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 14. When this manuscript is in preparation, a report of similar studies on the photophysical and photochemical processes of Ru(bpy)₃²⁺ in PMA solutions focusing the conformational aspects of the polymer was appeared (Ref. 15). Our results shown in this article agree well with much of the report, but the effects of PMA on I_E and quenching rate are much more pronounced in this paper. Also, more detailed informations on the effects of PMA are given here.
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 22. Because of partial hydrophobic character of nitrobenzene, some of NB molecules might be dissolved in the hydrophobic region of PMA. However, the large K value at pH 2, at which Ru(bpy)₃²⁺ does not bind to PMA suggests that most of NB molecules are in aqueous bulk water phase.

Vinylation of β -Acetoxyvinyl Mercurials with Olefins by Palladium (II) Salt

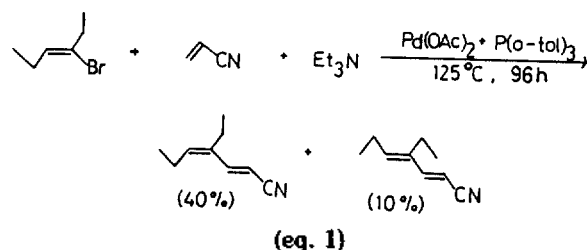
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Vinylation of highly hindered β -acetoxyvinyl mercurials with olefins in acetonitrile at room temperature in the presence of cupric chloride, as a reoxidant for the palladium, and a catalytic amount of LiPdCl₃ gave the corresponding conjugated dienes in moderate to good yields. The (E) or (Z) geometry in vinyl mercurials was retained in the vinylated products. The reaction was tolerant of a wide variety of functional groups (CO₂R, CN, OR, OAc) on either the vinyl mercurial or olefin compounds.

Introduction

The stereo- and regiospecific synthesis of conjugated dienes are of considerable importance in organic chemistry.¹ The palladium catalyzed vinylation of vinylic bromides or iodides with olefins in the presence of an amine, usually triethylamine or piperidine, has been shown to be a useful method for the synthesis of conjugated dienes.²⁻⁵ While the reactions are successful in most instances, they have some limitations. One of the limitations is that the reaction of (Z) isomers of sterically hindered vinylic bromides, such as (Z)-3-bromo-3-hexene, with acrylic acid derivatives proceeds very slowly even at 125°C and gives a mixture of (E,Z)- and (E,E)-conjugated dienes (eq. 1).⁵



The vinylic palladium halide intermediates in the above reaction may also be prepared by another method, the exchange reaction of palladium (II) salts with vinylic derivatives

of the main group elements. A number of other methods utilizing organometallic compounds for the preparation of conjugated dienes have been developed.⁶ However, there are only a few reports as to the vinylation of organometallic compounds with olefins by the exchange reaction of palladium (II) salts. For example, reaction of vinyl silanes with palladium (II) salts,^{7,8} allylation of alkenylpentafluorosilicates⁹ and arylation of olefins with arylmercuric salts¹⁰⁻¹² have been reported. Larock *et al.*¹³ have reported that the reaction of vinylmercuric chlorides with LiPdCl₃ and olefins gives high yields of the corresponding π -allylpalladium compounds.

We recently reported that the reaction of (E)-1-alkenylboronic acids with LiPdCl₃ and olefins in the presence of triethylamine gives good yields of (E,E)-conjugated dienes.¹⁴ The reaction also proceeded well catalytically with aid of a reoxidant for the palladium.

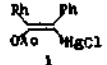
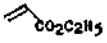
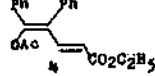

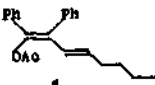
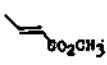
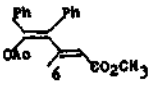

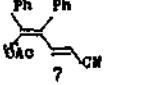
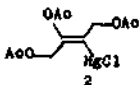
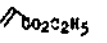
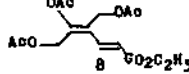

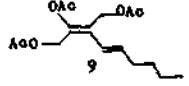
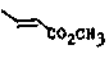
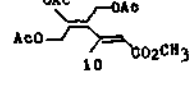

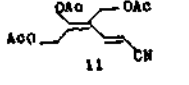
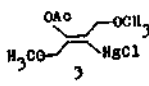
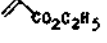
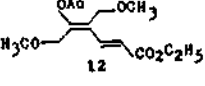

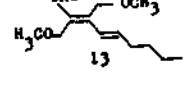
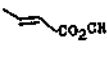
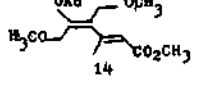

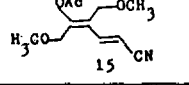
In this paper, we wish to report the vinylation of highly hindered (E)- or (Z)- β -acetoxyvinyl mercurials, prepared by acetoxymercuration of internal alkynes,^{15,16} with several olefins in the presence of cupric chloride, as a reoxidant for the palladium, and a catalytic amount of LiPdCl₃.

