

SYNTHESIS OF 1,4-DISUBSTITUTED (*E,Z*)-1,3-DIENES FROM LITHIUM DICYCLOHEXYL(*trans*-1-ALKENYL)(1-ALKYNYL)BORATES *

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Summary

Treatment of lithium dicyclohexyl(*trans*-1-alkenyl)(1-alkynyl)borates with either boron trifluoride etherate or tri-*n*-butyltin chloride results in the preferential migration of the alkenyl group from boron to the adjacent alkynyl carbon atom. Protonolysis of the resultant organoboron intermediates with acetic acid affords the corresponding 1,4-disubstituted (*E,Z*)-1,3-dienes in good yields, provided that the (*Z*)-alkenyl moiety of the diene does not contain a tertiary alkyl group. Demonstration that this novel procedure is applicable for the preparation of (*E,Z*)-1,3-dienes containing functional groups has been shown by the synthesis in 66% yield of methyl (10*E*,12*Z*)-hexadecadienoate, a precursor via lithium aluminium hydride reduction of the sex pheromone of the female silk moth, *Bombyx mori*.

Introduction

The (*E,Z*)-1,3-dienyl moiety is encountered as a part-structure of many natural products and insect pheromones. Considerable attention has been given to the synthesis of such compounds, and a number of attractive methods have been published in recent years. For example, monohydroboration of mono- and di-substituted acetylenes with thexylborane (2,3-dimethyl-2-butylborane) produces the corresponding thexyl bis(alkenyl)boranes. Sequential treatment of these with anhydrous amine oxide and iodine in the presence of a base provides (*E,Z*)-1,3-dienes in good yields and with high isomeric purities [1].

Unfortunately, the above simple procedure is only applicable for the preparation of symmetrically substituted dienes. However, Negishi and coworkers have recently developed two useful methods for preparing unsymmetrically substituted (*E,Z*)-conjugated dienes. These are: via hydroboration-protonolysis of enynes

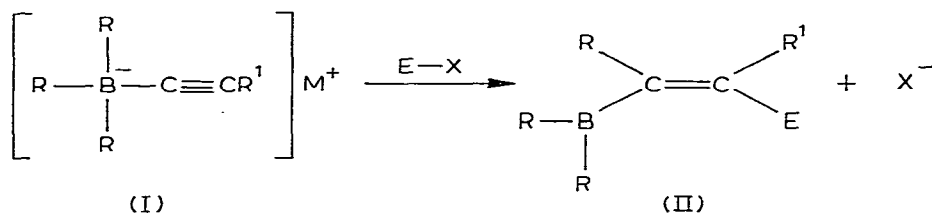
* Dedicated to Professor Herbert C. Brown, an inspiring teacher and scientist.

[2], and via coupling of (*E*)-alkenylalanes with (*Z*)-alkenyl halides in the presence of palladium or nickel complexes [3]. In quest of an operationally simple synthesis of (*E,Z*)-1,3-dienes that would not require the separate preparation of stereochemically defined precursors, we have now investigated the possibility of using the readily accessible lithium dialkyl(*trans*-1-alkenyl)(1-alkynyl)borates.

We wish to report below experimental data which illustrate the synthetic utility of these versatile alkenylalkynylborate intermediates for the preparation of (*E,Z*)-conjugated dienes.

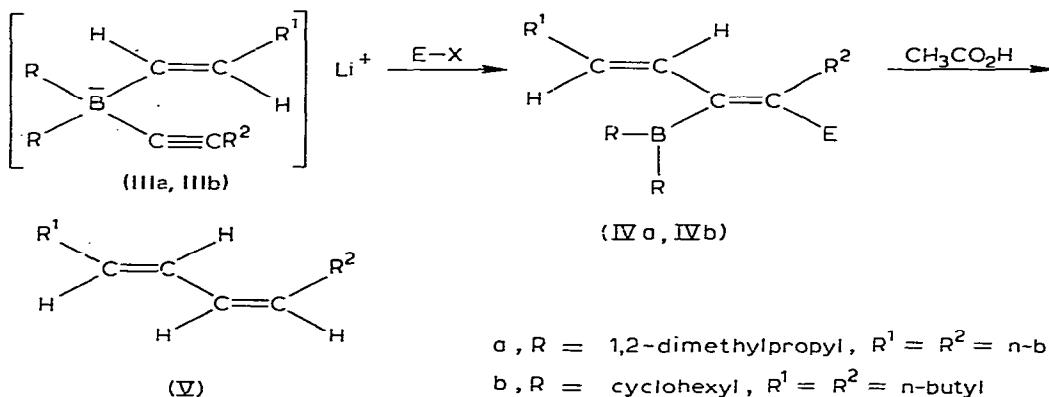
Results and discussion

It has been shown that sodium or lithium trialkyl(1-alkynyl)borates (I) react with a variety of electrophiles undergoing transfer of one alkyl group from boron to the adjacent carbon to produce the corresponding alkenylboranes II [4]. Specifically, substituted alkenylboranes in which the migrating group R and the entering electrophile E-X are *trans* have been obtained on treatment of I with propionic acid [4d,e], trimethylsilyl chloride [4b], or tri-*n*-butyltin chloride [4f].



