Selective Hydroboration of Conjugated Divnes with Dialkylboranes. A Convenient Route to Conjugated cis-Enynes, α , β -Acetylenic Ketones, and *cis,cis*-Dienes¹

George Zweifel and Norman L. Polston

Contribution from the Department of Chemistry, University of California, Davis, California 95616. Received December 19, 1969

Abstract: The monohydroborations of dodeca-5,7-diyne, 2,7-dimethylocta-3,5-diyne, and 2,2,7,7-tetramethylocta-3,5-diyne with disiamylborane [bis(3-methyl-2-butyl)borane] proceed to place the boron preferentially at the internal positions of the divne system. The organoboron intermediates upon protonolysis with acetic acid give the corresponding cis-envnes in high yields. Oxidation of the monohydroboration products with alkaline hydrogen peroxide affords the corresponding α,β -acetylenic ketones in better than 70% yields. Dihydroboration of dodeca-5,7-diyne, 2,7-dimethylocta-3,5-diyne, and 2-methyldodeca-3,5-diyne with dicyclohexylborane followed by protonolysis produces the corresponding cis, cis-dienes. For hindered diynes such as 2,2,7,7-tetramethylocta-3,5diyne, however, reduction to the diene has to be carried out stepwise. Thus, the diyne is first converted to the enyne via the hydroboration-protonolysis reaction. Subsequent hydroboration of the cis-enyne followed by protonolysis with acetic acid affords cis, cis-2, 2, 7, 7-tetramethylocta-3, 5-diene.

The hydroboration of conjugated dienes has been the subject of numerous investigations and has resulted in new routes to a large number of acyclic and cyclic organoboranes which undergo versatile chemical transformations.² The hydroboration of conjugated diynes and the chemistry of the resultant organoboranes, on the other hand, has remained essentially unexplored.

In connection with our studies concerning the syntheses of vinylboranes and their conversions to functional derivatives, we became interested in the possibility of converting conjugated diynes to the corresponding enynylboranes via the hydroboration reaction. It was anticipated that the protonolysis of these monohydroboration products would afford enynes, and oxidation would yield α,β -acetylenic ketones. Moreover, dihydroboration of conjugated diynes appeared to offer a route to 1.3-butadiene systems containing two boron atoms. Combined with protonolysis of the intermediate organoboranes, this would provide a method for a noncatalytic reduction of diynes to the corresponding dienes.

Results and Discussion

Preparation of Conjugated cis-Enynes. Preliminary experiments revealed that the hydroboration of dodeca-5,7-diyne with 2 equiv of disiamylborane resulted in a fast uptake of one hydride per diyne molecule. Further addition of B-H was very slow, indicating that the addition of disiamylborane to the diyne could be controlled to give the monohydroboration product.

It has been shown that protonolysis of vinylboranes with acetic acid occurs readily at room temperature. The reaction proceeds with retention of configuration to give the corresponding alkenes,³ thus providing a convenient tool for the elucidation of vinylborane structures. In applying the protonolysis reaction to the

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 G. Zweifel, K. Nagase, and H. C. Brown, J. Amer. Chem. Soc., 84, 183, 190 (1962); G. Zweifel and H. C. Brown, *ibid.*, 85, 2066 (1963); R. Köster, Advan. Organometal. Chem., 2, 257 (1964); H. C. Brown and C. D. D. Stationard Science (1964); H. C. Brown and C. D. Pfaffenberger, J. Amer. Chem. Soc., 89, 5475 (1967); H. C. Brown and E. Negishi, ibid., 89, 5477 (1967).

monohydroboration product derived from dodeca-5,7divne, however, it was observed that the cleavage of the vinyl carbon-boron bond occurred very slowly. Hence the protonolysis of the intermediate organoborane was carried out at 55-60° for 5 hr.

