Stereospecific Synthesis of 2,4-Dienoic Acid Derivatives from Vinylmercuric Chlorides and Acrylic Acid Derivatives by Palladium(II) Salt

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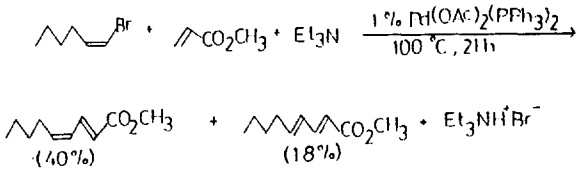
The reaction of (E)- or (Z)-1-alkenylmercuric chlorides with acrylic acid derivatives in the presence of 10 mol% of lithium trichloropalladate ($LiPdCl_3$) and an equimolar amount of cupric chloride, as a reoxidant for the palladium, in acetonitrile at room temperature gave the corresponding (E,E)- or (E,Z)-2,4-dienoic acid derivatives stereospecifically in moderate to good yields. The reaction of (E)- or (Z)-3-chloromercuripropenoic acid with olefins under the reaction condition described above similarly gave good yields of (E,E)- or (Z,E)-2,4-dienoic acids stereospecifically. A side reaction, the homocoupling of alkenylmercuric chlorides, could be minimized by employing the condition described above. However, in the reaction of 3-chloromercuripropenoic acid with olefins under the present condition, the homocoupled side reaction product was not produced.

Introduction

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 2,4-dienoic acids and their derivatives,[1-3] 2,4-dienals[4] and related polyenes.[5] Reaction conditions are 100-125°C for a few hours to several days depending upon the structures of the reactants. These reactions are very useful for the preparation of a wide variety of compounds of value in the synthesis of numerous natural products. While the reactions are successful in most instances, they have some limitations. One limitation is that (Z)-1-bromo-1-alkenes give mixtures of (E,Z)- and (E,E)-2,4-dienoates when they reacted with acrylic acid derivatives[1] (eq. 1).



(eq. 1)

Another problem is that (Z,E)-2,4-dienoates could not be obtained by these reactions because 3-bromoacrylate esters and other similar derivatives easily dehydrohalogenated under the reaction conditions.

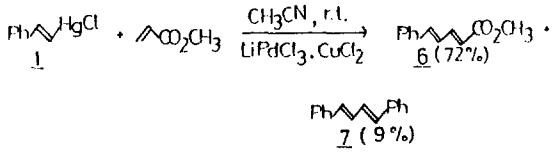
The vinylic palladium halide intermediates generated from the oxidative addition of palladium(0) catalysts to the vinylic halides in the above reaction may also be prepared by another method, the exchange reaction of palladium(II) salts with vinylic derivatives of the main group elements.

We have shown that the reaction of (E)-1-alkenylboronic acids,[6] highly hindered (E)- or (Z)-β-acetoxyvinylmercuric chlorides[7] and (E)-β-chloro-γ-hydroxyvinylmercuric chlorides[8] with funtionalized olefins in the presence of a catalytic amount of palladium(II) salt and cupric chloride, as a reoxidant for the palladium, afforded the corresponding (E,E)-conjugated dienes, substituted (E,E)-conjugated dienes and (E,E)-2,4-dienols respectively. These reactions are extremely mild and stereospecific, with tolerance of a wide variety of functional groups.

Herein, we report the stereospecific synthesis of 2,4-dienoic acid derivatives from vinylmercuric chlorides and acrylic acid derivatives by palladium(II) salt.

Results and Discussion

The reaction between (E)-styrylmercuric chloride(**1**) and methyl acrylate at room temperature in acetonitrile in the presence of 10 mol % of lithium trichloropalladate($LiPdCl_3$) and an equimolar amount of cupric chloride afforded a 72% yield of (E,E)-methyl 5-phenyl-2,4-pentadienoate(**6**) and a 9% yield of (E,E)-1,4-diphenyl-1,3-butadiene(**7**) (eq. 2).