(M = Li, Na; E-X = EtCO₂H, Me₃SiCl, *n*-Bu₃SnCl)

In view of these results, it was of interest to explore whether treatment of lithium dialkyl(*trans*-1-alkenyl)(1-alkynyl)borates (III) with suitable electrophiles would induce selective migration of the *trans*-alkenyl moiety from boron to the adjacent alkynyl carbon to produce dienylboranes IV. Provided that the electrophile used is either a protic acid or a moiety which undergoes protonolysis under mild conditions, treatment of IV with excess acetic acid should then afford the desired (*E,Z*)-1,3-dienes V.



a, R = 1,2-dimethylpropyl, R¹ = R² = *n*-butyl;
b, R = cyclohexyl, R¹ = R² = *n*-butyl

TABLE 1

PRODUCT DISTRIBUTION RESULTING FROM THE REACTIONS OF IIIa (10 mmol) WITH VARIOUS ELECTROPHILES (11 mmol) FOLLOWED BY PROTONOLYSES WITH ACETIC ACID

Electrophile	Product distribution (%)		
	(5 <i>E</i> ,7 <i>Z</i>)-Hexa- decadiene ^a	2,3-Dimethyl- 4-nonene ^b	1-Hexyne
HCl	18	71	17
CH ₃ CO ₂ H	20	66	18
BF ₃ · OEt ₂	57(97)	11	10
n-Bu ₃ SnCl	28(99)		59

^a Values in parentheses indicate the isomeric purity of the diene. ^b Mixtures of *cis*- and *trans*-alkenes were observed.

It should be pointed out that the nearly selective intramolecular transfer of the *trans*-1-alkenyl group to the triple bond in the presence of the bis(1,2-dimethylpropyl)boryl moiety in IIIa has been achieved previously using iodine as the electrophile. In this case, however, the resultant organoboron intermediates underwent deboroniodination to produce *trans*-enynes [2].

For our preliminary investigations we selected bis(1,2-dimethylpropyl)(*trans*-1-hexenyl)(1-hexynyl)borate (IIIa). This organoborate is readily available by hydroboration of 1-hexyne with disiamylborane [bis(1,2-dimethylpropyl)borane] followed by treatment of the resultant dialkylalkenylborane with lithium 1-hexynylide. To determine the relative migrating aptitudes of the 1,2-dimethylpropyl and *trans*-1-hexenyl groups as a function of the electrophile, IIIa was treated in separate experiments at -78°C with 1.1 equivalent of hydrogen chloride, acetic acid, boron trifluoride etherate, and tri-*n*-butyltin chloride. The reaction mixtures were then allowed to come to room temperature, and were maintained for an additional hour at this temperature before being treated with an excess of glacial acetic acid. The hydrocarbon products obtained were analyzed by GLC and the results are shown in Table 1.

Several interesting points are apparent from this study. Thus, protonation of the triple bond in IIIa with either hydrogen chloride or acetic acid induces preferential migration of the alkyl group. This is evidenced by the formation of 2,3-dimethyl-4-nonene as the main product. Under similar experimental conditions, but using boron trifluoride etherate as the electrophile the reaction proceeds with the preferential transfer of the *trans*-1-hexenyl moiety to afford, after protonolysis, a 57% yield of the (5*E*,7*Z*)-dodecadiene V, containing only 3% of the corresponding (*E,E*)-isomer. Finally, treatment of IIIa with tri-*n*-butyltin chloride causes extensive displacement of the 1-hexynyl moiety with concomitant formation of the dialkyl(*trans*-1-hexenyl)borane (VIa) and tri-*n*-butyl(1-hexynyl)stannane (VIIa). It should be noted here that protonolysis of the reac-

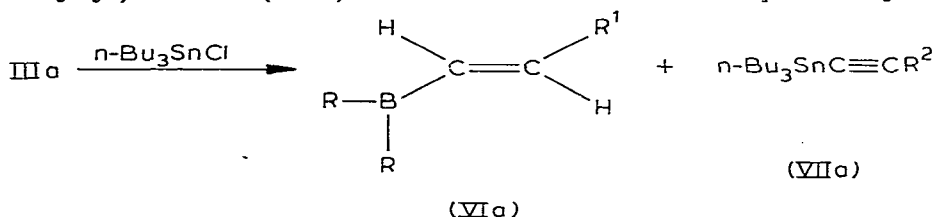


TABLE 2

PRODUCT DISTRIBUTION RESULTING FROM THE REACTIONS OF IIIb (10 mmol) WITH VARIOUS ELECTROPHILES (11 mmol) FOLLOWED BY PROTONOLYSIS WITH ACETIC ACID

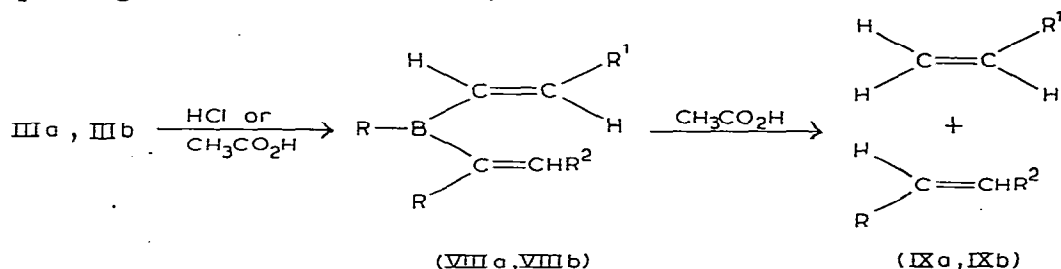
Electrophile	Product distribution (%)		
	(5 <i>E</i> ,7 <i>Z</i>)-Hexa- decadiene ^a	1-Cyclohexyl- 1-hexene	1-Hexyne
HCl	9	81 ^b	16
CH ₃ CO ₂ H	17	60 ^b	24
BF ₃ · OEt ₂	71(97)	8 ^b	8
n-Bu ₃ SnCl	86(99)	6	10

^a Values in parenthesis indicate the isomeric purity of the diene. ^b Mixtures of the *cis*- and *trans*-alkenes were observed.

tion mixture produces some of the desired diene Va and that it was essentially free of the (*E,E*)-isomer, albeit in modest yield (28%).

