

riers, $\Delta E_{X,X}^{\ddagger}$, and $\Delta E_{Y,Y}^{\ddagger}$, and the energy change, ΔE . The $\Delta E_{X,Y}^{\ddagger}$ value obtained by MINDO/3 calculations and by the Marcus equation (3) are summarized in Table 6. The Marcus equation is seen to apply satisfactorily to the MINDO/3 results of energy barriers and energy change involved in the hydrogen atom transfer reaction.

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Syntheses of Conjugated Dienes from 1-Alkenylboronic Acids by Palladium (II) Salt

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The reactions of (E)-1-hexenylboronic acid (1) or (E)- β -phenylethenylboronic acid (2) with various olefins in acetonitrile at room temperature in the presence of lithium palladium chloride and triethylamine gave the corresponding (E, E)-conjugated dienes stereospecifically in good yields. (E)- β -Phenylethenylboronic acid (2) was more reactive than (E)-1-hexenylboronic acid (1) in these vinylations. And these vinylations were also carried out catalytically when 10 mol % of lithium palladium chloride and cupric chloride, as the reoxidant of palladium, or 10 mol % of palladium acetate and mercuric acetate were added instead of stoichiometric amount of lithium palladium chloride.

Introduction

The conjugated dienes are important intermediates in the syn-

thesis of a wide variety of compounds of value, as well as in their utilization in other reactions such as Diels-Alder reaction.¹ A number of methods for the preparation of conjugated

dienes have been developed using organometallic compounds, magnesium,² aluminum,³ silicon,⁴ copper,^{5,6} silver,⁶ mercury,⁷ zirconium⁸ and boron^{9,10} reagents. Although these methods have their own excellence, many of these methods can be used only for the preparation of symmetrical dienes^{4-7,9} or unfunctionalized dienes¹ because of the reactant or the procedure employed.

Vinylation of organometallic compounds with olefins by exchange reaction of palladium also could be the promising method for the convenient stereospecific preparation of conjugated dienes containing a variety of functional groups. Although this vinylation needs stoichiometric amount of palladium, it can be done catalytically when the reoxidant of palladium such as cupric chloride or mercuric salts (except halides) is added.¹¹ But, only a few of studies about this vinylation, such as arylation of aryl mercuric salts¹¹⁻¹³ and vinylation of vinylsilanes,¹⁴ were carried out up to present. And it is well-known that stereodefined 1-alkenylboranes are readily prepared by monohydroboration of terminal alkynes.

Thus, we attempted to synthesize the various functionalized (E,E)-conjugated dienes by the vinylation of such stereodefined (E)-1-alkenylboronic acids with olefins in the presence of palladium (II) salt. And comparison of the reactivity according to the reactants are also discussed in this paper.

TABLE 1: Vinylation of 1-Alkenylboronic Acids with Olefins by Palladium (II) Salt^a

1-Alkenylboronic Acid	Olefin	Time, h	Product (% yield of isolated product)
		24	(78)
1		24	(48)
1		24	(75)
1		48	(40)
		24	(80)
2		24	(75)
2		24	(72)
2		24	(15)
2		48	(49)
2		24	(63)
2		24	7 (64) ^b
2		24	7 (40) ^c

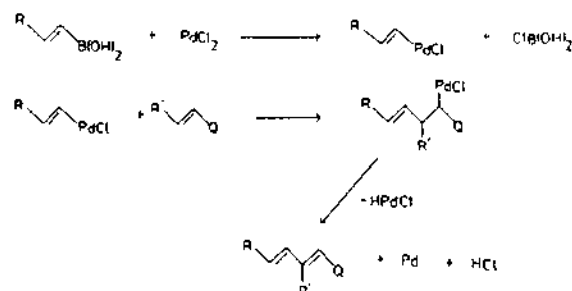
^a Reactions were carried out in acetonitrile containing 5 mmol of 1-alkenylboronic acid, 8 mmol of olefin, 15 mmol of triethylamine and 5 mmol of LiPdCl₄ at room temperature. ^b Reaction was carried out in acetonitrile containing 5 mmol of 2, 8 mmol of methyl acrylate, 0.5 mmol of LiPdCl₄ and 5 mmol of cupric chloride at room temperature. ^c Reaction was carried out in acetonitrile containing 5 mmol of 2, 8 mmol of methyl acrylate, 0.5 mmol of Pd(OAc)₂ and 5 mmol of mercuric acetate at room temperature.

Results and Discussion

(E)-1-Hexenylboronic acid (1), prepared by the hydroboration of 1-hexyne with catecholborane, and (E)-β-phenylethenylboronic acid (2), prepared by the hydroboration of phenylacetylene with catecholborane, were reacted with various olefins such as methyl acrylate, methyl crotonate, dimethyl fumarate, N-t-butylacrylamide, styrene and 1-hexene in acetonitrile at room temperature in the presence of lithium palladium chloride and triethylamine. (E,E)-Conjugated dienes were obtained conveniently in all reactions. Results are summarized in Table 1.