(eq. 2)

The mechanism of the present vinylation between vinylmercuric chlorides and olefins is outlined in Scheme 1.[9] Transmetallation between palladium(II) salt with vinylmercuric chloride gives a vinylchloropalladium(II) complex. Sequential addition of vinylchloropalladium(II) complex to the olefinic double bond and internal elimination to yield the vinylated product, palladium metal and hydrogen chloride. Cupric chloride simply serves to reoxidize the palladium(0) back to palladium(II) chloride.

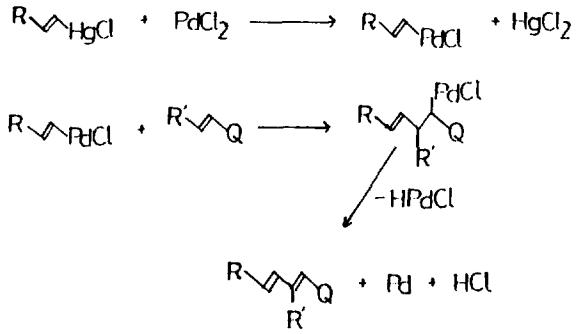
The undesired side product of homocoupling of vinylmercuric chloride is produced as illustrated in Scheme 2.[10] This coupling reaction proceeds through initial exchange to form a dichlorodivinylpalladium dianion which then reductively eliminates the diene, chloride anion and palladium metal.

The effects of varying the reaction conditions on the yield of **6** were studied (Table 1). Initially, the effects of the amounts of reoxidant and solvent upon reactions catalyzed by 10 mol% of $LiPdCl_3$ at room temperature were considered. The reaction in the presence of 2 equiv of cupric chloride gave a slightly

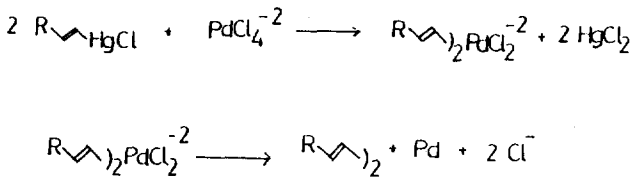
Table 1. Condition Study: Vinylation of (E)-Styrylmercuric Chloride(1) with Methyl Acrylate[a]

Entry	Catalyst (mol %)[b]	Reoxidant (equiv)[c]	Solvent	Temp, °C	Products, % Yield[d]	
					Diene(**6**)	Homocoupled Product(**7**)
1	$LiPdCl_3$(10)	$CuCl_2$(1)	CH_3CN	r. t.	72	9
2[e]	$LiPdCl_3$(10)	$CuCl_2$(1)	CH_3CN	r.t.	69	11
3	$LiPdCl_3$(10)	$CuCl_2$(2)	CH_3CN	r. t.	69	10
4[f]	$LiPdCl_3$(100)	—	CH_3CN	r. t.	39	25
5[g]	$LiPdCl_3$(1)	$CuCl_2$(1)	CH_3CN	r. t.	20	trace
6[h]	$LiPdCl_3$(10)	$CuCl_2$(2)	CH_3CN	r. t.	60	8
7	$Pd(OAc)_2$(10)	$Hg(OAc)_2$(1)	CH_3CN	r. t.	35	trace
8	$PdCl_2$(10)	$CuCl_2$(1)	CH_3CN	r. t.	27	trace
9	$PdCl_2$(10)	$CuCl_2$(1)	Benzene	r. t.	23	trace
10	$PdCl_2(PPh_3)_2$(10)	$CuCl_2$(1)	THF	r. t.	0	35
11	$PdCl_2(CH_3CN)_2$(10)	$CuCl_2$(1)	Benzene	r. t.	48	trace
12	Li_2PdCl_4(10)	$CuCl_2$(1)	THF	r. t.	53	5
13	Li_2PdCl_4(10)	$CuCl_2$(1)	Acetone	r. t.	50	11
14	Li_2PdCl_4(10)	$CuCl_2$(1)	DMF	r. t.	55	13
15	Li_2PdCl_4(10)	$CuCl_2$(1)	MeOH	r. t.	50	trace
16	$LiPdCl_3$(10)	$CuCl_2$(1)	CH_3CN	50	44	7