It has been noted previously that the success of tri-*n*-butyltin chloride mediated alkyl transfer reactions of lithium trialkylalkynylborates I is strongly dependent on the size of the alkyl group, proceeding satisfactorily only for trialkylboryl moieties of moderate steric requirements [4f]. Therefore, in the hope of improving formation of the diene precursor IV, the sterically less hindered cyclohexyl analog IIIb was treated with the aforementioned electrophiles.

A comparison of the results shown in Tables 1 and 2 reveals that substituting the 1,2-dimethylpropyl groups by cyclohexyl groups (IIIb) does not improve 1-hexenyl group migration in hydrogen chloride and acetic acid mediated transfer reactions. Alkyl group migrations in both cases are still favored and lead, after protonolysis of the resultant alkenylboranes VIIa, VIIb, to the corresponding disubstituted alkenes IXa, IXb and 1-hexene.

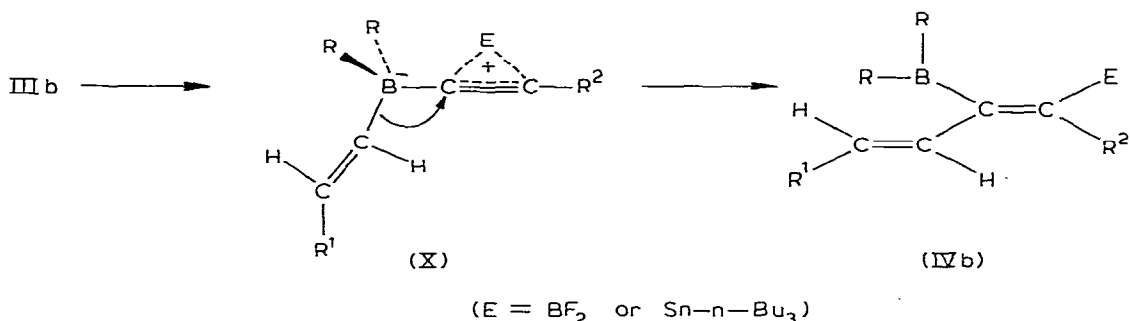


On the other hand, the size of the alkyl groups present in the alkenylalkynylborates III has a remarkable effect upon the product distribution in tri-*n*-butyltin chloride mediated transfer reactions. Thus treatment of IIIb with this electrophile results in the nearly exclusive migration of the 1-hexenyl group to produce, after protonolysis, an 86% yield of the isomerically pure (5*E*,7*Z*)-dodecadiene. The cyclohexyl group participated in the migration from boron to the adjacent alkynylcarbon atom only to a minor extent as evidenced by the formation of 6% of 1-cyclohexyl-1-hexene. A similar efficient diene synthesis was also achieved with IIIb and boron trifluoride etherate.

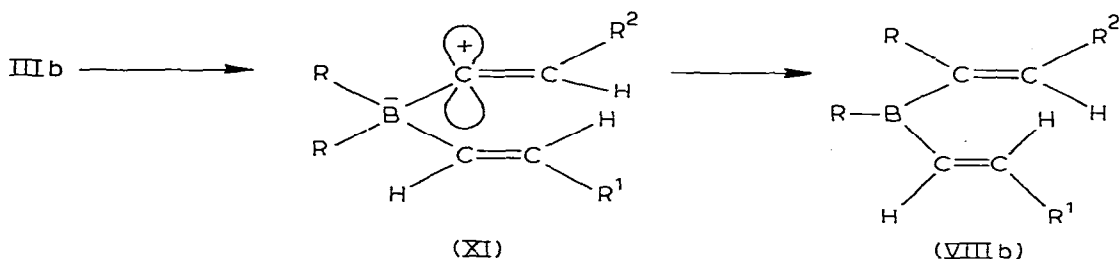
The ¹H NMR spectra of the organoboron intermediate IVb (E = *n*-Bu₃Sn) exhibited a doublet at δ 6.5 ppm (*J* 17 Hz) and a doublet of triplets at δ 4.9

ppm (J 17 and 6 Hz), indicating the *trans*-1-hexenyl group must have migrated with retention of configuration. Furthermore, the (*E,Z*)-stereochemistries of unsymmetrically substituted dienes obtained from IIIb, in which R^1 and R^2 were different, via sequential treatment with either boron trifluoride etherate or tri-*n*-butyltin chloride followed by acetic acid clearly demonstrate that the transfer of the alkenyl groups proceeded with retention (*vide infra*). Unfortunately, we do not have direct evidence regarding the stereochemistry of the double bond at the migration terminus. However, it is well documented that protonolyses of vinyl C—B and C—Sn bonds occur with retention of configuration. Consequently, the (*E,Z*)-configuration of the 5,7-dodecadiene obtained on protonolysis of IVb ($E = \text{BF}_2$ or BF_3 ; $\text{Sn-}n\text{-Bu}_3$) is compatible with retention of configuration of the migrating group and that the entering electrophile being *trans* to the migrating 1-hexenyl group.

