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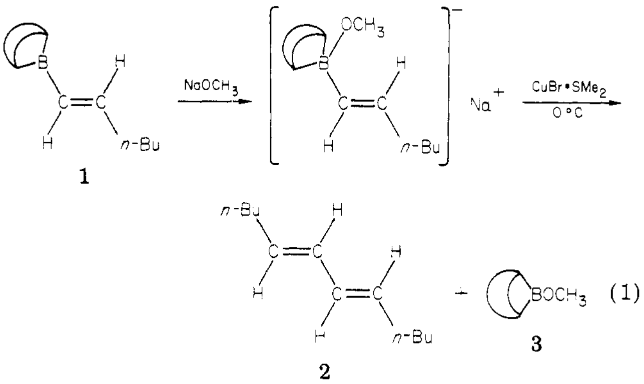
Communications

Stereospecific Synthesis of Symmetrical Conjugated Dienes with Alkenylcopper Intermediates from Alkenyldialkylboranes

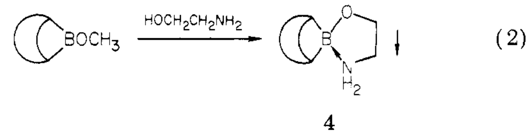
Summary: Sodium methoxyalkenyldialkylborates, obtained in the simple treatment of alkenyldialkylboranes with sodium methoxide, react readily with cuprous bromide–methyl sulfide at 0 °C to afford symmetrical conjugated dienes. The dienes are formed with retention of configuration predetermined from the stereochemistry of the initial alkenylborane intermediate.

Sir: Recent investigations in our laboratories have been directed toward developing alkenylmetallic methods for stereospecific carbon–carbon bond formation via alkenylboranes.[1] Of especial interest is the preparation of other more reactive alkenylmetallic reagents directly from alkenylboranes for stereospecific olefin synthesis. The initial study involved the possible transmetalation from boron to copper, influenced by the demonstrated synthetic utility of organocopper compounds.[2]

Toward this objective, we discovered that the borate complex, formed by addition of sodium methoxide to *B*-(1*E*)-1-hexen-1-yl-9-borabicyclo[3.3.1]nonane[3] (**1**), reacts rapidly with $CuBr{\cdot}SMe_2$ at 0 °C to give a 95% yield of (5*E*,7*E*)-5,7-dodecadiene (eq 1). The fact that the diene **2** is exclusively the *E*,*E* isomer was established by comparison of its spectral characteristics with those of an authentic sample.[4]



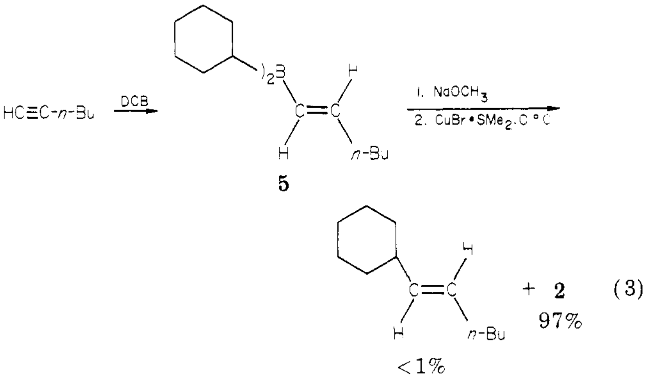
The reaction proceeds very cleanly, yielding only the diene and *B*-MeO-9-BBN (**3**).[5] Dicyclohexylborane derivatives of acetylenes can also be utilized. The methyl dialkylborinate byproduct can be conveniently removed by adding ethanolamine to the mixture upon completion of the reaction. The resulting air-stable adduct (**4**) precipitates, leaving the pure diene in solution (eq 2).



Apparently an alkenylcopper compound or a copper complex with boron is formed during the reaction. Stereospecific homocoupling then affords the corresponding conjugated dienes. Such "thermally induced" dimerizations of alkenylcopper reagents to give 1,3-dienes have been well documented.[6]

Recently alkenylchloroborane–methylcopper complexes were reported to produce (*E*,*E*)-1,3-dienes in excellent yields and with high stereochemical purity.[4] The reaction proceeds well with freshly distilled dialkenylchloroboranes. However, in our hands failure to purify these borane intermediates results in a considerable decrease in the yield of diene. Also, use of the more accessible alkenyldialkylboranes as precursors gives complex reaction mixtures. Presumably, substantial alkyl migration from boron can compete with alkenyl-group transfer in this reaction.

Our procedure involving the sodium methoxyalkenyldialkylborates does not require isolation of any borane precursor and gives only small amounts of competing alkyl-group transfer. The extent of alkyl-group migration was demonstrated and quantitatively established by treating the sodium methoxide addition compound of (1*E*)-1-hexen-1-yldicyclohexylborane (**5**) with $CuBr{\cdot}SMe_2$ at 0 °C (eq 3). A 97% yield of the diene **2** was obtained by GC analysis with less than 1% detected of the product derived from alkyl–group transfer.