[a] General condition: 3 mmol of **1**, 5 mmol of methyl acrylate, 3 mmol of cupric chloride, 3m*l* of 0.1 M $LiPdCl_3$ in acetonitrile, and 20m*l* of acetonitrile for 24h. [b] Mol% per **1**. [c] Equivalents per **1**. [d] % Yield of isolated product. [e] 30m*l* of acetonitrile was used. [f] 3 equiv of triethylamine per **1** was added. [g] Reacted for 48h. [h] 1 equiv of K_2CO_3 per **1** was added.



Scheme 1



Scheme 2

lower yield of **6** than the reaction under an equimolar amount of cupric chloride and increased amount of solvent had no effect on the yield of **6**(entries 1-3). When the reaction proceeded at room temperature in acetonitrile in the presence of stoichiometric amount of $LiPdCl_3$ and 3 equiv of triethylamine, a 39% yield of **6** and a 25% yield of **7** were obtained(entry 4). Reduced amount of catalyst slowed the reaction(entry 5). Addition of an equimolar amount of inorganic base to the reaction mixture reduced the yield of **6**(entries 1,6).

Employing palladium(II) acetate, palladium(II) chloride, dichlorobis(triphenylphosphine)palladium(II)($PdCl_2(PPh_3)_2$) or dichlorobis(acetonitrile)palladium(II)($PdCl_2(CH_3CN)_2$) instead of $LiPdCl_3$ gave a lower yield of **6**(entries 1,7-11). Particularly, the reaction under 10 mol% of $PdCl_2(PPh_3)_2$ and an equimolar amount of cupric chloride in THF at room temperature afforded a 35% yield of **7** only(entry 10). Also, the effect of solvent upon the reactions was investigated (entries 1,12-15). Acetonitrile produced the highest yield of **6**(entry 1). The reaction proceeded at 50°C afforded a lower yield of **6** than when the reaction was run at room temperature(entries 1,16).

Table 2. Vinylation of (E)-Styryl Derivatives of Main Group Elements with Methyl Acrylate[a]

Ph-M, M =	Products, % Yield[b]	
	Diene(**6**)	Homocoupled Product(**7**)
HgCl	72	9
$SiMe_3$	38	trace
$SnBu_3$	45	trace
$B(OH)_2$[c]	64	7

[a] 3 mmol of (E)-styryl derivative of main group element, 5 mmol of methyl acrylate, 3 mmol of cupric chloride, 3m*l* of 0.1M $LiPdCl_3$ in acetonitrile, room temperature, and 20m*l* of acetonitrile for 24h. [b] % Yield of isolated product.

In table 2 are summarized the results of the vinylation of (E)-styryl derivatives of main group elements with methyl acrylate in the presence of 10 mol% of $LiPdCl_3$ and an equimolar amount of cupric chloride in acetonitrile at room temperature. It is apparent from the table that (E)-styrylmercuric chloride(**1**) is most reactive and gives highest yield

Table 3. Synthesis of (E,E)-2,4-Dienoic Acid Derivatives[a]

Vinylmercuric Chloride	Olefin	Time, h	Products (% Yield)[b]		
			Diene		Homocoupled Product
Ph HgCl (1)	CO_2CH_3	24	Ph CO_2CH_3 (6)	(72)	(9)
1	CN	24	Ph CN (8)	(50)	(13)
1	$CONH_2$	24	Ph $CONH_2$ (9)	(60)	(11)
1	CO_2CH_3	48	Ph CO_2CH_3 (10)	(trace)	(15)
1	COOH	48	Ph COOH (11)	(trace)	(15)
HOOC HgCl (2)	Ph	20	Ph COOH (12)	(80)	(0)
2	COOH	20	HOOC COOH (13)	(83)	—
HgCl (3)	CO_2CH_3	36	CO_2CH_3 (14)	(63)[c]	(12)[c]
3	$CONH_2$	36	$CONH_2$ (15)	(55)	(13)[c]

[a] 3 mmol of vinylmercuric chloride, 5 mmol of olefin, 3 mmol of cupric chloride, 3m*l* of 0.1M $LiPdCl_3$ in acetonitrile, room temperature, and 20m*l* of acetonitrile. [b] % Yield of isolated product. [c] Determined by GLC analysis using an internal standard.

