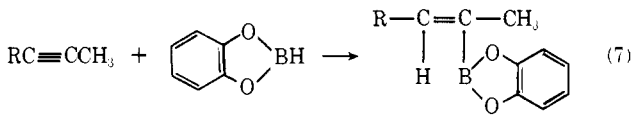
Fortunately, our recent work in this area has revealed that 1,3,2-benzodioxaborole (**1**) hydroborates olefins rapidly at 100° to give the corresponding alkaneboronic esters, 2-alkyl-1,3,2-benzodioxaboroles, in almost quantitative yields.[1] This prompted us to investigate the selective monohydroboration of alkynes with this new reagent in the hope of obtaining the corresponding cyclic esters of alkeneboronic acids, 2-alkenyl-1,3,2-benzodioxaboroles (**2**). Indeed, this reaction proceeds in a highly satisfactory manner, without observable dihydroboration, and the desired products **2** are readily isolated by distillation and can be stored under nitrogen for prolonged periods without polymerization or disproportionation.

In addition to the reactions of alkenylboroles **2**, pyridine forms stable 1:1 addition compounds with **2**. These products serve as easily identified solid derivatives of the alkenylboroles **2**.

The hydroboration of alkynes with catecholborane proceeds in a stereospecific cis manner[10] with the boron being attached regioselectively at the less hindered carbon atom of the triple bond. The reaction of the reagent with 4,4-dimethyl-2-pentyne, for example, proceeded almost exclusively (95%) to place the boron atom at the less hindered position (R = *tert*-butyl, eq 7). The



(7)

reaction is slightly less selective in the case of 1-cyclohexylpropyne, where a 92:8 distribution of the two isomers is observed (R = cyclohexyl, 92%, eq 7). Even in the case of 1-phenylpropyne, the boron atom goes preferentially to the less hindered position, in spite of the strong directive influence of the phenyl group in simple alkenes[2] (R = phenyl, 73%, eq 7).

Results on the conversion of several representative alkynes into the corresponding alkeneboronic esters and acids *via* the present method are summarized in Table I.[11]

The conversion of 1-cyclohexylpropyne into the corresponding derivative of **2** is illustrative of this new, simple hydroboration procedure. A mixture of 1-cyclohexylpropyne (12.2 g, 100 mmol) and catecholborane (12.0 g, 100 mmol) was stirred at 70° under nitrogen for 4 hr (terminal alkynes require 1 hr, internal alkynes require 2–4 hr). Distillation yielded 20.8 g (86%) of pure *cis*-2-(2-cyclohexyl-1-methyl)ethenyl-1,3,2-benzodioxaborole: bp 124° (0.15 mm); n^{20}D 1.5400.[11]

To achieve the protonolysis of this derivative, 7.2 g (30 mmol) was stirred under nitrogen with acetic acid (15 ml) at 100° for 2 hr. The resulting yellow solution was poured over ice water and extracted with pentane. The pentane extract was washed with ice-cold 1 *N* sodium hydroxide and then with brine, and dried over magnesium sulfate. Evaporation of the solvent gave 3.55 g (95%) of *cis*-propenylcyclohexane: bp 150° (750 mm); n^{20}D 1.4535.[11]

(10) This was confirmed by the trans relationship of the two vinylic protons in **2**, as indicated by pmr spectroscopy,[3,7] and also by the deuterolysis experiments.

(11) All the compounds gave concordant ir and nmr spectra. New compounds, in addition, gave satisfactory (within 0.3%) carbon–hydrogen analyses and mass spectra.