Results and Discussion

Vinylation of highly hindered (E)- or (Z)- β -acetoxyvinyl mercurials with olefins such as ethyl acrylate, acrylonitrile, methyl crotonate, and 1-hexene in acetonitrile at room

temperature in the presence of an equimolar amount of cupric chloride and 10 mol % of LiPdCl₃ gave the corresponding (E,E)-conjugated dienes stereospecifically in moderate

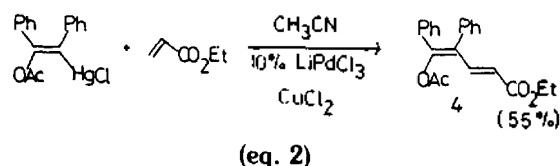
Table 1. Vinylation of β -Acetoxyvinyl Mercurials with Olefins by Palladium(II) Salt^a.

β -Acetoxyvinyl mercurial	Olefin	Product (% yield of isolated product)
		 (55)
1		 (50)
1		 (45)
1		 (44)
		 (75)
2		 (66)
2		 (57)
2		 (50)
		 (61)
3		 (55)
3		 (55)
3		 (47)

^aReactions were carried out in acetonitrile containing 5 mmol of β -acetoxyvinyl mercurial, 8 mmol of olefin, 5 mmol of cupric chloride and 0.5 mmol of LiPdCl₃ at room temperature for 48 h.

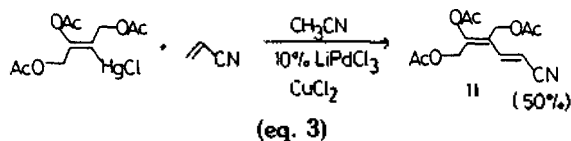
to good yields. (Z)- α -Acetoxy- β -(chloromercuri) stilbene(1), (E)-1,2,4-triacetoxy-3-(chloromercuri)-2-butene(2) and (E)-2-acetoxy-3-(chloromercuri)-1, 4-dimethoxy-2-butene (3) were used as β -acetoxyvinyl mercurials. Several experimental results are summarized in Table 1.

Table 1 shows that this vinylation is tolerant of a wide variety of reactive functional groups such as ester, acetate, nitrile, and ether on either the vinyl mercurial or olefin compounds. The reaction also proceeds with retention of double bond geometry in the vinyl mercurial compounds. In general, this vinylation proceeded well and gave good yields of conjugated dienes when reactants are substituted with electron withdrawing groups. Also, internal olefins were less reactive than terminal olefins in these reactions. However, acrylonitrile revealed poor reactivity even less than 1-hexene or methyl crotonate and gave low yields of conjugated dienes. For example, reaction of (Z)- α -acetoxy- β -(chloromercuri) stilbene (1), prepared by acetoxymercuration of diphenylacetylene, with a slight excess amount of ethyl acrylate in acetonitrile at room temperature in the presence of 10 mol % of LiPdCl₃ and an equimolar amount of cupric chloride gave (E,E)-ethyl 4,5-diphenyl-5-acetoxy-2,4-pentadienoate(4) in 55% yield (eq. 2).

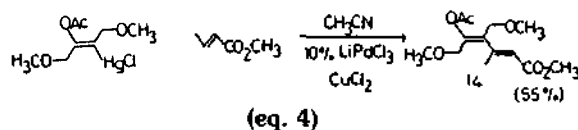


But, reaction of 1 with acrylonitrile under the present condition described above gave (E,E)-4,5-diphenyl-5-acetoxy-2,4-pentadienenitrile(7) in only 44% yield. Reaction of 1 with 1-hexene selectively gave (E,E)-1-acetoxy-1,2-diphenyl-1,3-octadiene(5) in 50% yield.