Table 4. Synthesis of (E,Z)- and (Z,E)-2,4-Dienoic Acid Derivatives[a]

Vinylmercuric Chloride	Olefin	Time, h	Products (% Yield)[b]		
			Diene		Homocoupled Product
HgCl (4)	CO_2CH_3	36	CO_2CH_3 (16)	(65)	(8)
4	CN	48	CN (17)	(45)	(10)
4	$CONH_2$	36	$CONH_2$ (18)	(60)[c]	(8)
4	CO_2CH_3	48	CO_2CH_3 (19)	(28)	(15)
4	H_3CO_2C CO_2CH_3	48	CO_2CH_3 CO_2CH_3 (20)	(45)	(12)
HOOC HgCl (5)	Ph	20	Ph COOH (21)	(70)[c]	(0)
5	COOH	20	HOOC COOH (22)	(75)[c]	—

[a] 3 mmol of vinylmercuric chloride, 5 mmol of olefin, 3 mmol of cupric chloride, 3m*l* of 0.1M $LiPdCl_3$ in acetonitrile, room temperature, and 20m*l* of acetonitrile. [b] Determined by GLC analysis using an internal standard. [c] % Yield of isolated product.

of **6**.

(E)-Styrylmercuric chloride(**1**), (E)-3-chloromercuripropenoic acid(**2**) and 2-methyl-1-propenylmercuric chloride(**3**) were treated individually with acrylic acid derivatives in the

presence of 10 mol% of $LiPdCl_3$ and an equimolar amount of cupric chloride in acetonitrile at room temperature. (E,E)- and (E)-2,4-dienoic acid derivatives were obtained stereospecifically. Results are summarized in Table 3. Reaction of **1** with methyl acrylate, acrylonitrile and acrylamide gave the corresponding (E,E)-2,4-dienoic acid derivatives in moderate to good yields(**6**,**8**, and **9**) together with 9-13% yields of homocoupled (E,E)-1,4-diphenyl-1,3-butadiene(**7**). Similar reaction of **3** with methyl acrylate and acrylamide also gave the corresponding (E)-2,4-dienoic acid derivatives in moderate to good yields (**14** and **15**) together with 12-13% yields of homocoupled 2,5-dimethyl-2,4-hexadiene. However, reaction of **1** with methyl methacrylate and crotonic acid gave only trace amounts of (E,E)-2,4-dienoic acid derivatives(**10** and **11**) and 15% yields of **7**. Reaction of **2** with styrene gave a 80% yield of (E,E)-5-phenyl-2,4-pentadienoic acid(**12**) only and homocoupled product was not produced. Reaction of **2** with acrylic acid also proceeded well and yielded (E,E)-2,4-hexadienedioic acid(**13**) in 83% yield.

(Z)-1-Butenylmercuric chloride(**4**) and (Z)-3-chloromercuripropenoic acid(**5**) were reacted with acrylic acid derivatives for the synthesis of (E,Z)- and (Z,E)-2,4-dienoic acid derivatives. Results are summarized in Table 4. Reaction of **4** with methyl acrylate under the reaction condition described above gave a 65% yield of (E,Z)-methyl 2,4-heptadienoate (**16**) and a 8% yield of homocoupled (Z,Z)-3,5-octadiene. GLC analysis indicated that the isomeric purity of **16** was 98%. Similar results were obtained with acrylonitrile, acrylamide and methyl fumarate (**17**, **18**, and **20**). However, reaction with methyl methacrylate gave only a 28% yield of (E,Z)-methyl 2-methyl-2,4-heptadienoate(**19**) and a 15% yield of (Z,Z)-3,5-octadiene. On the other hand, reaction of **5** with styrene gave a 70% yield of (Z,E)-5-phenyl-2,4-pentadienoic acid(**21**) only and homocoupled product was not produced. Similar result was obtained with acrylic acid(**22**).