Table I. The Synthesis of Alkeneboronic Esters **2** and Acids **3** from Alkynes *via* the Hydroboration with Catecholborane

Alkyne hydroborated	Yield, %[a]	Bp, °C (mm)	n^{20}D
1-Pentyne	92 (80)	67 (0.4)	1.5225
1-Hexyne	90 (75)	82 (0.25)	1.5180
Cyclohexylethyne	93 (82)	114 (0.2)	1.5430
Phenylethyne	(85)	78–78.5[b]	
3,3-Dimethyl-1-butyne	94 (85)	74 (0.3)	1.5145
3-Chloro-1-propyne	85 (70)	80 (0.25)	1.5560
5-Chloro-1-pentyne	(82)	114 (0.6)	1.5435
3-Hexyne	92 (85)	81 (0.2)	1.5160
1-Cyclohexylpropyne	95 (86)	124 (0.15)	1.5400
4,4-Dimethyl-2-pentyne	97 (89)	86 (0.5)	1.5180
trans-2-Phenyletheneboronic acid	(80)	163–164[b]	
trans-5-Chloro-1-penteneboronic acid	(95)	94[b]	
trans-2-Cyclohexyletheneboronic acid	(97)	104–105[b]	

[a] By glpc analysis. The yields by isolation are given in parentheses. [b] Melting point of the compound.

Oxidation of 4.8 g (20 mmol) of *cis*-2-(2-cyclohexyl-1-methyl)ethenyl-1,3,2-benzodioxaborole with alkaline hydrogen peroxide was carried out in a THF–ethanol solution at 25–30° for 2 hr. The reaction mixture was extracted with pentane, and the pentane extract was washed with ice-cold 1 *N* sodium hydroxide and then with brine, and then dried over magnesium sulfate. The removal of the solvent gave cyclohexylacetone in 98% yield (glpc), essentially free of other products.

The following synthesis of 2-cyclohexyletheneboronic acid from the corresponding cyclohexyletheneboronic ester is representative. A mixture of **2** (R = cyclohexyl, 2.3 g, 10 mmol) and water (10 ml) was stirred rapidly at 25° for 1 hr. The white crystalline product thus formed was filtered and recrystallized from hot water to give 1.5 g (97%) of the desired acid: mp 104–105°.[11]

The reaction of 2-alkenyl-1,3,2-benzodioxaboroles with pyridine is illustrated by the following example. The alkenylborole **2** from 4,4-dimethyl-2-pentyne (2.16 g, 10 mmol) was dissolved in hexane (20 ml) and pyridine (0.8 g, 10 mmol) was added to it with stirring at 25° under nitrogen. A crystalline precipitate was formed almost immediately. After cooling with ice, it was filtered and recrystallized from hexane to give 2.8 g (94%) of the adduct: mp 97–98°.[11]

It is evident that this development of catecholborane as a selective, rapidly reacting, monofunctional hydroboration reagent for alkynes should have wide application and make the highly useful vinylboronic acid far more readily available.

(12) Postdoctorate research associate on Grant No. GM-10937, supported by the National Institutes of Health.

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Reaction of 2-Alkenyl-1,3,2-benzodioxaboroles with Mercuric Acetate. A Convenient Stereospecific Procedure for the Conversion of Alkynes into Alkenylmercuric Salts

Sir:

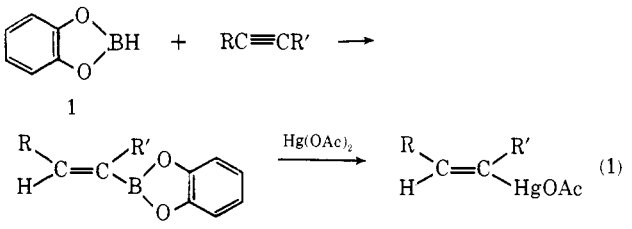
2-Alkenyl-1,3,2-benzodioxaboroles (**2**), readily available *via* hydroboration of alkynes with 1,3,2-benzodioxa-