The formation of the organoboron intermediate IVb ($E = \text{BF}_2$ or $n\text{-Bu}_3\text{Sn}$) from its precursor IIIb may be depicted to proceed via initial complexation of the electrophile with the triple bond (X) followed by intramolecular transfer of the alkenyl group.



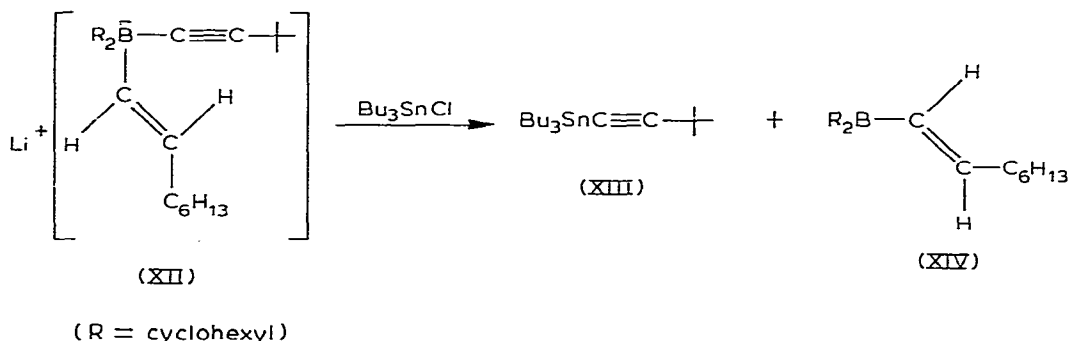
It is apparent that the presence of bulky substituents at the triple bond (R^2) as well as at the tetrahedral boron (R) would interfere with complexation of the electrophile, especially in the case of the tri-*n*-butyltin moiety. This is in accord with the observation that the presence of the bulky bis(1,2-dimethylpropyl) moiety of IIIa impairs migration of the alkenyl group (Table 1). The question remains, however, as to why alkenyl group transfer is favored over alkyl group migration with the Lewis acids BF_3 and $n\text{-Bu}_3\text{SnCl}$, whereas the reverse trend is observed when IVb is treated with hydrogen chloride or acetic acid (Table 2). It is conceivable that the reaction of IIIb with protic acids proceeds via an intermediate XI with more charge development at the vinylic carbon as compared to that in X.



The intermediacy of XI has previously been proposed in carboxylic acid induced migrations of alkyl groups in lithium trialkylalkynylborates I [4d]. In the case of intermediate XI, the group with the greater electron-donating ability should migrate preferentially. Thus, the sp^3 carbon of the cyclohexyl group would better satisfy the electron demand at the vinyl cation center of the inverse boron-ylide XI as compared with the sp^2 carbon of the alkenyl group. On the other hand, migration in complex X, in which the positive charge is more delocalized, should be governed by the relative carbanion stabilities of the participating groups, thus favoring transfer of the alkenyl group.

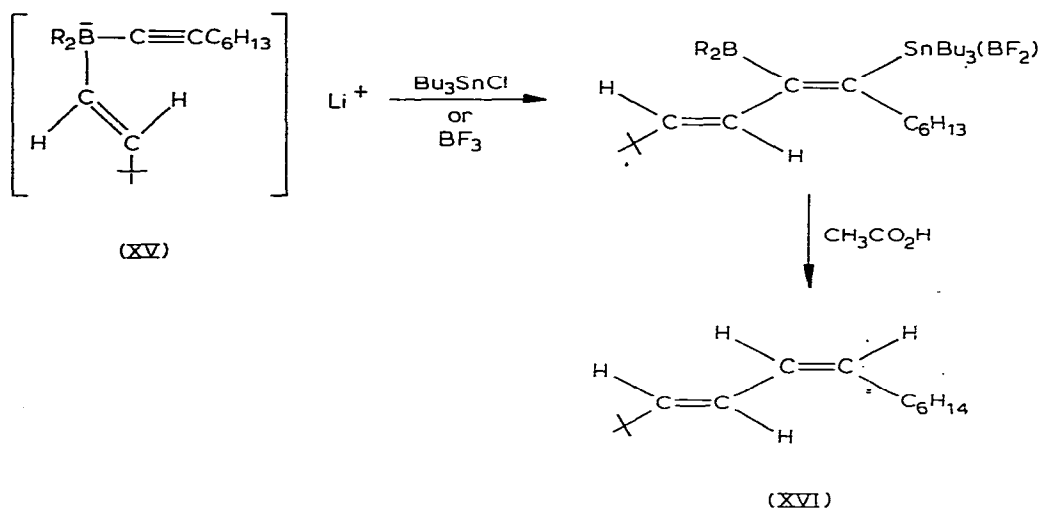
These preliminary investigations have thus revealed that treatment of lithium dicyclohexyl(*trans*-1-alkenyl)(1-alkynyl)borates with either boron trifluoride etherate or tri-*n*-butyltin chlorides provides viable stereoselective syntheses of (*E,Z*)-1,3-dienes.