(E)-1,2,4-triacetoxy-3-(chloromercuri)-2-butene(2), prepared by acetoxymercuration of 1,4-butyndiol diacetate, was more reactive than 1 or 3 and its reaction with ethyl acrylate under the similar condition described above gave (E,E)-ethyl 4-acetoxymethyl-5,6-diacetoxy-2,4-hexadienoate(8) in 75% yield. Reaction of 2 with acrylonitrile also proceeded well and yielded (E,E)-4-acetoxymethyl-5,6-diacetoxy-2,4-hexadienenitrile(11) in 50% yield (eq. 3).



(E)-2-Acetoxy-3-(chloromercuri)-1,4-dimethoxy-2-butene(3), prepared by acetoxymercuration of 1,4-butyndiol dimethyl ether, also reacted well with olefins under the reaction condition described above. Reaction of 3 with ethyl acrylate gave 61% of (E,E)-ethyl 4-methoxymethyl-5-acetoxy-6-methoxy-2,4-hexadienoate(12). A similar reaction of 3 with methyl crotonate gave (E,E)-methyl 3-methyl-4-methoxymethyl-5-acetoxy-6-methoxy-2,4-hexadienoate (14) in 55% yield selectively (eq. 4).



Even though the present method has several limitations such as the use of Cu(II) salt as a cocatalyst to reoxidize the Pd(0) to make the reaction catalytic and only moderate yields are obtained in some cases it should be useful for the preparation of substituted conjugated dienes in a stereospecific manner. Also, the tolerance of reaction with a variety of functional groups provides a valuable method for preparing polyfunctional compounds without the need of employing protecting groups.

Experimental

The ^1H NMR spectra were measured with a Varian Model S-60T spectrometer. Chemical shifts are given in δ units relative to tetramethylsilane as an internal standard. Splitting patterns are designated as s(singlet), d(doublet), t(triplet), q(quartet), m(multiplet) or bs(broad singlet). Infrared spectra were recorded on a Beckman Model 18-A spectrophotometer and the frequencies are given in reciprocal centimeters. 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. Ethyl acrylate (Tokyo Kasei Co.), 1-hexene (Sigma Chemical Co.), methyl crotonate (Tokyo Kasei Co.), acrylonitrile (Tokyo Kasei Co.), cupric chloride (Tokyo Kasei Co.) and palladium chloride (Aldrich Chemical Co.) were commercial products and used without further purification. Acetonitrile was distilled from calcium hydride before use. (Z)- α -Acetoxy- β -(chloromercuri) stilbene(1),¹⁶ (E)-1,2,4-triacetoxy-3-(chloromercuri)-2-butene(2),¹⁶ (E)-2-acetoxy-3-(chloromercuri)-1,4-dimethoxy-2-butene(3)¹⁶ and 0.1 M LiPdCl₃ in acetonitrile¹⁰ were prepared according to the literature methods.

General Procedure for the Preparation of Conjugated Dienes. The following procedure for the preparation of (E,E)-ethyl 4,5-diphenyl-5-acetoxy-2,4-pentadienoate(4) is representative.

In a dry 100 ml flask equipped with a magnetic bar were placed 0.8 g(8 mmol) of ethyl acrylate, 0.673 g(5 mmol) of cupric chloride, 25 ml of dry acetonitrile and 5 ml of 0.1 M LiPdCl₃ in acetonitrile. After cooling to 0°C, 2.365 g(5 mmol) of (Z)- α -acetoxy- β -(chloromercuri) stilbene was added to the flask and flushed with nitrogen which was capped. The reaction mixture was allowed to warm to room temperature and stirred for 48 h. Ether (50 ml) and saturated ammonium chloride solution (10 ml) were added to the reaction mixture and filtered. The filtrate was washed with saturated ammonium chloride solution and dried over anhydrous magnesium sulfate. After removal of the solvent, the crude product was purified by column chromatography (silica gel, ethyl acetate/cyclohexane = 1/3(v/v)). 0.93 g(55%) of pure (E,E)-ethyl 4,5-diphenyl-5-acetoxy-2,4-pentadienoate was obtained. ^1H NMR(CDCl₃) δ 1.25(t, J = 7Hz, 3H), 1.80(s, 3H), 4.15(q, J = 7Hz, 2H), 5.64(d, J = 16Hz, 1H), 7.20-7.62(m, 10H), 7.82(d, J = 16Hz, 1H); IR(KBr) 3050, 2900, 1770, 1710, 1000, 910, 700 cm⁻¹; mp. 91-92°C.