Conclusion

The palladium catalyzed vinylation of vinylmercuric chlorides with acrylic acid derivatives in the presence of cupric chloride, as a reoxidant for the palladium, has been demonstrated to proceed readily and stereospecifically to give 2,4-dienoic acid derivatives in moderate to good yields. The configurations of vinylmercuric chlorides are retained during the reaction, thus providing versatile and convenient procedures for the synthesis of (E,E)-, (E,Z)- and (Z,E)-2,4-dienoic acid derivatives.

However, reaction with hindered olefins such as methyl methacrylate or crotonic acid gave only in low yields or trace amounts of 2,4-dienoic acid derivatives.

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. Infrared spectra were recorded on a Nicolet 5-DX spectrophotometer and the frequences are given in reciprocal centimeters. Melting points were determined on a Fisher-Johns electrothermal melting point apparatus without correction. Gas chromatographic analyses were carried out on a Perkin Elmer Model Sigma-3B using 10% SE-30/Chromosorb W NAW, 2 m × 1/4 in. column and helium as a carrier gas. Analytical thin layer chromatography was performed on precoated silica gel plates (0.2 mm, $60F_{254}$, E. Merck) and silica gel(Kieselgel 60, 70-230 mesh, E. Merck) was used for column chromatography.

Acetonitrile was distilled from calcium hydride and stored over 4A molecular sieves. Tetrahydrofuran was freshly distilled from sodium/benzophenone prior to use. Acrylic acid and its derivatives, styrene, cupric chloride, palladium(II) acetate and palladium(II) chloride were commercial products. (E)-Styryltrimethylsilane,[11] (E)-styryltributyltin,[11] (E)-styrylboronic acid,[12] dichlorobis(triphenylphosphine)palladium(II) ($PdCl_2(PPh_3)_2$)[13], dichlorobis(acetonitrile)palladium(II) ($PdCl_2(CH_3CN)_2$)[14] and 0.1 M lithium trichloropalladate($LiPdCl_3$) in acetonitrile[9] were prepared according to the literature methods.

Vinylmercuric Chlorides. (E)-Styrylmercuric chloride(**1**) was prepared according to the literature method.[15]

(Z)-1-Butenylmercuric Chloride(**4**). In a 300m*l* flask, equipped with a stirrer, reflux condenser, addition funnel and protected by an nitrogen atmosphere, was placed 1.58g (65mmol) of magnesium turnings. The turnings were covered with 100m*l* of dry THF and reaction was initiated by addition of several drops of 1,2-dibromoethane. A solution of 8.10g(60 mmol) of (Z)-1- bromobutene[16] in 25m*l* of dry THF was added dropwise over a half hour period. When the addition was complete, the mixture was refluxed for 2h. After cooling to 0°C, 14.90g (55 mmol) of mercuric chloride in 30m*l* of dry THF was added dropwise to the mixture and stirred overnight at room temperature. Saturated ammonium chloride solution was added and THF layer was seperated, and dried over anhydrous magnesium sulfate. After removal of THF, the crude product was recrystallized from 95% ethanol. 12.32g (63%) of (Z)-1- butenylmercuric chloride was obtained. mp. 46-47°C; ^1H NMR($CDCl_3$)δ 1.26(t, J = 7Hz, 3H); 2.43(m, 2H), 6.08(d, J = 9Hz, 1H), 6.78(q, J = 7Hz, 1H); IR(KBr) 2930, 1610, 1460, 710 cm^{-1}.