However, as pointed out in the preceding discussion, not only does the size of the alkyl groups on boron influence the course of the reaction, but also the steric requirement of the alkyl group on the alkyne (R^2 in IVb) should play a decisive role in boron trifluoride and tri-*n*-butyltin chloride mediated (*E,Z*)-diene syntheses. Thus, we included in our study of the scope of the diene synthesis the organoborate XII derived from the reaction of dicyclohexyl(*trans*-1-octenyl)-borane with lithium *t*-butylacetylide. Treatment of XII with tri-*n*-butyltin chloride resulted in displacement of the alkyne to give the tri-*n*-butyltin derivative XIII and the alkenylborane XIV. This was evidenced by the formation of 1-octene (80%) and *t*-butylacetylene on protonolysis of the reaction mixture.



Transfer of the *trans*-1-octenyl group was slightly higher with boron trifluoride as the electrophile. In this case, GLC analysis of the reaction mixture revealed, after treatment with acetic acid, 20% of the anticipated diene and 56% of 1-octene. Therefore, the present procedure does not permit the synthesis of (*E,Z*)-1,3-dienes in which the (*Z*)-alkenyl moiety contains a tertiary alkyl group. However, the presence of a secondary alkyl group on the triple bond as in isopropyl or cyclohexylacetylene does not impede alkenyl group migration when the corresponding lithium dicyclohexylalkenylalkenylborates are treated with either tri-*n*-butyltin chloride or boron trifluoride. In these cases, protonolysis of the reaction mixture affords the corresponding (*E,Z*)-dienes in good yields.

Interestingly, a tertiary alkyl group can be accommodated in the alkenyl moiety of the organoborate XV without a detrimental effect on the yield of the dienes XVI.



Finally, incorporation of a disubstituted (*Z*)-alkenyl group into the lithium dicyclohexylalkenylalkynylborate by treating dicyclohexylborane with 3-hexyne results on treatment of the organoborate with tri-*n*-butyltin chloride in the preferential migration of the cyclohexyl group to produce, after protonolysis, mainly the corresponding cyclohexyl substituted olefins.

A summary of the types and yields of dienes obtained via treatment of lithium dicyclohexyl(*trans*-1-alkenyl)(1-alkynyl)borates with boron trifluoride etherate or tri-*n*-butyltin chloride is shown in Table 3. Included to demonstrate that this novel procedure is also applicable for the preparation of (*E,Z*)-1,3-dienes

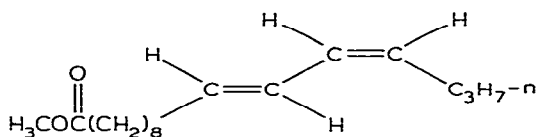
TABLE 3

YIELDS OF CONJUGATED (*E,Z*)-DIENES FROM REACTIONS OF LITHIUM DICYCLOHEXYL- (*trans*-1-ALKENYL)(1-ALKYNYL)BORATES WITH BF_3 AND $n-Bu_3SnCl$ FOLLOWED BY PROTONOLYSIS

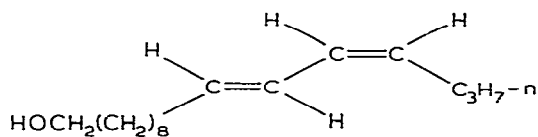
Alkenylborane derived from	Lithium alkynylide derived from	Lewis acid	Diene product (%) ^a	Isolated yield (%) ^b
1-Hexyne	1-Hexyne	BF_3	(5 <i>E</i> ,7 <i>Z</i>)-Dodecadiene (98)	67
1-Hexyne	1-Hexyne	Bu_3SnCl	(5 <i>E</i> ,7 <i>Z</i>)-Dodecadiene (99)	68
1-Octyne	1-Hexyne	BF_3	(5 <i>Z</i> ,7 <i>E</i>)-Tetradecadiene (97)	68
1-Octyne	1-Hexyne	Bu_3SnCl	(5 <i>Z</i> ,7 <i>E</i>)-Tetradecadiene (99)	74
1-Hexyne	1-Octyne	BF_3	(5 <i>E</i> ,7 <i>Z</i>)-Tetradecadiene (97)	72
3,3-Dimethyl-1-butyne	1-Octyne	BF_3	(3 <i>E</i> ,5 <i>Z</i>)-2,2-Dimethyldodeca-3,5-diene (98)	71
3,3-Dimethyl-1-butyne	1-Octyne	Bu_3SnCl	(3 <i>E</i> ,5 <i>Z</i>)-2,2-Dimethyldodeca-3,5-diene (99)	70
Cyclohexylethyne	3-Methyl-1-butyne	BF_3	(1 <i>E</i> ,3 <i>Z</i>)-1-Cyclohexyl-5-methylhexa-1,3-diene (97)	60
1-Hexyne	Cyclohexylethyne	Bu_3SnCl	(1 <i>Z</i> ,3 <i>E</i>)-1-Cyclohexyl-octa-1,3-diene (98)	53
Methyl 10-undecynoate	1-Pentyne	BF_3	Methyl(10 <i>E</i> ,12 <i>Z</i>)hexadecadienoate (98)	66

^a Values in parentheses are isomeric purities. ^b The dienes contained 3–8% of the corresponding cyclohexylalkene.

containing functional groups in the synthesis of methyl (10*E*,12*Z*)-hexadecadienoate (XVII), a precursor of the sex pheromone XVIII of the female silk moth, *Bombyx mori* [2,5]. Thus, methyl 10-undecynoate was hydroborated with dicyclohexylborane. The resultant alkenylborane was sequentially treated with lithium pentynylide followed by boron trifluoride etherate. Protonolysis of the reaction mixture afforded the desired diene XVII in 66% yield.