Spectral Data of Conjugated Dienes. (E,E)-1-Acetoxy-1,2-diphenyl-1,3-octadiene(5): ^1H NMR(CDCl₃) δ 0.85(bs, 7H), 1.43(bs, 2H), 1.80(s, 3H), 5.10-5.45(m, 1H), 7.15-7.53(m, 11H); IR(KBr) 3035, 2950, 1760, 970, 710 cm⁻¹; mp. 85-86°C.

(E,E)-Methyl-3-methyl-4,5-diphenyl-5-acetoxy-2,4-pentadienoate(6): ^1H NMR(CDCl₃) δ 1.80(s, 3H), 2.23(s, 3H), 3.75(s, 3H), 5.62(s, 1H), 7.10-7.65(m, 10H); IR(KBr) 3030, 2950, 1770, 1710, 1000, 900, 720 cm⁻¹; mp. 96-97°C.

(E,E)-4,5-Diphenyl-5-acetoxy-2,4-pentadienenitrile(7): ^1H NMR(CDCl₃) δ 1.80(s, 3H), 5.00(d, J = 16Hz, 1H), 7.15-7.62(m, 11H); IR(KBr) 3030, 2950, 2240, 1770, 970, 715 cm⁻¹.

(E,E)-Ethyl-4-acetoxymethyl-5,6-diacetoxy-2,4-hexadienoate(8): ^1H NMR(CDCl₃) δ 1.24(t, J = 7Hz, 3H), 2.02(s, 6H), 2.23(s, 3H), 4.25(q, J = 7Hz, 2H), 4.85(bs, 4H), 6.12(d, J = 16Hz, 1H), 7.55(d, J = 16Hz, 1H); IR(neat) 2910, 1750, 1710, 980 cm⁻¹.

(E,E)-1,2-Diacetoxy-3-acetoxymethyl-2,4-nonadiene(9): ^1H NMR(CDCl₃) δ 0.82(bs, 7H), 1.35(bs, 2H), 2.02(s, 6H), 2.22(s, 3H), 4.52-4.50(m, 5H), 5.63(d, J = 16Hz, 1H); IR(neat) 2970, 1750, 970 cm⁻¹.

(E,E)-Methyl-3-methyl-4-acetoxymethyl-5,6-diacetoxy-2,4-hexadienoate(10): ^1H NMR(CDCl₃) δ 1.62(s, 3H), 2.01(s, 6H), 2.24(s, 3H), 3.74(s, 3H), 4.85(bs, 4H), 5.42(s, 1H); IR(neat) 2950, 1760, 1720, 950 cm⁻¹.

(E,E)-4-Acetoxymethyl-5,6-diacetoxy-2,4-hexadienenitrile(11): ^1H NMR(CDCl₃) δ 2.05(s, 6H), 2.18(s, 3H), 4.55-5.05(m, 5H), 6.23(d, J = 16Hz, 1H); IR(neat) 2950, 2220, 1750, 970 cm⁻¹.

(E,E)-Ethyl-4-methoxymethyl-5-acetoxy-6-methoxy-2,4-hexadienoate(12): ^1H NMR(CDCl₃) δ 1.25(t, J = 7Hz, 3H), 2.18(s, 3H), 3.35(s, 6H), 4.23(q, J = 7Hz, 2H), 4.35(bs, 4H), 5.95(d, J = 16Hz, 1H), 7.35(d, J = 16Hz, 1H); IR(neat) 2975, 1750, 1720, 960 cm⁻¹.

(E,E)-1-Methoxy-2-acetoxy-3-methoxymethyl-2,4-nonadiene(13): ^1H NMR(CDCl₃) δ 0.78(bs, 7H), 1.25(bs, 2H), 2.23(s, 3H), 3.35(s, 6H), 4.42-5.05(m, 5H), 5.56(d, J = 16Hz, 1H); IR(neat) 2975, 1760, 970 cm⁻¹.

(E,E)-Methyl-3-methyl-4-methoxymethyl-5-acetoxy-6-methoxy-2,4-hexadienoate(14): ^1H NMR(CDCl₃) δ 1.64(s, 3H), 2.21(s, 3H), 3.36(s, 6H), 3.47(s, 3H), 4.35(bs, 4H), 5.35(s, 1H); IR(neat) 2920, 1760, 1725, 960 cm⁻¹.