2-Methyl-1-Propenylmercuric Chloride(**3**). This compound was prepared from 2-methyl-1-propenylmagnesium bromide and mercuric chloride following a procedure for the preparation of (Z)-1-butenylmercuric chloride(**4**) in 65% yield. mp. 70-72°C; ^1H NMR($CDCl_3$)δ 1.98 (s, 6H), 5.52 (s, 1H); IR(KBr) 2930, 1630, 1445, 790 cm^{-1}.

(E)-3-Chloromercuripropenoic Acid(**2**). n-Butyllithium (60 mmol, 26.8m*l* of a 2.24M solution in hexane) was added dropwise over 1.5h to a rapidly stirred solution of 4.53g (30 mmol) of (E)-3-bromopropenoic acid[17] in 300 ml of dry ether at -78°C under nitrogen. The mixture was stirred for 1.5h at -78°C and 8.13g(30 mmol) of mercuric chloride in 20m*l* of dry THF was added dropwise with stirring. The mixture was stirred for 2h at -78°C, allowed to warm to room temperature, and treated with 50m*l* of water. The layers were seperated and the organic layer was extracted with an additional 50m*l* portion of water. The aqueous solution was washed with ether, cooled to 0°C and acidified with cold 5% hydrochloric acid, and saturated with sodium chloride. The precipitated product was filtered and dried in a vacuum oven overnight. 2.76g (30%) of (E)-3-chloromercuripropenoic acid was obtained. mp. 204-205°C; ^1H NMR(DMSO-d_6)δ 6.43 (d, J = 14Hz, 1H), 7.58 (d, J = 14Hz, 1H), 10.75 (bs, 1H); IR(KBr) 3441, 1670, 1600, 959, 870, 774, 658 cm^{-1}.

(Z)-3-Chloromercuripropenoic Acid(**5**). This compound was prepared from (Z)-3-bromopropenoic acid[17] by the same pro-

cedure as described for the (E) isomer in 25% yield. mp. 181~182°C; ^{1}H NMR(DMSO-d_6)δ 6.68 (d, J=8Hz, 1H), 7.18 (d, J=8Hz, 1H), 10.70 (bs, 1H); IR(KBr) 3441, 1680, 1615, 909, 830, 734, 637 cm^{-1}.

General Procedure for the Preparation of (E,E)-2,4-Dienoic Acid Derivatives (Table 3). The following procedure for the preparation of (E,E)-methyl 5-phenyl-2,4-pentadienoate(**6**) is representative.

In a dry 100m*l* flask equipped with a magnetic bar were placed 0.43g(5 mmol) of methyl acrylate, 0.40g(3 mmol) of cupric chloride, 20m*l* of acetonitrile and 3m*l* of 0.1M $LiPdCl_3$ in acetonitrile. After cooling to 0°C, 1.01g(3 mmol) of (E)-styrylmercuric chloride was added to the flask and capped. The reaction mixture was allowed to warm to room temperature and stirred for 24h. Ether(50m*l*) and saturated ammonium chloride solution(10m*l*) were added to the reaction mixture and stirred for 1h. The organic layer was washed with saturated ammonium chloride solution and dried over anhydrous magnesium sulfate. After removal of the solvent, the residue was seperated by column chromatography(ethyl acetate/n-hexane=1/9(v/v)). 0.40g(72%) of (E,E)-methyl 5-phenyl-2,4-pentadienoate and 0.03g(9%) of (E,E)-1,4-diphenyl-1,3-butadiene were obtained. (E,E)-methyl 5-phenyl-2,4-pentadienoate(**6**):[19] R_f 0.54; mp. 69-70°C(lit.[18] 70-71°C); ^{1}H NMR($CDCl_3$)δ 3.78(s, 3H), 6.15 (d, J=15Hz, 1H), 6.76-7.08 (m, 2H), 7.12-7.78 (m, 6H); IR(KBr) 3040, 2960, 1745, 1630, 970 cm^{-1}. (E,E)-1,4-diphenyl-1,3-butadiene(**7**):[20] R_f 0.78; mp. 153-154°C(lit.[20] 153°C); ^{1}H NMR ($CDCl_3$)δ 6.4-7.1 (m, 4H), 7.15-7.44 (m, 10H); IR(KBr) 3030, 1595, 985 cm^{-1}.