The recent accessibility of (1*Z*)-1-alkenyldicyclohexylboranes[7] also permits preparation of (*Z*,*Z*)-1,3-dienes (eq cyclohexylborane (**6**) as a precursor proved to be exclu- 4). The diene obtained by using (1*Z*)-1-hexen-1-yldi- sively the *Z*,*Z* isomer, indicating again complete retention of configuration from the starting alkenylborane.

The mild and general nature of both the hydroboration and the coupling reaction permits a variety of alkynes, both terminal and internal, to be employed as precursors (Table I). Numerous sensitive functional groups can also be

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[1] (a) Brown, H. C.; Jacob, P., III. *J. Am. Chem. Soc.* **1976**, *98*, 7832. (b) Brown, H. C.; Jacob, P., III. *J. Org. Chem.* **1977**, *42*, 579.

[2] (a) Posner, G. H. *Org. React.* **1972**, *19*, 1. (b) Posner, G. H. *Ibid.* **1975**, *22*, 253.

[3] Prepared by hydroboration of 1-hexyne with 9-borabicyclo[3.3.1]nonane (9-BBN).

[4] Yamamoto, Y.; Yatagai, H.; Sonoda, A.; Murahashi, S. I.; Moritani, I. *J. Am. Chem. Soc.* **1977**, *99*, 5652.

[5] The *B*-MeO-9-BBN was identified by ^{11}B NMR and proved to be identical with a sample prepared by methanolysis of 9-BBN.

[6] (a) Kauffman, T.; Sahm, W. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 85. (b) Whitesides, G. M.; Casey, C. P.; Krieger, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 1379.

[7] (a) Negishi, E.; Williams, R. M.; Lew, G.; Yoshida, T. *J. Organomet. Chem.* **1975**, *92*, C4. (b) Campbell, J. B., Jr.; Molander, G. A. *Ibid.* **1978**, *156*, 71.

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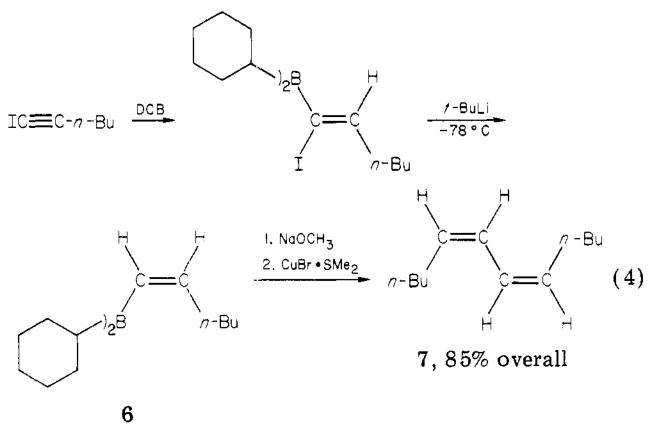
Table I. Preparation of Symmetrical Conjugated Dienes

alkyne	hydroborating reagent	product	yield,[c] %
1-hexyne	9-BBN[a]	(5*E*,7*E*)-5,7-dodecadiene (2)	95
	DCB[b]	(5*E*,7*E*)-5,7-dodecadiene (2)	97
3-hexyne	DCB	(3*E*,5*E*)-4,5-diethyl-3,5-octadiene	99 (91)
3,3-dimethyl-1-butyne	9-BBN	(3*E*,5*E*)-2,2,7,7-tetramethyl-3,5-octadiene	98
4-acetoxy-1-butyne	DCB	(3*E*,5*E*)-1,8-diacetoxy-3,5-octadiene	80
phenylethyne	DCB	(1*E*,3*E*)-1,4-diphenyl-1,3-butadiene	(79)
5-chloro-1-pentyne	DCB	(4*E*,6*E*)-1,10-dichloro-4,6-decadiene	95
1-iodo-1-hexyne	DCB[d]	(5*Z*,7*Z*)-5,7-dodecadiene (7)	85

[a] 9-Borabicyclo[3.3.1]nonane. [b] Dicyclohexylborane. [c] Yields are by GC analysis. Numbers in parentheses are yields by isolation. [d] The intermediate, (1-iodo-1-hexenyl)dicyclohexylborane, was treated with *t*-BuLi to provide (1*Z*)-1-hexen-1-yldicyclohexylborane.



(4)

7, 85% overall

6

tolerated by the reaction procedure.