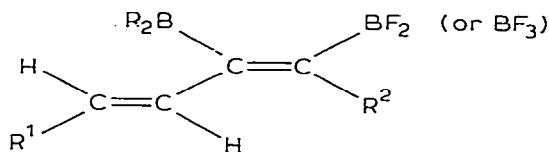
(XVII)



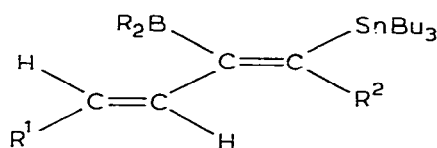
(XVIII)

Conclusions

The reactions of the readily available lithium dicyclohexyl(*trans*-1-alkenyl)-(1-alkynyl)borates III with either boron trifluoride or with tri-*n*-butyltin chloride provide an operationally simple procedure for preparing 1,4-disubstituted (*E,Z*)-1,3-dienes, with the only restriction being that the (*Z*)-double bond does not contain a tertiary alkyl substituent. Since the hydroboration reaction is known to tolerate many functional groups, the present procedure should be amenable to the synthesis of a variety of functionally substituted natural products and insect pheromones. Also, it is important to note that the reaction of III with boron trifluoride or tri-*n*-butyltin chloride produces intermediates containing either the 1,2-diboryl (XIX) or the 1-boryl-2-stannyl (XX) moieties. Although



(XIX)



(XX)

we have not yet explored the synthetic potentials of these novel classes of dienylboranes, it is evident they represent attractive intermediates for further functionalization.

Experimental

Materials

All boiling points are uncorrected. Infrared spectra were obtained on a Beckman IR-8 spectrometer. ¹H NMR spectra were recorded on a Varian A-60 spectrometer, and chemical shifts are reported in ppm downfield from Me₄Si internal standard. High-resolution mass measurements were obtained on a Dupont 21-492B mass spectrometer. GLC analyses were performed on a Varian 940 gas chromatograph equipped with 5-ft columns, packed with Carbowax 20M or SF-96 on Gas-Chrom R or Q, respectively, or on a Varian 1400 gas chromatograph

equipped with either a 55 m OV-101 or a 55 m SE-30 glass capillary column.

The alkenes (Philips) and the alkynes (Farchan) were used directly after checking their ^1H NMR spectra, indices of refractions and GLC retention times. Methyl 10-undecynoate was prepared by treatment of 10-undecynoic acid with methyl iodide in the presence of HMPA in 6 *N* sodium hydroxide [6]. Boron trifluoride etherate was freshly distilled from calcium hydride prior to use and stored under nitrogen. Tri-*n*-butyltin chloride (Aldrich) was purified by distillation (b.p. $95^\circ\text{C}/0.3$ Torr) and stored under nitrogen. The concentration of methyl-lithium (Ventron) was determined by the improved double titration method [7] prior to use. Solutions of borane in THF [8] were transferred from the storage vessel into the reaction flask by means of a syringe.

All glassware for reactions involving organoboron or organolithium reagents were oven-dried at 140°C for 6 h, assembled hot, and cooled under a stream of purified nitrogen before use. All reactions involving these organometallics were stirred magnetically and carried out under an atmosphere of nitrogen.

Preparation of dialkylboranes

Disiamylborane was prepared by adding a solution of 2-methyl-2-butene (40 mmol, 5.0 *M*) in THF to a precooled (-15 to -20°C) solution of borane (20 mmol, 2.0 *M*) while maintaining the temperature during the addition below 0°C . The reaction mixture was allowed to stand for 2 h at ambient temperature, then was standardized by measuring the hydrogen evolved on hydrolysis.

Dicyclohexylborane was prepared by adding to a solution of borane (10 mmol, 2.27 *M*) in THF at -15° ($\text{CCl}_4/\text{Dry ice bath}$) a solution of cyclohexene (20 mmol, 2.50 *M*) in THF at such a rate as to maintain the temperature below 0°C . The resultant white slurry was stirred for 1 h at 0 – 5°C and then used *in situ*.

The 1-lithioacetylides used in the study were prepared by adding at such a rate as to keep the temperature during the addition below -5°C , a solution of methyl-lithium (10.0 mmol, 1.90 *M*) in ether to the appropriate 1-alkyne (10 mmol) in THF maintained at -25°C . The 1-lithioacetylide thus obtained was used shortly after its preparation.

General procedure for the preparation of dienes using boron trifluoride etherate

(5*E*,7*Z*)-Dodecadiene. To a freshly prepared slurry of dicyclohexylborane (10 mmol) in THF maintained at -15°C was added a solution of 1-hexyne (0.82 g, 10.0 mmol) in 2.5 ml of THF. After stirring for 2 h at 0 – 5°C , the reaction mixture became homogeneous. To the dicyclohexyl(*trans*-1-hexenyl)borane formed was added at -25 to -10°C the lithium 1-hexynylide (10 mmol) by means of the double-ended needle technique [9]. The resultant lithium dicyclohexyl(*trans*-1-hexenyl)(1-hexynyl)borate was stirred for 1 h at ambient temperature, then treated at -25°C with boron trifluoride etherate (1.4 ml, 11 mmol). The reaction mixture was allowed to exotherm to room temperature, stirred for 1 h, and treated with glacial acetic acid (2.3 ml, 40 mmol). After maintaining the mixture for 1 h at room temperature, it was treated consecutively with methanol (10 ml) and 6 *N* sodium hydroxide (10 ml). Then the mixture was oxidized at 30 – 50°C by adding dropwise a 30% solution of hydrogen peroxide (2.4 ml). This oxidative work up avoids co-distillation of boron-containing by-products with the diene. After stirring vigorously for 30 min at ambient