Spectral Data of (E,E)-2,4-Dienoic Acid Derviatives.

(E,E)-5-Phenyl-2,4-pentadienenitrile(**8**):[22] TLC(ethyl acetate/n-hexane=1/5(v/v)) R_f 0.48; mp. 104°C(lit.[21] 104-105°C); ^{1}H NMR($CDCl_3$)δ 5.95 (d, J=16.5Hz, 1H), 6.70-7.15 (m, 2H), 7.28-7.82 (m, 6H); IR(KBr) 3030, 2928, 2212, 1622, 967 cm^{-1}.

(E,E)-5-Phenyl-2,4-pentadieneamide(**9**): mp. 183-184°C (lit.[23] 185°C); ^{1}H NMR(DMSO-d_6)δ 5.98 (d, J=16Hz, 1H), 6.42 (bs, 2H), 6.60-7.12 (m, 2H), 7.18-7.82 (m, 6H); IR(KBr) 3400, 3160, 3020, 1660, 960 cm^{-1}.

(E,E)-5-Phenyl-2,4-pentadienoic acid(**12**): TLC(ethyl acetate/methanol=1/1(v/v)) R_f 0.87; mp. 166-167°C(lit.[24] 168°C); ^{1}H NMR(DMSO-d_6)δ 6.09 (d, J=15Hz, 1H), 6.80-7.15 (m, 2H), 7.20-7.80 (m, 6H), 10.98 (s, 1H); IR(KBr) 3010, 1675, 1615, 1000, 960 cm^{-1}.

(E,E)-2,4-Hexadienedioic acid(**13**): mp. 292°C(dec.) (lit.[25] 301°C); ^{1}H NMR(DMSO-d_6)δ 6.00-6.68 (m, 2H), 7.02-7.70 (m, 2H); IR(KBr) 3100, 1675, 1020, 925 cm^{-1}.

(E)-Methyl 5-methyl-2,4-hexadienoate(**14**):[26] TLC(ethyl acetate/n-hexane=1/2(v/v)) R_f 0.82; ^{1}H NMR($CDCl_3$)δ 1.90 (bs, 6H), 3.82 (s, 3H). 5.67 (d, J=15Hz, 1H), 5.94 (d, J=10Hz, 1H), 7.45 (dd, J=12 and 15Hz, 1H); IR(neat) 2974, 1709, 1634, 985 cm^{-1}.

(E)-5-Methyl-2,4-hexadieneamide (**15**): TLC(ethyl acetate/methanol=10/1(v/v)) R_f 0.79; ^{1}H NMR($CDCl_3$)δ 1.98 (bs, 6H), 5.86-6.42 (m, 2H), 6.12 (bs, 2H), 7.62 (dd, J=11.5 and 15.5Hz, 1H); IR(KBr) 3291, 3245, 1671, 1604, 985 cm^{-1}.

General Procedure for the Preparation of (E,Z)- and (Z,E)-2,4-Dienoic Acid Derviatives (Table 4). The following procedure for the preparation of (E,Z)-methyl 2,4-heptadienoate (**16**) is representative.