A possible mechanism of this reaction (Scheme 1) involves sequential (a) exchange reaction of palladium compound with boronic acid group, (b) addition to the olefinic double bond, and (c) internal elimination, as studied in detail by Heck.¹¹

Reaction of (E)-1-hexenylboronic acid (1) with slight excess of methyl acrylate in acetonitrile at room temperature in the presence of equimolar amount of lithium palladium chloride and 3 equiv. of triethylamine gave (E,E)-methyl 2,4-nonenadienoate (3) in 78% yield (eq. 1).



R = alkyl and aryl

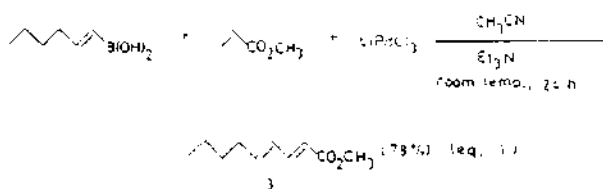
R' = H, alkyl and CO₂CH₃

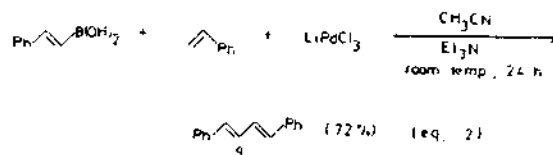
Q = alkyl, aryl, CO₂CH₃, and CONH(t-Bu)

Scheme 1.

But, reaction of 1 with 1-hexene under condition described above gave (E,E)-5,7-dodecadiene (4) in only 48% yield. These results indicate that this vinylation depended on the electronic effects of the substituents on olefins. Thus, reaction of 1 with N-t-butylacrylamide was proceeded well and gave (E,E)-N-t-butyl 2,4-nonadienamide (5) in 75% yield. On the other hand, internal olefins were less reactive than terminal olefins and reaction of 1 with methyl crotonate gave (E,E)-methyl 3-methyl-2,4-nonadienoate (6) in 40% yield.

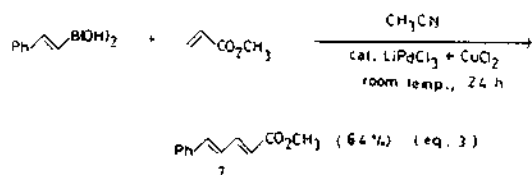
(E)-β-Phenylethenylboronic acid (2) was more reactive than 1 and its reaction with methyl acrylate gave (E,E)-methyl 5-phenyl-2,4-pentadienoate (7) in 80% yield. Similar reaction of 2 with N-t-butylacrylamide gave (E,E)-N-t-butyl 5-phenyl-2,4-pentadienamide (8) in 75% yield. Reaction of 2 with styrene also proceeded well and yielded (E,E)-1,4-diphenyl-1,3-butadiene (9) in 72% yield (eq. 2).





However, reaction of 2 with 1-hexene, like reaction of 1, gave (E,E)-1-phenyl-1,3-octadiene (10) only in 54% yield. And reaction of 2 with methyl crotonate gave (E,E)-methyl 3-methyl-5-phenyl-2,4-pentadienoate (11) in 49% yield, but reaction with dimethyl fumarate yielded (E,E)-methyl 3-carbamethoxy-5-phenyl-2,4-pentadienoate (12) in 63% yield. These results also clearly indicate that this vinylation proceeds well and give high yields of (E,E)-dienes when reactants are substituted with electron withdrawing groups.

This vinylation was also proceeded catalytically with aid of reoxidant of palladium. Reaction of 2 with methyl acrylate in acetonitrile at room temperature in the presence of 10 mol % of lithium palladium chloride and equimolar amount of cupric chloride gave 7 in 64% yield (eq. 3).



When 10 mol % of palladium acetate and equimolar amount of mercuric acetate were used instead of lithium palladium chloride and cupric chloride under same condition, reaction of 2 with methyl acrylate gave 7 in 40% yield.

Although this vinylation of 1-alkenylboronic acids with olefins in the presence of palladium (II) salt has several limitations, it has been demonstrated to proceed readily and stereospecifically to give various functionalized conjugated dienes.

Experimental Section

The ¹H NMR spectra were obtained on Varian Model S-60T spectrometer. Chemical shifts are given in δ units relative to tetramethylsilane as an internal standard. Infrared spectra were obtained on Beckman Model 18-A spectrometer. Analytical thin layer chromatography was performed on precoated silica gel plates (0.2 mm, 60F₂₅₄, E. Merck) and silica gel (Kieselgel 60, 70-230 mesh, E. Merck) was used for column chromatography. Melting points were determined on a Fisher-Johns electrothermal melting point apparatus.