temperature, the phases were separated, and the aqueous layer was extracted with n-pentane. The combined pentane extracts were washed with brine, dried (MgSO_4), and concentrated. The cyclohexanol by-product was removed by column chromatography on Florisil (60–100 mesh) using n-hexane. Distillation of the diene fraction gave 1.12 g (67%) of (5*E*,7*Z*)-dodecadiene containing 8% of 1-cyclohexyl-1-hexene: b.p. 60–61°C (1 Torr); n_D^{23} 1.4646 (lit. [1] b.p. 68–69°C/0.8 Torr, n_D^{22} 1.4652); IR (neat): 3030, 980, 950 and 730 cm^{-1} ; UV_{max} (cyclohexane) 234 (25,600) nm; ^1H NMR (CCl_4): δ 0.92 (t, 6H, J 6 Hz), 1.3 (m, 8H), 2.1 (m, 4H), and 5.0–6.6 ppm (m, 4H).

(5*Z*,7*E*)-Tetradecadiene. Using the procedure described above, 1-octyne (2.20 g, 20.0 mmol) was hydroborated with dicyclohexylborane (20 mmol). The organoborane formed was treated sequentially with lithium 1-hexynylide (20 mmol) and boron trifluoride etherate (2.8 ml, 22 mmol). After protonolysis and oxidation, the diene product obtained was distilled from a small amount of calcium carbonate to give 2.64 g (68%) of (5*Z*,7*E*)-tetradecadiene: b.p. 68–69°C/0.3 Torr; n_D^{24} 1.4664; IR (neat): 3035, 985, 950, and 730 cm^{-1} ; UV_{max} (cyclohexane): 234 (26,000) nm; ^1H NMR (CCl_4): δ 0.9 (m, 6H), 1.3 (m, 12H), 2.1 (m, 4H), and 5.0–6.6 ppm (m, 4H); exact mass m/e 194.2030 (calcd. 194.2036).

(5*E*,7*Z*)-Tetradecadiene. 1-Hexyne (20 mmol) was hydroborated with dicyclohexylborane, the resultant organoborane was treated with lithium 1-octynylide (20 mmol), and then with boron trifluoride etherate. Protonolysis and oxidation yielded 2.81 g (72%) of (5*E*,7*Z*)-tetradecadiene containing 8% of 1-cyclohexyl-1-octene: b.p. 65–66°C/0.3 Torr; n_D^{25} 1.4650; IR (neat): 3030, 980, 950, and 730 cm^{-1} ; UV_{max} (cyclohexane): 233 (24,200) nm; ^1H NMR (CCl_4): δ 0.9 (m, 6H), 1.3 (m, 12H), 2.1 (m, 4H), and 5.0–6.4 ppm (m, 4H).

(3*E*,5*Z*)-2,2-Dimethyldodeca-3,5-diene. 3,3-Dimethyl-1-butyne (1.64 g, 20.0 mmol) was hydroborated with dicyclohexylborane (20 mmol). The organoborane obtained was treated with lithium 1-octynylide (20 mmol), then with boron trifluoride etherate (2.8 ml, 22 mmol). Protonolysis and oxidation produced 2.77 g (71%) of (3*E*,5*Z*)-2,2-dimethyldodeca-3,5-diene containing 4% of 1-cyclohexyl-1-octene: b.p. 59–60°C/0.4 Torr; n_D^{21} 1.4632; IR (neat): 3020, 985, 950, and 740 cm^{-1} ; UV_{max} (cyclohexane): 233 (25,900) nm; ^1H NMR (CCl_4): δ 0.89 (t, 3H), 1.03 (J, 9H), 1.3 (m, 8H), 2.1 (m, 2H), and 4.9–6.4 ppm (m, 4H); exact mass m/e 194.2012 (calcd. 194.2036).

(1*E*,3*Z*)-1-Cyclohexyl-5-methylhexa-1,3-diene. Cyclohexylethyne (1.08 g, 10.0 mmol) was hydroborated with dicyclohexylborane (10 mmol). To the resultant organoborane was added sequentially lithium 3-methyl-1-butynylide (10 mmol) followed by boron trifluoride etherate (1.4 ml, 11 mmol). The concentrated reaction products were chromatographed on Florisil, and the hydrocarbon fraction obtained was distilled to afford 1.07 g (60%) of (1*E*,3*Z*)-1-cyclohexyl-5-methylhexa-1,3-diene: b.p. 52–53°C/0.3 Torr; n_D^{22} 1.4905; IR (neat) 3020, 985, 950 and 750 cm^{-1} ; UV_{max} (cyclohexane): 232 (27,700) nm; ^1H NMR (CCl_4): δ 0.96 (d, 6H, J 7 Hz), 1.0–2.1 (m, 11H), 2.70 (m, 1H), and 4.8–6.4 ppm (m, 4H); exact mass m/e 178.1733 (calcd. 178.1723).