(E,E)-4-Methoxymethyl-5-acetoxy-6-methoxy-2,4-hexadienenitrile(15): ^1H NMR(CDCl₃) δ 2.21(s, 3H), 3.35(s, 6H), 4.55-5.13(m, 5H), 6.02(d, J = 16Hz, 1H); IR(neat) 2985, 2250, 1765, 980 cm⁻¹.

Acknowledgement. We are grateful to the Korea Science and Engineering Foundation for financial support of this work.

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Dichlororhodium(III) Complexes of N,N'-Dimethylethylenediamine-N,N'-diacetic Acid

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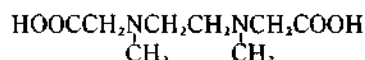
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Dichlororhodium(III) complexes of a flexible quadridentate ligand, N,N'-dimethylethylenediamine-N,N'-diacetic acid (dmedda), have been prepared. Both *cis-α* and *cis-β* isomers have been yielded in the $K[Rh(dmedda)Cl_2]$ complexes, which were characterized with elemental analyses, electronic absorption and proton nuclear magnetic resonance spectroscopic data.

Introduction

Legg and Cooke¹ prepared N,N'-dimethylethylenediamine-N,N'-diacetic acid(dmedda).



They isolated the *cis-α* isomer for the ethylenediaminecobalt(III) complex of dmedda out of the three possible geometric isomers shown in Figure 1. Diammine and trimethylenediamine cobalt(III) complexes of dmedda were prepared, in which only the *cis-α* isomer could be obtained.² Later Maricondi and Douglas reported the synthesis of the oxalato and ethylenediamine cobalt(III) complexes of dmedda,³ while Jordan and Douglas prepared the dinitro, diammine, and trimethylenediamine cobalt(III) complexes of dmedda,⁴ all of which yielded the *cis-α* isomer only. Recently, the dichloro cobalt(III) complex of dmedda was prepared, in which the only isomer obtained had the *cis-α* configuration.⁵

Although such variety of cobalt(III) complexes of dmedda have been obtained, no metal complexes of dmedda have been reported other than cobalt.^{6,7} We have therefore been interested in seeing what isomers would be obtained from the preparation of rhodium(III) complexes of the dmedda ligand, and this paper is the first report on the preparation of any rhodium(III) complexes of this dmedda ligand. The stereochemistry of the complexes prepared in this study was investigated through ion-exchange chromatography, electronic absorption spectroscopy, and proton nuclear magnetic resonance spectroscopy. It is shown here that both *cis-α* and *cis-β* geometric isomers have been obtained during the course of

our preparation of the dichloro rhodium(III) complexes of dmedda.

Experimental

Physical Measurements. Electron absorption spectra were obtained with a Shimadzu UV-240 Spectrophotometer. Pmr spectra were recorded on a Varian EM 360 L Spectrometer. Infrared spectra were taken with a Shimadzu IR-435 Spectrophotometer. Elemental analyses were performed by Micro-Tech Analytical Laboratories, Skokie, Illinois, U.S.A.

Preparation of Barium N,N'-Dimethylethylenediamine-N,N'-diacetate (Badmedda). This was prepared essentially by the method of Legg and Cooke¹ with some modification as described previously.⁵

Preparation of Potassium Dichloro-N,N'-dimethylethylenediamine-N,N'-diacetatorhodate(III). 0.34g of Badmedda were dissolved in 10 ml of water, to which 1.0 ml of 1.0 M

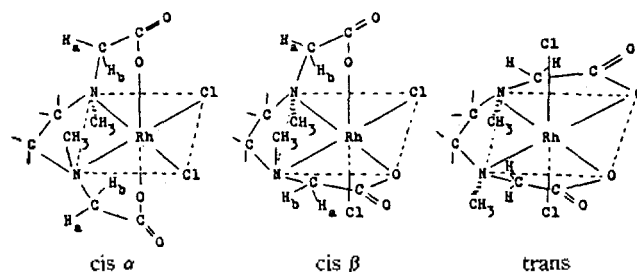


Figure 1. Three possible geometric isomers for the $[Rh(dmedda)Cl_2]$ complexes.