Materials. 1-Hexene (Sigma Chemical Co.), methyl acrylate (Tokyo Kasei Co.), methyl crotonate (Tokyo Kasei Co.), dimethyl fumarate (Tokyo Kasei Co.), Styrene (Tokyo Kasei Co.), palladium chloride (Aldrich Chemical Co.) and palladium acetate (Aldrich Chemical Co.) were commercial products and used without further purification. Acetonitrile was purified by distillation from calcium hydride and anhydrous lithium chloride was dried in vacuum oven at 150°C before use. N-t-Butylacrylamide,¹⁵ (E)-1-hexenylboronic acid¹⁴ and (E)-β-phenylethenylboronic acid¹⁷ were prepared according to the literature methods.

Preparation of 0.1 M LiPdCl₃ in acetonitrile. 5 mmol (0.887g) of palladium chloride and 5.5 mmol (0.233g) of anhydrous

lithium chloride were added to 50 ml of dry acetonitrile and stirred overnight at room temperature. After filtering the excess lithium chloride, the resulting red solution was used as 0.1 M LiPdCl₃ in acetonitrile.

General procedure for the preparation of (E,E)-conjugated dienes. The following procedure for the preparation of (E,E)-methyl 2,4-nonadienoate (3) is representative.

In a dry 100 ml flask equipped with a magnetic bar was placed 50 ml of 0.1 M LiPdCl₃ in acetonitrile. 0.64g (5 mmol) of (E)-1-hexenylboronic acid, 0.688g (8 mmol) of methyl acrylate and 1.515g (15 mmol) of triethylamine were added to the flask and flushed with nitrogen and capped. The reaction mixture was stirred for 24 h at room temperature, and then diluted with 150 ml of ether and filtered. The filtrate was washed with water several times and dried over anhydrous magnesium sulfate. Remove solvent under reduced pressure and the crude product was purified by column chromatography (silica gel, ethyl acetate/n-hexane = 1/10 (v/v)). 0.655g (78%) of pure (E,E)-methyl 2,4-nonadienoate (3) was obtained. ¹H NMR (CDCl₃) 0.8 (bs, 3H), 1.3 (bs, 4H), 2.1 (bs, 2H), 3.6 (s, 3H), 5.5-6.2 (m, 3H), 6.9-7.4 (m, 1H); IR (neat) 2940, 1710, 1635, 1000 cm⁻¹.

The dienes prepared by employing the above procedure are as follows. (E,E)-5,7-dodecadiene (4): ¹H NMR (CDCl₃) 0.9 (bs, 6H), 1.4 (bs, 8H), 3.8 (m, 4H), 4.9-5.4 (m, 4H); IR (neat) 2900, 1680, 965 cm⁻¹.

(E,E)-N-t-butyl 2,4-nonadienamide (5): ¹H NMR (CDCl₃) 0.8 (bs, 3H), 1.2 (bs, 13H), 1.9 (bs, 2H), 5.5-6.0 (m, 4H), 6.8-7.2 (m, 1H); IR (KBr) 3260, 2900, 1655, 1640, 995 cm⁻¹; mp 93-94°C.

(E,E)-methyl 3-methyl-2,4-nonadienoate (6): ¹H NMR (CDCl₃) 0.8 (bs, 3H), 1.3 (bs, 4H), 1.5 (bs, 3H), 2.3 (bs, 2H), 3.7 (s, 3H), 5.5-6.2 (m, 3H); IR (neat) 2900, 1715, 1640, 990 cm⁻¹.

(E,E)-methyl 5-phenyl-2,4-pentadienoate (7): ¹H NMR (CDCl₃) 3.8 (s, 3H), 5.9-6.2 (d, J = 16Hz, 1H), 6.9 (m, 3H), 7.5 (bs, 5H); IR (KBr) 3020, 2950, 1715, 1630, 1000 cm⁻¹; mp 67-70°C.

(E,E)-N-t-butyl 5-phenyl-2,4-pentadienamide (8): ¹H NMR (CDCl₃) 1.45 (s, 9H), 5.6 (bs, 1H), 5.8-6.1 (d, J = 16Hz, 1H), 6.8-6.95 (m, 2H), 7.3 (m, 6H); IR (KBr) 3310, 3030, 2950, 1650, 1620, 1000 cm⁻¹; mp 170-172°C.

(E,E)-1,4-diphenyl-1,3-butadiene (9): ¹H NMR (CDCl₃) 6.7-7.0 (m, 3H), 7.4 (m, 11H); IR (KBr) 3030, 1630, 1000 cm⁻¹; mp 148-150°C.