Table I. Mercuration of 2-Alkenyl-1,3,2-benzodioxaboroles

2-Alkenyl-1,3,2-benzodioxaborole derived from	Product	Isolated yield, %	Mp,[a] °C
1-Pentyne	*trans*-1-Pentenylmercuric chloride	98	130–130.5
5-Chloro-1-pentyne	*trans*-5-Chloro-1-pentenylmercuric chloride	98	94.5–95.0
Cyclohexylethyne	*trans*-Cyclohexylethenylmercuric chloride	99	134–135
3-Hexyne	*cis*-3-Hexenylmercuric chloride	98	47.5–48.0
4,4-Dimethyl-2-pentyne	*cis*-4,4-Dimethyl-2-pentenylmercuric chloride	97	108–108.5

[a] Recrystallized from 95% ethanol.

borole (catecholborane) (**1**),[1] undergo a very rapid stereospecific reaction at 0° with mercuric acetate to give the corresponding alkenylmercuric acetates (eq 1). Treat-



1

2

(1)

ment with aqueous sodium chloride provides 97–99% isolated yields of the alkenylmercuric chlorides. This remarkably simple procedure readily accommodates both internal and terminal alkynes and provides a convenient stereospecific route for their conversion into isomerically pure *cis*- and *trans*-alkenylmercuric salts, respectively.[2]

Alkenylmercury compounds are generally prepared by the reaction of alkenylmagnesium or -lithium compounds with mercuric halides (eq 2).[3] The reaction of

$$\begin{aligned} \text{RCH=CHMgX} + \text{HgX}_2 &\longrightarrow \text{RCH=CHHgX} \\ \text{RCH=CHLi} + \text{HgX}_2 &\longrightarrow \text{RCH=CHHgX} \end{aligned} \quad (2)$$

alkenylboronic acids or esters also appears to provide excellent yields of alkenylmercuric halides (eq 3).[4-7]

$$\text{RCH=CHB(OH)}_2 + \text{HgX}_2 \longrightarrow \text{RCH=CHHgX} \quad (3)$$

Until recently, however, the alkenylboronic acids and esters generally had to be prepared from the corresponding lithium or magnesium compounds, so that there was no particular advantage to be gained by using the organoboron intermediates.

Recently, we reported several new general syntheses of alkylboronic acids and esters from olefins *via* hydroboration.[8,9] The discovery that 1,3,2-benzodioxaborole (**1**) will readily hydroborate alkynes to give good yields of the stereospecific and regioselective 2-alkenyl-1,3,2-benzodioxaboroles (**2**)[1] has now provided a new route to alkenylmercurials *via* hydroboration–mercuration of alkynes.

The mercuration of the 2-alkenyl-1,3,2-benzodioxaboroles with mercuric acetate provides quantitative yields of the corresponding alkenylmercurials (see Table I). This hydroboration–mercuration sequence works equally well for both internal and terminal alkynes and should readily accommodate a number of functional groups which could not be present in the usual organolithium and -magnesium procedures.

A representative procedure is that utilized for the preparation of *cis*-4,4-dimethyl-2-pentenylmercuric chloride. Mercuric acetate (7.97 g, 25 mmol) was added to a well-stirred solution of 25 mmol of the 2-alkenyl-1,3,2-benzodioxaborole (derived from 4,4-dimethyl-2-pentyne and catecholborane)[1] (5.40 g) in 25 ml of tetrahydrofuran at 0°, while flushing with nitrogen. The solution was stirred several minutes until all mercuric acetate had disappeared and then poured into 100 ml of ice water containing 25 mmol of sodium chloride. The tetrahydrofuran was removed under vaccum and the resulting white solid was filtered, washed very thoroughly with water, and dried overnight under vacuum. There was obtained 8.04 g (97%) of *cis*-4,4-dimethyl-2-pentenylmercuric chloride, mp 108–108.5° (95% ethanol).

Anal. Calcd for $C_7H_{13}HgCl$: C, 25.23; H, 3.93; Hg, 60.20. Found: C, 25.50; H, 3.85; Hg, 60.29.

The experimental results are summarized in Table I.