In a dry 100m*l* flask equipped with a magnetic bar were placed 0.43g(5 mmol) of methyl acrylate, 0.40g(3 mmol) of cupric chloride, 20m*l* of acetonitrile and 3m*l* of 0.1M $LiPdCl_3$ in acetonitrile. After cooling to 0°C, 0.87g(3 mmol) of (Z)-1-butenylmercuric chloride was added to the flask and capped. The reaction mixture was allowed to warm to room temperature and stirred for 36h. Ether(50m*l*) and saturated ammonium chloride solution(10m*l*) were added and stirred for 1h. The organic layer was washed with saturated ammonium chloride solution and dried over anhydrous magnesium sulfate. Analysis of the organic phase by GLC using n-decane as an internal standard indicated that 0.27g(65%) of (E,Z)-methyl 2,4-heptadienoate and 0.01g(8%) of homocoupled (Z,Z)-3,5-octadiene were formed. Analytically pure samples were obtained by column chromatography(ethyl acetate/n-hexane=1/1(v/v)). (E,Z)-methyl 2,4-heptadienoate(**16**):[27] R_f 0.80; ^{1}H NMR($CDCl_3$)δ 1.04 (t, J=7Hz, 3H), 2.32 (m, 2H), 3.74 (s, 3H), 5.54-6.32 (m, 2H), 5.85 (d, J=15Hz, 1H), 7.64 (dd, J=10 and 15Hz, 1H); IR(neat) 2980, 1730, 1641, 978 cm^{-1}. (Z,Z)-3,5-octadiene: R_f 0.85; ^{1}H NMR($CDCl_3$)δ 0.96 (t, J=7Hz, 6H), 1.90-2.30 (m, 4H), 5.05-6.45 (m, 4H); IR(neat) 3045, 3010, 1630 cm^{-1}.

Spectral Data of (E,Z)- and (Z,E)-2,4-Dienoic Acid Derivatives.

(E,Z)-2,4-Heptadienenitrile(**17**): TLC(ethyl acetate/n-hexane=1/1(v/v)) R_f 0.78; ^{1}H NMR($CDCl_3$)δ 0.98 (t, J=7Hz, 3H), 1.94 (m, 2H), 5.05-5.86 (m, 3H), 7.62 (dd, J=10 and 15Hz, 1H); IR(neat) 2980, 2240, 1663, 970 cm^{-1}.

(E,Z)-2,4-Heptadieneamide(**18**): TLC(ethyl acetate) R_f 0.60; mp. 122-123°C; ^{1}H NMR($CDCl_3$)δ 0.97 (t, J=7Hz, 3H), 1.78 (m, 2H), 5.22-6.28 (m, 3H), 5.72 (bs, 2H), 7.66 (dd, J=10 and 15Hz, 1H); IR(KBr) 3370, 3190, 2980, 1670, 1635, 985 cm^{-1}.

(E,Z)-Methyl 2-methyl-2,4-heptadienoate(**19**): TLC(ethyl acetate/n-hexane=1/4(v/v)) R_f 0.78; ^{1}H NMR($CDCl_3$)δ 1.15 (t, J=7Hz, 3H), 1.80 (s, 3H), 1.96 (m, 2H), 3.80 (s, 3H), 5.52-6.31 (m, 2H), 7.62 (d, J=15Hz, 1H); IR(neat) 2985, 1744, 1655, 975 cm^{-1}.

(E,Z)-Methyl 3-carbamethoxy-2,4-heptadienoate(**20**): TLC(ethyl acetate/n-hexane=1/1.5(v/v)) R_f 0.52; ^{1}H NMR ($CDCl_3$)δ 1.12 (t, J=7Hz, 3H), 1.98 (m, 2H), 3.74 (s, 3H), 3.80 (s, 3H), 5.54-6.30 (m, 3H); IR(neat) 2982, 1736, 1645, 976 cm^{-1}.

(Z,E)-5-Phenyl-2,4-pentadienoic acid(**21**): mp. 137°C(lit.[28] 138°C); ^{1}H NMR(DMSO-d_6)δ 6.22 (d, J=8Hz, 1H), 6.82-7.15 (m, 2H), 7.32-7.80 (m, 6H), 10.95 (s, 1H); IR(KBr) 3440, 3010, 1674, 1645, 965 cm^{-1}.

(Z,E)-2,4-Hexadienedioic acid(**22**): mp. 190°C(lit.[25] 190-191°C); ^{1}H NMR(DMSO-d_6)δ 6.25-6.70 (m, 2H), 6.95-7.40 (m, 2H); IR(KBr) 3098, 1670, 1010, 900 cm^{-1}.

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