In a representative experiment a solution of disiamylborane (11 mmol) in tetrahydrofuran was added to a solution of dodeca-5,7-diyne (10 mmol) in tetrahydrofuran. The reaction was maintained at $0-5^{\circ}$ for 3 hr. Protonolysis of the intermediate organoborane with an excess of acetic acid at 55-60° for 5 hr afforded, by glpc analysis, 83% cis-5-dodecen-7-yne, 7% cis, cis-dodeca-5,7-diene, and only traces of unreacted diyne. The 10% excess of disiamylborane was found, from pre-



liminary experiments, to be necessary to ensure complete utilization of the diyne.⁴

In extending the monohydroboration-protonolysis reaction to 2,7-dimethylocta-3,5-diyne and to the sterically hindered 2,2,7,7-tetramethylocta-3,5-diyne, it was gratifying to observe that the corresponding cisenynes were also formed in high yields in both cases. Moreover, the side-product dienes were formed in less than 1% yields.⁵ The results of these experiments are summarized in Table I.

In order to determine the position of the boron in the monohydroboration product, dodeca-5,7-diyne was treated with 1 equiv of disiamylborane. The resultant organoborane was treated with deuterioacetic acid. Nmr examination of the cis-envne obtained revealed

⁽³⁾ H. C. Brown and G. Zweifel, ibid., 83, 3834 (1961).

⁽⁴⁾ Attempted monohydroboration of dodeca-5,7-diyne with dicyclohexylborane gave after protonolysis an 80-20 mixture of enyne and diene. Thus, disiamylborane is clearly the reagent of choice for monohydroboration of diynes.

⁽⁵⁾ For catalytic reductions of diacetylenes to enynes, see P. N. Rylander, "Catalytic Hydrogenation Over Platinum Metals," Academic Press, New York, N. Y., 1967, p 71.

 Table I. The Yields of the Protonolysis and Oxidation Products

 Obtained from Several Monohydroborated

 Disubstituted 1,3-Diynes^a

Diyne	cis-Enyne, % ^b	α,β - Acetylenic ketone, $\%^b$
$\overline{n - C_4 H_9 C} \equiv C - C \equiv C C_4 H_9 - n$	76	75
>-c=c-c=c-<	77	74
	75	80°

^a Using a 10% excess of disiamylborane. ^b By isolation. ^c By glpc analysis.

that $95 \pm 3\%$ of deuterium was attached at the internal position of the double bond. This result indicates



that the boron preferentially attacks the sterically lesshindered internal positions of the diyne system. A similar selectivity was observed in the hydroboration of dodeca-5,7-diyne with dicyclohexylborane where nmr examination of the *cis*-enyne obtained after deuterolysis of the intermediate organoborane indicated that 97 \pm 3% of the deuterium was attached at the internal position of the double bond.⁴

In connection with the observed mode of addition of dialkylboranes to diynes it should be noted that the boron does not discriminate between the triple bonds in unsymmetrically substituted diynes. Thus, monohydroboration of 2,2-dimethyldeca-3,5-diyne with disiamylborane gave, after protonolysis, the two possible *cis*-enynes in nearly equal amounts.

$$(CH_3)_3CC = C - C = CC_4H_9 \cdot n \xrightarrow{1. R_4BH} \xrightarrow{2. CH_3COOH} (CH_3)_3CCH = CHC = CC_4H_9 \cdot n + (CH_3)_3CC = C - CH = CHC_4H_9 \cdot n$$

Preparation of α,β -Acetylenic Ketones. It has been shown that vinyl organoboranes react readily with alkaline hydrogen peroxide to afford the corresponding carbonyl derivatives.³ Thus, the observation that B-H addition to symmetrically disubstituted diynes is selective suggested that it should be possible to synthesize α,β -acetylenic ketones by oxidation of the diyne monohydroboration products. To explore the



scope of this novel reaction, the 1,4-di-*n*-butyl-, 1,4-diisopropyl-, and 1,4-di-*t*-butyldiynes were monohydroborated with disiamylborane. The resultant organoboranes were treated at 25-35° with sodium hydroxide followed by addition of 30% hydrogen peroxide. The α,β -acetylenic ketones were separated from the contaminant 3-methyl-2-butanol by distillation. The results of these experiments are also summarized in Table I. In view of the ready availability of symmetrically substituted diynes via the Glaser reaction⁶ it is apparent that the hydroboration-oxidation reaction represents an efficient route to acetylenic ketones.⁷