Methyl (10*E*,12*Z*)-hexadecadienoate. Methyl 10-undecynoate (3.92 g, 20.0 mmol) was treated with dicyclohexylborane (20 mmol). To the resultant organoborane was added at –70 to –60° lithium 1-pentynylide (20 mmol). After adding boron trifluoride etherate (2.8 ml, 22 mmol), the reaction product

was protonolyzed with acetic acid (6.9 ml) at 50°C for 1 h. Oxidation at 30–50°C in the presence of methanol (20 ml) with sodium hydroxide (25 ml, 6 *N*) and 30% hydrogen peroxide (4.8 ml) yielded, after work up and short path distillation, 3.46 g (66%) of methyl (10*E*,12*Z*)-hexadecadienoate: b.p. 108–111°C/10^{−4} Torr; n_D^{25} 1.4738 (lit. [10] b.p. 105–110°C/10^{−3} Torr; n_D^{25} 1.4745); IR (neat): 3035, 1740, 985, 950, and 730 cm^{−1}; ν_{max} (cyclohexane): 233 (26,100) nm (lit. [10]: 233 (25,000) nm); ¹H NMR (CCl₄): δ 0.92 (t, 3H, *J* 6 Hz), 1.3 (m, 14H), 2.1 (m, 6H), 3.56 (s, 3H), 4.9–6.5 ppm (m, 4H); exact mass *m/e* 266.2242 (calcd. 266.2247).

General procedure for the preparation of dienes using tri-n-butyltin chloride

(5*E*,7*Z*)-Dodecadiene. The lithium (*trans*-1-hexenyl)(1-hexynyl)borate (10 mmol) was prepared in an analogous fashion to that described for the corresponding boron trifluoride mediated transfer reaction, and then was treated at 0–5°C with tri-*n*-butyltin chloride (3.0 ml, 11 mmol). The reaction mixture was brought to room temperature (15 min), stirred for one additional h, and diluted with glacial acetic acid (2.3 ml). After being heated at 50°C for 1 h, the mixture was oxidized at 30–50°C by adding consecutively methanol (10 ml), sodium hydroxide (8 ml, 6 *N*), and 30% hydrogen peroxide (2.4 ml). After work up, the dried extract (MgSO₄) was concentrated and then chromatographed on Florisil using petroleum ether (30–60°C) as the eluent. It should be noted that the tri-*n*-butyltin chloride mediated diene syntheses produced, in addition to cyclohexanol, after protonolysis and oxidative work up, bis(tributyltin) oxide (Bu₃SnOSnBu₃). In those cases in which their by-products interfered in isolation of the diene product, the concentrated extracts were chromatographed on Florisil. Distillation of the eluant afforded 1.12 g (68%) of (5*E*,7*Z*)-dodecadiene containing 6% of 1-cyclohexyl-1-hexene. The physical constants of the diene were similar to those observed in the corresponding boron trifluoride mediated reaction.

(5*Z*,7*E*)-Tetradecadiene. Sequential treatment of dicyclohexyl(*trans*-1-octenyl)-borane (10 mmol) with lithium 1-hexynylide (10 mmol), tri-*n*-butyltin chloride (11 mmol), glacial acetic acid, and alkaline hydrogen peroxide yielded, after work up, passage of the concentrated extract through Florisil and distillation, 1.44 g (74%) of (5*Z*,7*E*)-tetradecadiene containing 5% of the 1-cyclohexyl-1-hexene. The physical constants of the diene obtained were similar to those observed for the diene produced in the corresponding boron trifluoride mediated reaction.

(3*E*,5*Z*)-2,2-Dimethyldodeca-3,5-diene. Dicyclohexyl(*trans*-3,3-dimethyl-1-butenyl)borane (10 mmol) was treated sequentially with lithium 1-octynylide (10 mmol), tri-*n*-butyltin chloride (11 mmol), glacial acetic acid, and alkaline hydrogen peroxide as described above. The concentrated organic extract was chromatographed on Florisil, and the eluant was distilled to give 1.35 g (70%) of the diene containing 6% of 1-cyclohexyl-1-octene. The physical constants of the diene were similar to those observed for the diene obtained in the corresponding boron trifluoride mediated reaction.

(1*Z*,3*E*)-1-Cyclohexylocta-1,3-diene. Dicyclohexyl(*trans*-1-hexenyl)borane (10 mmol) was treated sequentially with lithium cyclohexylethynylide (10 mmol), and tri-*n*-butyltin chloride (11 mmol). Since the diene isomerizes in the

presence of acetic acid at elevated temperatures, the protonolysis was carried out at 25°C for 30 min. After oxidation and passage of the concentrated organic extract through Florisil, there was obtained 1.02 g (53%) of the diene containing 4% of 1,2-dicyclohexylethene: b.p. 75–76°C/0.4 Torr, n_D^{25} 1.4916; IR (neat); 3020, 985, 950, and 740 cm^{-1} ; UV_{max} (cyclohexane): 235 (25.900) nm; ^1H NMR: δ 0.7–2.5 (m, 20H), 5.06 (dd, 1H, J 10 Hz and J 10 Hz), 5.52 (dt, 1H, J 15 Hz and J 6 Hz), 5.75 (dd, 1H, J 10 Hz and J 10 Hz), 6.26 ppm (dd, 1H, J 15 Hz and J 10 Hz); exact mass m/e 192.1890 (calcd.: 192.1879).

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