Elemental analyses and nmr and infrared spectra were all consistent with the assigned structures.[2] Although the alkenylmercuric chlorides derived from terminal alkynes all gave complicated nmr spectra in the vinyl hydrogen region from which proton–proton coupling constants could not readily be determined, ^{199}Hg–H coupling constants clearly showed these compounds to be trans. Thus, overlapping satellites due to both cis and geminal ^{199}Hg–H coupling were observed with coupling constants of $J_{^{199}\text{Hg-H}}$ = 292–303 Hz. Integration of the satellite areas gave 16–17% of the total vinyl hydrogen area (^{199}Hg has a relative abundance of 16.86%). These facts are only consistent with a trans configuration.[10] Furthermore, the infrared spectra of these derivatives exhibited a very strong band at 920–970 cm^{-1} indicative of a trans derivative.[11] The alkenylmercuric chlorides derived from internal alkynes also gave ^{199}Hg–H coupling constants only consistent with a cis Hg–H configuration. Thus, the mercuration reac-

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(2) The present procedure is more convenient and far more general than the reaction of mercuric acetate with the adducts of alkynes and dicyclohexylborane: R. C. Larock and H. C. Brown, *J. Organometal. Chem.*, **36**, 1 (1972).

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(10) Vinylmercuric acetate exhibits the following ^{199}Hg–H coupling constants: J_{gem} = 291 Hz, J_{cis} = 331 Hz, and J_{trans} = 658 Hz: P. R. Wells, W. Kitching, and R. F. Henzell, *Tetrahedron Lett.*, **18**, 1029 (1964).

(11) N. A. Chumaevskii and A. E. Borisov, *Dokl. Akad. Nauk SSSR*, **161**, 366 (1965).

tion proceeds with retention of the configuration present in the alkenylborane.[12]

Thus, the hydroboration–mercuration of alkynes provides a major new stereospecific route to the alkenylmercurials, which have proven invaluable for the synthesis of other alkenylmetallics.[3]

(12) Retention had previously been observed in the mercuration of alkenylboronic acids. See ref 4 and 6.

(13) National Science Foundation Fellow, 1967–1971.
(14) Postdoctorate Research Associate on Grant No. GM-10937 supported by the National Institutes of Health.

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Asymmetric Homogeneous Hydrosilylation with Chiral Phosphine–Palladium Complexes

Sir:

Recently we have reported the first example of asymmetric hydrosilylation of α-methylstyrene catalyzed by (*R*)-benzylmethylphenylphosphine complexes of platinum(II)[1] or nickel(II),[2] which, respectively, lead to a 5 or 17.6% excess of one enantiomer in the addition product, 2-phenylpropylmethyldichlorosilane. Experiments with the similar phosphine complex of palladium(II) showed it to be only slightly useful for the asymmetric synthesis in hydrosilylation of olefins, despite other studies on the effectiveness of tertiary phosphine complexes of palladium.[3,4]

Instead of using tertiary phosphines which are asymmetric at phosphorus, Morrison and coworkers[5] have reported that a chiral rhodium complex from neomenthyldiphenylphosphine ligands is very effective as an asymmetric homogeneous hydrogenation catalyst. The fact that a complex with ligands that are dissymmetric remote from phosphorus does fulfill the necessary condition for asymmetric catalysis[5,6] prompted us to investigate the asymmetric hydrosilylation using complexes with this type of chiral phosphine.

We wish to report that a palladium(II) complex of menthyldiphenylphosphine (MDPP)[7] or epimeric neomenthyldiphenylphosphine (NMDPP)[8] is especially useful to induce asymmetry in hydrosilylation of styrene and some cyclic conjugated dienes.