Preparation of Conjugated cis, cis-Dienes. As stated earlier, the addition of a second equivalent of disiamylborane to the monohydroboration product derived from dodeca-5,7-diyne was very slow. However, this difficulty could be circumvented by using the sterically less-hindered dicyclohexylborane. By maintaining the reaction at room temperature for 5 hr, two hydrides per diyne molecule were utilized. Protonolysis of the intermediate organoborane with acetic acid at 60° for 5 hr produced cis, cis-dodeca-5,7-diene in 79% yield.⁸

$$n \cdot C_{4}H_{9}C = C - C = CC_{4}H_{9} \cdot n \xrightarrow{1.(C_{4}H_{11})_{2}BH}_{2.CH_{3}COOH}$$

$$n \cdot C_{4}H_{9} \xrightarrow{H}_{C} = C \xrightarrow{H}_{C} \xrightarrow{H}_{C_{4}H_{9} \cdot n}$$

It should be noted here that whereas monohydroboration of unsymmetrically substituted diynes produces a mixture of organoboranes, the dihydroboration-protonolysis procedure is suitable for the conversion of unsymmetrical conjugated diynes to the corresponding cis, cis-dienes. Thus, bishydroboration of 2-methyldodeca-3,5-diyne with dicyclohexylborane followed by protonolysis gave a 74% isolated yield of the corresponding cis, cis-diene.

To investigate the scope of this noncatalytic reduction of divnes to dienes, the highly substituted 2,2,7,7tetramethylocta-3,5-diyne was treated at 25° with 2 equiv of dicyclohexylborane. The progress of the reaction was followed by periodically withdrawing aliquots from the reaction mixture and quenching them in a known amount of 1-hexene. Glpc analysis of the remaining 1-hexene indicated that the addition of the second B-H was extremely slow. Moreover, it was observed that the chromatogram of the protonolysis products of the organoboron intermediate exhibited additional peaks besides the expected components (diene, enyne, and diyne). Consequently, it was of interest to explore alternative hydroboration-protonolysis routes for reduction of the sterically hindered diynes. It was discovered that the *cis*-enyne resulting from the monohydroboration-protonolysis reaction of 2,2,7,7-tetramethylocta-3,5-diyne reacted readily with disiamylborane. Treatment of the intermediate organoborane with acetic acid afforded after distillation 75% of cis, cis-2,2,7,7-tetramethylocta-3,5-diene, representing a 56% overall isolated yield based on starting diyne.

In order to facilitate the isolation of the *cis,cis*-diene products by distillation, the siamyl or cyclohexyl moieties attached to boron must be oxidized to the corresponding alcohols prior to the work-up. There-

⁽⁶⁾ G. Eglinton and W. McCrae, Advan. Org. Chem., 4, 225 (1963). (7) F. Bohlman and H. G. Viehe, Chem. Ber., 88, 1017 (1955), reported that the acid-catalyzed hydration of disubstituted diynes affords α,β -acetylenic ketones.