The following procedure for the preparation of (3*E*,5*E*)-4,5-diethyl-3,5-octadiene is representative. To a freshly prepared suspension of dicyclohexylborane[8] (50.0 mmol) in THF at 0 °C is added 5.81 mL (51.0 mmol) of 3-hexyne over a period of 3–5 min. The cold-bath temperature is adjusted to 5–10 °C and the reaction stirred until the precipitate of the dicyclohexylborane completely disappears (ca. 1.5 h). The cooling bath is then removed and the reaction stirred an additional 30 min to ensure complete hydroboration. The solution is decanted onto a suspension of $NaOCH_3$ (53.0 mmol) in THF at 25 °C.[9] After being stirred for 30 min, the resultant solution is decanted dropwise via cannula onto a 0 °C suspension of $CuBr{\cdot}SMe_2$[10] (10.5 g, 51.0 mmol) in THF. The reaction is stirred 1 h each at 0 and 25 °C, followed by quenching with 10 mL of 3 N HCl. The clear organic layer is separated from the copper sediments, with the residue being washed with pentane (3 × 30 mL). Ethanolamine (3.06 mL, 51.0 mmol) is added, resulting in immediate precipitation of the ethanolamine–dicyclohexylborinate adduct. The precipitate is removed by centrifugation and washed with fresh pentane (2 × 30 mL). The clear organic phase is dried ($MgSO_4$) and concentrated to give a slightly yellow oil. Distillation affords 3.77 g (22.7 mmol) or 91% of the diene [bp 86–87 °C (18 mm Hg)]. The product was analytically pure by GC analysis and a single stereoisomer by ^1H and ^{13}C NMR.

The exact nature of the reactive species generated in the reaction is uncertain. The intermediacy of a copper(I) borate complex formed by cation exchange with sodium appears likely. Such borate complexes have been previously suggested as intermediates in reactions involving trialkylboranes and copper(I) complexes.[11] However, whether this intermediate decomposes directly to give a diene or dissociates to yield an alkenylcopper compound remains to be established. The cleanly defined stereospecificity of the hydroboration of alkynes, usually with very high regiospecificity, permits accurate prediction of the stereochemistry of the ultimate product. The tolerance for reactive functional groups is also promising for the scope and versatility of this synthesis.

Registry No. 1, 69322-45-8; 2, 30651-68-4; 3, 38050-71-4; 5, 37609-12-4; 6, 56962-83-5; 7, 6108-62-9; 1-hexyne, 693-02-7; 3-hexyne, 928-49-4; 3,3-dimethyl-1-butyne, 917-92-0; 4-acetoxy-1-butyne, 56703-55-0; phenylethyne, 536-74-3; 5-chloro-1-pentyne, 14267-92-6; 1-iodo-1-hexyne, 1119-67-1; (3*E*,5*E*)-4,5-diethyl-3,5-octadiene, 30651-70-8; (3*E*,5*E*)-2,2,7,7-tetramethyl-3,5-octadiene, 22430-49-5; (3*E*,5*E*)-1,8-diacetoxy-3,5-octadiene, 72161-00-3; (1*E*,3*E*)-1,4-diphenyl-1,3-butadiene, 538-81-8; (4*E*,6*E*)-1,10-dichloro-4,6-decadiene, 57404-73-6; 9-BBN, 280-64-8; DCB, 1568-65-6.

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[8] Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. "Organic Syntheses via Boranes"; Wiley-Interscience: New York, 1975.

[9] The $NaOCH_3$ must be free of any CH_3OH. Typically, a standard aliquot of $NaOCH_3$ in CH_3OH was "dried" by heating at 150 °C for 2 h under high vacuum (ca. 0.1 torr).

[10] House, H. O.; Chu, C. Y.; Wilkins, J. M.; Umen, M. J. *J. Org. Chem.* **1975**, *40*, 1460.

[11] (a) Miyaura, N.; Itoh, M.; Suzuki, A. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2199. (b) Miyaura, W.; Itoh, M.; Suzuki, A. *Tetrahedron Lett.* **1976**, 255.

[12] Graduate research assistant on Grant No. CHE 76-20846 provided by the National Science Foundation.

Stereospecific Synthesis of 1,4-Dienes by Cross-Coupling of Allyl Halides with Alkenylcopper Intermediates from Alkenyldialkylboranes

Summary: Alkenylcopper intermediates, generated from alkenyldialkylborane derivatives of 9-borabicyclo[3.3.1]-nonane (9-BBN) and dicyclohexylborane (DCB), undergo stereospecific cross-coupling with allylic halides to yield stereodefined 1,4-dienes.

Sir: In the preceding communication, a stereospecific synthesis of (*E*,*E*)- and (*Z*,*Z*)-1,3-dienes was described on the basis of alkenyldialkylborane precursors readily synthesized via hydroboration.[1] Treatment of such sterically defined alkenylboranes with sodium methoxide and $CuBr{\cdot}SMe_2$ provides excellent yields of dienes with defined stereochemistry. These dienes are postulated to be formed through the intermediacy of an alkenylcopper complex.

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