(E,E)-1-phenyl-1,3-octadiene (10): ¹H NMR (CDCl₃) 0.9 (bs, 3H), 1.8 (bs, 4H), 2.2 (bs, 2H), 5.9-6.8 (m, 3H), 7.3 (m, 6H); IR (KBr) 3025, 2910, 1600, 990 cm⁻¹.

(E,E)-methyl 3-methyl-5-phenyl-2,4-pentadienoate (11): ¹H NMR (CDCl₃) 2.2 (s, 3H), 3.8 (s, 3H), 5.7-5.9 (m, 2H), 7.3 (m, 5H), 8.3-8.6 (d, J = 16Hz, 1H); IR (KBr) 3025, 2990, 1715, 1630, 990 cm⁻¹.

(E,E)-methyl 3-carbamethoxy-5-phenyl-2,4-pentadienoate (12): ¹H NMR (CDCl₃) 3.6 (s, 3H), 3.8 (s, 3H), 5.8 (s, 1H), 6.8 (m, 2H), 7.3 (s, 5H); IR (KBr) 3040, 2950, 1720, 1615, 970 cm⁻¹; mp 73-75°C.

Preparation of (E,E)-methyl 5-phenyl-2,4-pentadienoate (7): by catalytic method. In a dry 100 ml flask equipped with a

magnetic bar was placed 0.699g (5 mmol) of (E)- β -phenylethylboronic acid, 0.688g (8 mmol) of methyl acrylate, 0.673g (5 mmol) of anhydrous cupric chloride and 25 ml of dry acetonitrile. 5 ml of 0.1 M LiPdCl₄ in acetonitrile was added to the flask and flushed with nitrogen and capped. The reaction mixture was stirred for 24 h at room temperature, and then diluted with 100 ml of ether and filtered. The filtrate was washed with water several times and dried over anhydrous magnesium sulfate. Remove solvent and the crude product was purified by column chromatography (silica gel, ethyl acetate/n-hexane = 1/10 (v/v)). 0.602g(64%) of pure (E,E)-methyl 2,4-pentadienoate (7) was obtained.

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The Stereochemistry of the Metal Complexes of Novel Stereospecific Quadridentate Ligands. Cobalt(III) Complexes of N,N'-Dimethylethylenediamine-N,N'-di- α -propionate and N,N'-Dimethylethylenediamine-N,N'-diacetate Ligands

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A new flexible quadridentate ligand, N,N'-dimethylethylenediamine-N,N'-di- α -propionic acid (dmedpa) has been synthesized, and diammine and ethylenediamine cobalt(III) complexes of dmedpa, [Co(dmedpa)(NH₃)₂]⁺ and [Co(dmedpa(en))]⁺, have been prepared. Only *s-cis* isomer has been yielded. A known N,N'-dimethylethylenediamine-N,N'-diacetic acid (dmedda) has also been prepared. Dichloro cobalt(III) complexes of both dmedda and dmedpa have been prepared. Only the *s-cis* isomer has been yielded in the [Co(dmedda)Cl₂]⁻ complex, while only the *uns-cis* isomer has been obtained for the [Co(dmedpa)Cl₂]⁻ complex.

Introduction

Octahedral cobalt(III) complexes of a linear flexible edda-type ligand (edda is ethylenediaminediacetic acid, HOOCCH₂NHCH₂CH₂NHCH₂COOH) can have three geometric isomers, *s-cis* (symmetric *cis*), *uns-cis* (unsymmetric *cis*), and *trans*, as depicted in Figure 1. The cobalt(III) complexes of edda were prepared by Mori *et al.*,¹ who have observed that the carbonate, diaqua, and dinitro complexes yielded the *s-cis* isomer only. On the other hand, Legg and Cooke² isolated both *s-cis* and *uns-cis* isomers for the [Co(edda)(am)]⁺

(am is ethylenediamine or (NH₃)₂). *Uns-cis* isomer of the cobalt(III) complexes of edda has also been observed by other workers.³⁻⁶

Liu and coworkers⁷ have prepared the first C-alkyl-substituted analogue of edda, ethylenediamine-N,N'-di-S- α -propionic acid (SS-eddp). Both *s-cis* and *uns-cis* isomers of [Co(SS-eddp)(L)]⁺ (L is en or R-pn) were isolated. Other C-alkyl-substituted edda ligands include S-stilbenediamine-N,N'-diacetate (S-sdda),⁸ ethylenediamine-N,N'-di-S- α -isovalerate (ven),^{9,10} and 2S, 2'S-1,1'-ethane-1,2-diylbis (pyrrolidine-2-carboxylate) (pren).^{11,12}