⁽⁸⁾ A. J. Hubert, *Chem. Soc.*, 6669 (1965), reported that the hydroboration of dodeca-5,7-diyne with disiamylborane yielded, after protonolysis with acetic acid, a mixture of products containing less than 10% of the desired *cis,cis*-diene. However, heating the diyne with triisobutylborane at 170° yielded, after protonolysis with acetic acid, 42% of *cis,cis*-dodeca-5,7-diene.



fore, difficulties may be encountered in cases where the diene exhibits a similar boiling point as the contaminant alcohol. This problem was encountered in the dihydroboration of 2,7-dimethylocta-3,5-diyne with dicyclohexylborane. Although the reduction proceeded to completion, the diene obtained after protonolysis and oxidation could not be distilled free from cyclohexanol. This difficulty was obviated by reducing the diyne with disiamylborane to the enyne stage. The enyne obtained was rehydroborated with an equimolar amount of disiamylborane. After protonolysis and oxidation, the diene obtained was readily separated from 3-methyl-2-butanol by distillation. A summary of the yields of dienes realized in these reactions is shown in Table II.

 Table II.
 The Yields of cis,cis-Dienes Obtained via the

 Hydroboration-Protonolysis Reactions of 1,3-Diynes

Diyne	Method of reduction ^a	Yield of cis,cis- diene, % ^b
$n-C_4H_9C \equiv C - C \equiv CC_4H_9 - n$	Α	79
	В	60
	В	56
$n \cdot C_6 H_{13} C = C - C = C - \langle$	Α	74

^a Method A, hydroboration with dicyclohexylborane in a 1:2 ratio. Method B, conversion of the diyne to the enyne with disiamylborane followed by subsequent reduction of the enyne with 1 equiv of disiamylborane. ^b By isolation. In all experiments the yields are based on the starting diynes.

In order to determine the distribution of the boron atoms in the dihydroboration product, dodeca-5,7diyne was hydroborated with 2 equiv of dicyclohexylborane. The resultant dihydroboration product was treated with deuterioacetic acid. Nmr examination of the *cis,cis*-dodeca-5,7-diene formed revealed the presence of 1.1 deuteriums at the internal and 0.9 deuterium at the terminal carbons of the diene system. Thus, the dihydroboration product contained the boron atoms in a 1,3 relationship. As mentioned earlier, addition of



the first B-H to the diyne proceeds to place the boron at an internal position of the 1,3-diyne system. Therefore, the second boron must add preferentially to the terminal carbon of the remaining triple bond of the monohydroboration product.

To illustrate the directive influence of the boron moiety in the enynylborane on the subsequent hydroboration to give the dihydroboration product, *cis*-5dodecen-7-yne was treated with 1 equiv of dicyclohexylborane. The resultant organoborane was protonolyzed with deuterioacetic acid. Nmr examination of the *cis,cis*-dodeca-5,7-diene formed indicated that only 29% of the boron had been attached to the terminal carbon of the triple bond. These results clearly point



to the marked directive effect of the boron moiety in the hydroboration of the monohydroboration product. The observed modes of addition of dialkylboranes to diynes can be accounted for in terms of stereochemical considerations.

Experimental Section

Materials. Tetrahydrofuran, diglyme, and boron trifluoride ethereate were purified as described previously.⁹ 2-Methyl-2butene and cyclohexene (99% pure grade) were obtained from the Phillips Petroleum Co. Acetic acid- d_1 (99%) was obtained from Diaprep, Inc.

Recording of Spectra. The infrared (ir) spectra were recorded on a Beckman Model IR-8 infrared spectrophotometer as liquid films. The ultraviolet (uv) spectra were obtained on a Cary Model 15 recording spectrophotometer in 1.00-cm cells with cyclohexane as solvent. The mass spectra were obtained with a double-focusing C.E.C. 21-104 mass spectrometer at 70 eV. The nuclear magnetic resonance (nmr) spectra were recorded on a Varian A-60 spectrometer with tetramethylsilane as an internal standard. Samples were run as 20% solutions in carbon tetrachloride.