Thus, addition of trichlorosilane (60 mmol) to styrene (30 mmol) was carried out in the presence of dichlorobis(benzonitrile)palladium(II) (6×10^{-2} mmol) and MDPP (1.2×10^{-1} mmol) in a degassed sealed glass tube at room temperature over a period of 5 hr. The reaction mixture was distilled to give α-phenylethyltrichlorosilane[9] as a sole addition product (87% yield), $[\alpha]^{20}D$ +2.72° (neat). The adduct was methylated to give α-phenylethyltrimethylsilane[10] ($[\alpha]^{20}D$ −5.30° (neat); $[M]^{20}D$ −9.44°), a 5.1% enantiomeric excess (ee) of the S isomer, which was estimated on the basis of predicted molecular rotations in a series of (*S*)-α-phenylethyl derivatives.[11]

When the NMDPP–palladium complex was used as catalyst, the enantiomeric *R* addition product (3.3% asymmetric bias) was obtained, as indicated in Table I.

Table I. Asymmetric Hydrosilylation of Styrene and Cyclic Dienes with $HSiCl_3$ Catalyzed by Chiral Phosphine–Palladium(II) Complexes[a]

Olefin	Catalyst Pd(II) plus[b]	Yield, %	$[\alpha]^{20}D$, deg, of product[c]	$[\alpha]^{20}D$, deg, of methylated	Config[d]
$PhCH{=}CH_2$	MDPP	87	+2.72	−5.30	*S*
$PhCH{=}CH_2$	NMDPP	87	−1.51	+3.38	*R*
$PhCH{=}CH_2$	R_3P^*[e]	70	−0.13	+0.25	*R*
Cyclopentadiene	MDPP	69	*f*	−11.84	*S*
Cyclopentadiene	NMDPP	81	*f*	−7.54	*S*
1,3-Cyclohexadiene	MDPP	64	*f*	−11.08	*S*
1,3-Cyclohexadiene	NMDPP	56	*f*	−3.66	*S*

[a] All new compounds gave satisfactory elemental analyses, and have correct structures assigned on the basis of infrared and nmr spectra. [b] $PdCl_2(PhCN)_2$–chiral phosphine (1:2); the molar ratio of the catalyst/olefin = 2×10^{-3}. [c] α-Phenylethyltrichlorosilane,[9] 2-cyclopentenyltrichlorosilane (bp 60–70° (23 mm)), and 2-cyclohexenyltrichlorosilane (bp 88–90° (23 mm)), respectively, from styrene, cyclopentadiene, and 1,3-cyclohexadiene. [d] Configuration of the predominant isomer. [e] R_3P^* = (*R*)-(+)-($PhCH_2$)MePhP (K. Neuman, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 7102 (1969)) (67% optical purity). *trans*-$[PdCl_2(R_3P^*)_2]$ (mp 166°) was used as catalyst (unpublished results by R. Ito of this laboratory). [f] Not determined.

Hydrosilylation of cyclic conjugated dienes with trichlorosilane catalyzed by a palladium(II) complex either with MDPP or with NMDPP required much higher reaction temperature. However, of particular interest was that the reaction always gave 2-cycloalkenyltrichlorosilanes with an enantiomeric excess of the *S*-(−) isomer,[12] regardless of the phosphine epimer used in the catalyst. This is not the case with styrene (see Table I).

Thus, addition of trichlorosilane (90 mmol) to cyclopentadiene (45 mmol) catalyzed by Pd(II)–NMDPP at 120° for 58 hr yielded almost exclusively 2-cyclopentenyltrichlorosilane (81% yield), which was not contaminated

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(8) Prepared according to a procedure by J. D. Morrison, *et al.*,[5] using menthyl chloride [$[\alpha]^{20}D$ −45.5° (neat); 86% epimeric purity based on a maximum rotation reported, $[\alpha]^{25}D$ −53.0°; E. D. Hughes, C. K. Ingold, and J. B. Rose, *J. Chem. Soc.*, 3839 (1953)]; $[\alpha]^{20}D$ +82.9° (*c* 1.20, CH_2Cl_2).
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(10) J. W. Ryan and J. L. Speier, *J. Org. Chem.*, **24**, 2052 (1959).
(11) D. D. Davis and F. R. Jensen, *ibid.*, **35**, 3410 (1970); (*S*)-(−)-$PhMeCHSiMe_3$, $[M]^{20}D$ −184° (±5%).