{18}$: C, 86.88; H, 13.12%. Mass: *m/e*=138 (M^+). IR (CCl_4): 3010, 965, 860 cm^{-1}. NMR (CCl_4): τ, 9.10 (3H, t, J=6 Hz), 8.5—8.8 (4H, m), 8.36 (3H, d, J=4 Hz), 7.9—8.15 (2H, m), 7.2—7.45 (2H, m), 4.5—4.7 (4H, m).

3-Methyl-1,4-nonadiene: $n_D^{22}=1.4390$. Found: C, 86.69: H, 13.21%. Calcd for $C_{10}H_{18}$: C, 86.88; H, 13.12%. Mass: *m/e*=138 (M^+). IR (CCl_4): 965, 910, 860 cm^{-1}. NMR (CCl_4): τ, 9.10 (3H, t, J=6 Hz), 8.93 (3H, d, J=7 Hz), 8.5—8.8 (4H, m), 7.85—8.1 (2H, m), 7.05—7.4 (1H, m), 5.09 (1H, d, J=12 Hz), 5.06 (1H, d, J=16 Hz), 4.55—4.70 (2H, m), 4.05—4.50 (1H, m).

1,4-Undecadiene: $n_D^{22}=1.4370$. Found: C, 86.70; H, 13.02%. Cacld for $C_{11}H_{20}$: C, 86.76; H, 13.24%. Mass: *m/e*=152 (M^+). IR (CCl_4): 3080, 1640, 965, 915, 860 cm^{-1}. NMR (CCl_4): τ, 9.10 (3H, t, J=6 Hz), 8.5—8.8 (8H, m), 7.85—8.1 (2H, m), 7.05—7.35 (2H, m), 5.01 (1H, d, J=10 Hz), 4.98 (1H, d, J=16 Hz), 4.51—4.64 (2H, m), 4.02—4.44 (1H, m).

1-(2-Cyclohexenyl)-1-octene: $n_D^{22}=1.4749$. Found: C, 87.38; H, 12.63%. Cacld for $C_{14}H_{24}$: C, 87.42; H, 12.58%. Mass: *m/e*=192 (M^+). IR (CCl_4): 3010, 970, 865 cm^{-1}. NMR (CCl_4): τ, 9.10 (3H, t, 6 Hz), 8.26—8.90 (12H, m), 7.89—8.17 (4H, m), 7.20—7.47 (1H, m), 4.58—4.73 (2H, m), 4.33—4.54 (2H, m).

1,2,7-Dodecatrien-5-yne: $n_D^{22}=1.5009$. Found: C, 89.93; H, 9.85%. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06%. Mass: *m/e*=160 (M^+). IR (CCl_4): 2180, 1955, 955, 855 cm^{-1}. NMR (CCl_4): τ, 9.11 (3H, t, J=6 Hz), 8.45—8.9 (4H, m), 7.75—8.10 (2H, m), 6.9—7.17 (2H, m), 5.25 (2H, dt, J=3 and 7 Hz), 4.93 (1H, tt, J=6 and 7 Hz), 4.62 (1H, d, J=16 Hz), 4.00 (1H, dt, J=6 and 16 Hz).

1,2,7-Tridecatrien-5-yne: $n_D^{22}=1.4972$. Found: C, 89.39; H, 10.35%. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41%. Mass: *m/e*=174 (M^+). IR (CCl_4): 2180, 1960, 950, 845 cm^{-1}. NMR (CCl_4): τ, 9.10 (3H, t, J=6 Hz), 8.5—8.85 (6H, m), 7.96 (2H, t, J=6 Hz), 6.91—7.13 (2H, m), 5.25 (2H, dt, J=3 and7 Hz), 4.93 (1H, tt, J=6 and7 Hz), 4.62 (1H, d, J=16 Hz), 3.99 (1H, dt, J=6 and 16 Hz).

1,2,7-Tetradecatrien-5-yne: $n_D^{22}=1.5012$. Found: H, 89.44; H, 10.78%. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71%. Mass: *m/e*=188 (M^+). IR (CCl_4): 2180, 1960, 955, 860 cm^{-1}. NMR (CCl_4): τ, 9.09 (3H, t, J=6 Hz), 8.44—8.84 (8H, m), 7.73—8.05 (2H, m), 6.87—7.08 (2H, m), 5.22 (2H, dt, J=3 and 7 Hz), 4.90 (1H, tt, J=6 and 7 Hz), 4.60 (1H, d, J=16 Hz), 3.98 (1H, dt, J=6 and 16 Hz).

7-Ethyl-1,2,7-dodecatrien-5-yne: $n_D^{22}=1.5012$. Found: C, 88.76; H, 10.10%. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06%. Mass: *m/e*=160 (M^+). IR (CCl_4): 2180, 1960, 860 cm^{-1}. NMR (CCl_4): τ, 9.02 (3H, t, J=6 Hz), 8.97 (3H, t, J=6 Hz), 7.76—8.07 (2H, m), 6.90—7.11 (2H, m), 5.25 (2H, dt, J=3 and 7 Hz), 4.93 (1H, tt, J=6 and 7 Hz), 4.37 (1H, t, J=6 Hz).

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