Preparation of Diynes. The symmetrically disubstituted diynes were prepared *via* the Glaser reaction. The following procedure is representative.¹⁰ A steady stream of oxygen was passed into a well-stirred mixture of 0.10 mol of cuprous chloride, 50 ml of pyridine, 100 ml of acetone, and 0.20 mol of 1-hexyne over a period of 3 hr. The exothermic reaction was controlled between 20 and 40°. The mixture was then acidified with 75 ml of 6 N hydrochloric acid. After work-up there was obtained a 97% yield of dodeca-5,7-diyne: bp 78–79° (1 mm); n^{23} D 1.4880 [lit.¹¹ bp 110° (10 mm), n^{25} D 1.4890]. By a similar procedure, oxidative coupling of 3-methyl-1-butyne produced 97% of 2,7-dimethylocta-3,5-diyne: bp 84–85° (20 mm); n^{23} D 1.4787 [lit.¹² bp 74° (12 mm)]. Also, from 3,3-dimethyl-1-butyne mp 129–130° [lit.¹³ mp 130–132°].

The unsymmetrically substituted 2,2-dimethyldeca-3,5-diyne (48%) [bp 71-72° (2 mm); n^{23} D 1.4796] and 2-methyldodeca-3,5-diyne (44%) [bp 78-80° (0.03 mm); n^{24} D 1.4821] were synthesized via the Chodkiewicz–Cadiot reaction.¹⁴

Preparation of Disiamylborane. Disiamylborane was prepared by adding 29.6 ml of a 1.86 M solution of borane (55 mmol) in tetrahydrofuran to a solution of 2-methyl-2-butene (0.12 mol) in 20 ml of tetrahydrofuran maintained at $-5-0^{\circ}$. The reaction mixture was stirred at $0-5^{\circ}$ for 2 hr, then transferred to the reaction flask by means of a hypodermic syringe.

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⁽⁹⁾ G. Zweifel and H. C. Brown, Org. Reactions, 13, 1 (1963).

⁽¹⁰⁾ This procedure represents a modification of that given by L. F.
Fieser in "Organic Experiments," Raytheon Education Co., Lexington, Mass., 1968, p 82.
(11) H. K. Black, D. H. S. Horn, and B. C. L. Weedon, J. Chem.

⁽¹¹⁾ H. K. Black, D. H. S. Horn, and B. C. L. Weedon, J. Chem. Soc., 1704 (1954).

⁽¹²⁾ V. V. Gravilenko, L. L. Ivanov, and L. I. Zakharkin, Zh. Obshch. Khim., 37, 515 (1967).

⁽¹³⁾ F. Bohlmann, Chem. Ber., 86, 657 (1953).

Preparation of Enynes. cis-5-Dodecen-7-yne. To a solution of 8.10 g of dodeca-5,7-diyne (50 mmol) in 20 ml of tetrahydrofuran was added at $-5-0^{\circ}$ a solution of disiamylborane (55 mmol) in tetrahydrofuran. The reaction mixture was stirred at 0° (icewater bath) for 2 hr, then diluted with 12.5 ml of glacial acetic acid, and maintained at 55-60° for 5 hr. After the protonolysis reaction was complete the reaction mixture was made basic by adding 45 ml of 6 N sodium hydroxide. The disiamylborinate formed was oxidized at 35-40° with 13 ml of 30% hydrogen peroxide. After stirring the reaction mixture at room temperature for 30 min, sodium chloride was added and the upper phase formed was separated. The aqueous phase was extracted with n-pentane, and the combined extracts were dried (MgSO₄). Distillation of the product mixture through an annular Teflon spinning band column gave besides 3-methyl-2-butanol, 6.2 g of cis-5-dodecen-7-yne (76%): bp 70° (3.5 mm); $n^{22}D$ 1.4626; uv max (cyclohexane) 227 (ϵ 15,100) and 235 mµ (sh, e 12,300) [lit.15 bp 114-115° (25 mm), uv max (ethanol) 227 mµ].

2,7-Dimethyl-*cis*-**3-octen-5-yne.** 2,7-Dimethylocta-3,5-diyne was subjected to the hydroboration-protonolysis procedure as described above. Distillation of the product mixture through an annular Teflon spinning band column afforded 77% of 2,7-dimethyl-*cis*-3-octen-5-yne: bp 84° (90 mm); n^{24} D 1.4471; uv max (cyclohexane) 227 (ϵ 14,660) and 235 m μ (sh, ϵ 12,400); ir (neat) 2220 (C=C), 1610 (C=C), and 750 cm⁻¹ (*cis*-CH=CH). The nmr and mass spectra were consistent with the assigned structure.

Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.15; H, 12.22.

2,2,7,7-Tetramethyl-*cis*-**3-octen-5-yne.** Hydroboration of 2,2,7,7-tetramethylocta-3,5-diyne with disiamylborane followed by protonolysis of the intermediate organoborane yielded, after distillation through a short Vigreux column, 75% of 2,2,7,7-tetramethyl-*cis*-3-octen-5-yne: bp 62° (13 mm); n^{24} D 1.4477; uv max (cyclohexane) 228 (ϵ 15,000) and 237 m μ (sh, ϵ 12,600); ir (neat) 2230 (C=C), 1615 (C=C), and 740 cm⁻¹ (*cis*-CH=CH). The nmr and mass spectra were consistent with the assigned structure.

Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.64; H, 12.23.

Preparation of Ketones. 7-Dodecyn-6-one. Dodeca-5,7-diyne (50 mmol) was monohydroborated with 55 mmol of disiamylborane at 0-5° for 2 hr. The organoborane formed was oxidized at 25-35° by adding 18 ml of 3 N sodium hydroxide and 18 ml of 30% hydrogen peroxide. Distillation through a short Vigreux column gave, besides 3-methyl-2-butanol, 75% of 7-dodecyn-6-one: bp 107-108° (4 mm); $n^{22}D$ 1.4521 [lit.¹⁶ bp 102 (3 mm); $n^{20}D$ 1.4515]; uv max (cyclohexane) 217 (ϵ 8140) and 226 m μ (sh, ϵ 6660); ir (neat) 2200 (C=C) and 1665 cm⁻¹ (C=O).

2,7-Dimethyl-5-octyn-4-one. The ketone was obtained in 74% yield from 2,7-dimethylocta-3,5-diyne *via* the monohydroboration-oxidation reaction: bp 67° (5 mm); $n^{23}D$ 1.4403; uv max (cyclohexane) 218 (ϵ 7830) and 226 m μ (sh, ϵ 6450); ir (neat) 2200 (C=C) and 1665 cm⁻¹ (C=O). The nmr and mass spectra were in agreement with the assigned structure.

Anal. Calcd for C₁₀H₁₆O: C, 78.90; H, 10.59. Found: C, 79.26; H, 10.43.

2,2,7,7-Tetramethyl-5-octyn-4-one. 2,2,7,7-Tetramethylocta-3,5diyne was converted to the ketone as described by above: bp 80–81° (7 mm); n^{24} D 1.4404; 2,4-dinitrophenylhydrazone, mp 137–138°; uv max (cyclohexane), 220 (ϵ 7250) and 227 m μ (sh, ϵ 5590) [lit.⁷ bp 60° (0.05 mm), 2,4-dinitrophenylhydrazone, mp 137–138°, uv max 225 m μ (ϵ 6900)]; ir (neat) 2210 (C=C) and 1665 cm⁻¹ (C=O).

Preparation of Dienes. cis, cis-Dodeca-5,7-diene. To a solution of cyclohexene (0.22 mol) in 25 ml of tetrahydrofuran was added at $-5-0^{\circ}$ a solution of borane (0.11 mol) in tetrahydrofuran. The resultant precipitate was stirred at 0-5° for 1 hr. To the dicyclohexylborane (0.11 mol) formed was added at $-5-0^{\circ}$ a solution of dodeca-5,7-diyne (50 mmol) in 30 ml of tetrahydrofuran. The reaction mixture was allowed to come to room temperature, then was maintained at this temperature for 5 hr. The homogeneous, red solution formed was diluted with 25 ml of glacial acetic acid, then heated at 55-60° for 5 hr. Oxidation of the resulting dicyclohexylborinate was achieved by adding 85 ml of 6 N sodium hydroxide followed by dropwise addition of 26 ml of 30% hydrogen peroxide at a rate to maintain the reaction mixture of 30-35°. The mixture was then stirred for an additional 30 min before working up. Distillation of the product through a Vigreux column afforded 6.5 g of cis, cis-dodeca-5,7-diene (79%): bp 80-81° (4 mm); n^{23} D 1.4650; uv max (cyclohexane) 236 m μ (ϵ 24,600); ir (neat) 1760, 1690, 1600 (C=C), and 710 cm⁻¹ (cis-CH=CH) [lit.8 bp 120° (3 mm), uv max 236 mµ (e 24,000); ir 1600 and 715 cm⁻¹]. The nmr and mass spectra agreed with the assigned structure.

2-Methyl-*cis,cis***-dodeca-3,5-diene.** Dihydroboration of 2methyldodeca-3,5-diyne (50 mmol) with dicyclohexylborane (0.11 mol) followed by protonolysis of the intermediate organoborane yielded, after oxidation, 74% of 2-methyl-*cis,cis*-dodeca-3,5-diene: bp 80° (3 mm); n^{24} D 1.4616; uv max (cyclohexane) 235 mµ (¢ 26,700); ir (neat) 1760, 1675, and 1595 cm⁻¹ (C=C), and 730 cm⁻¹ (*cis*-CH=CH). The nmr and the mass spectra agreed with the assigned structure.

Anal. Calcd for $C_{13}H_{24}$: C, 86.59; H, 13.41. Found: C. 86.41; H, 13.19.

2,7-Dimethyl-*cis*,*cis*-**octa-3,5-diene.** To a solution of 6.85 g of 2,7-dimethyl-*cis*-3-octen-5-yne (50 mmol) in 30 ml of tetrahydro-furan was added at $-5-0^{\circ}$ a solution of disiamylborane (55 mmol) in tetrahydrofuran. The mixture was stirred at $0-5^{\circ}$ for 3 hr, then diluted with 12.5 ml of acetic acid, and heated at $55-60^{\circ}$ for 5 hr. The disiamylborinate was oxidized at $30-35^{\circ}$ by adding 45 ml of 6 N sodium hydroxide and 13 ml of 30% hydrogen peroxide. Distillation through an annular Teflon spinning band column gave 5.42 g (78%) of 2,7-dimethyl-*cis*,*cis*-octa-3,5-diene: bp 68° (35 mm); n^{23} D 1.4514; uv max (cyclohexane) 233 m μ (ϵ 25,000); ir (neat) 1770, 1690, 1600 (C=C), 935 and 740 cm⁻¹ (*cis*-CH=CH). The nmr and mass spectra were consistent with the assigned structure.

Anal. Calcd for C₁₀H₁₅: C, 86.88; H, 13.12. Found: C, 86.99; H, 13.50.

2,2,7,7-Tetramethyl-*cis*,*cis*-**octa-3,5-diene**. Under similar experimental conditions as described above, 10 mmol of 2,2,7,7-tetramethyl-*cis*-3-octen-5-yne was treated with 11 mmol of disiamylborane. The organoborane formed was treated with acetic acid, then with alkaline hydrogen peroxide. Distillation through a Vigreux column yielded 1.36 g (75%) of 2,2,7,7-tetramethyl-*cis*,*cis*-octa-3,5-diene: bp 67 (10 mm); n^{24} D 1.4590; uv max (cyclohexane) 238 and 234 m μ (ϵ 23,700); ir (neat) 1760, 1680, 1580 (C=C), 900, and 730 cm⁻¹ (*cis*-CH=CH). The nmr and mass spectra were in agreement with the assigned structure.

Anal. Calcd for $C_{12}H_{22}$: C, 86.62; H, 13.33. Found: C, 86.63; H, 13.06.

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