Pergamon

SCIENCE DIRECT®

Tetrahedron 59 (2003) 3635–3641

TETRAHEDRON

Highly chemoselective coupling of allenylstannanes with organic iodides promoted by $Pd(PPh_3)_4$/LiCl: an efficient method for the synthesis of substituted allenes

Chih-Wei Huang, Muthian Shanmugasundaram, Hao-Ming Chang and Chien-Hong Cheng*

Department of Chemistry, Tsing Hua University, Hsinchu 300, Taiwan, ROC

Received 4 December 2002; revised 25 February 2003; accepted 27 March 2003

Abstract—An efficient method for the preparation of various monosubstituted arylallenes, disubstituted allenes and alkenylallenes via palladium-catalyzed coupling of allenylstannanes with aryl iodides or alkenyl iodides is described. The coupling reaction was carried out in the presence of $Pd(PPh_3)_4$ and LiCl using DMF as solvent. The possible role of LiCl in this coupling process is discussed based on the ^{119}Sn NMR studies. © 2003 Published by Elsevier Science Ltd.

1. Introduction

Allenes are highly useful synthetic intermediates in organic synthesis because of their unique structure and reactivity.[1] In particular, transition-metal-catalyzed reactions based on allenes have attracted considerable interest for the past two decades.[2] Examples of metal-mediated allene chemistry include metal–metal bond addition to allenes,[3] three-component coupling reaction of allenes,[4] carbonylation reaction of allenes[5] and nickel-catalyzed [2+2+2] cycloaddition with allenes.[6]

In view of the broad utility of allenes, an efficient and general method for the preparation of allenes is in great demand. The most commonly used method involves the S_N2' displacement of propargylic ether derivatives with organometallic reagents.[7] However, this traditional method is limited by the incompatibility with many functional groups, the requirement of a large excess of organometallic and the sensitivity of the organometallic to moisture and air. Other methods for the preparation of allenes include dehydrohalogenation of vinylhalides,[8] reductive elimination of halogenated cyclopropanes,[9] elimination of enol phosphates,[10] S_N2' substitution of 2-bromo-1,3-butadiene derivatives catalyzed by palladium complexes[11] and radical β-elimination of vinyl sulfoxides.[12] Disubstituted allenes can be prepared by the Horner–Wadsworth–Emmons olefination of hydroxyalkenyl phosphonates.[13] The disadvantage of this method is the formation of alkyne as a side product and the requirement of more than one reaction step.

Although the palladium-catalyzed Stille coupling of aryl iodides with allenylstannanes has been reported, the method often results in low yields of allenes with limited examples.[14] The palladium-catalyzed coupling of aryl triflates with allenylstannanes has also been reported, but the reaction required higher temperature and gave moderate yields of allenes.[15] Allenylstannane derivatives have the advantage over traditional Grignard reagents because of their easy availability, air- and moisture-stability as well as their compatibility with functional groups. The need for an efficient and general method for the preparation of substituted allenes for the study of allene chemistry prompted us to develop an improved procedure for the palladium-catalyzed coupling of allenylstannanes with organic iodides. Herein, we report a complementary method for the preparation of monosubstituted arylallenes, disubstituted allenes and alkenylallenes via a Stille coupling of allenylstannanes with organic iodides promoted by the $Pd(PPh_3)_4$/LiCl system. The yields of allene products are much higher than those for the previously reported palladium-catalyzed Stille coupling reactions.[14]

2. Results and discussion

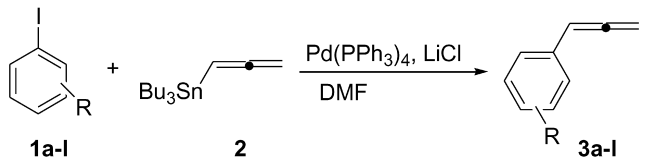
Treatment of iodobenzene (**1a**) with tributyl(1,2-propadienyl)stannane (**2**) in the presence of $Pd(PPh_3)_4$ (5 mol%) and LiCl (1.2 equiv.) in DMF at ambient temperature led to the formation of phenylallene (**3a**) in quantitative yield (Scheme 1, Table 1, entry 8). Control experiments revealed that in the absence of palladium catalyst, no coupling product **3a** was observed. The structure of **3a** was completely characterized by spectroscopic data.

To further understand the nature of the catalytic reaction, we

Keywords: palladium and compounds; coupling reactions; lithium and compounds; allenes.

* Corresponding author. Tel.: +886-3-5721454; fax: +886-3-5724698; e-mail: chcheng@mx.nthu.edu.tw

0040–4020/03/$ - see front matter © 2003 Published by Elsevier Science Ltd.
doi:10.1016/S0040-4020(03)00516-7



Scheme 1.

Table 1. Effects of catalysts, additives and solvents on the coupling of iodobenzene **1a** with *n*-tributylallenyl stannane **2**

Entry	Catalyst	Additive	Solvent	Yield of **3a** (%)[a]
1	$NiCl_2(PPh_3)_2/Zn$[b]	LiCl	DMF	0
2	$Ni(dppe)Br_2/Zn$[b]	LiCl	DMF	0
3	$Pd(OAc)_2$	LiCl	DMF	0
4	$Pd(dba)_2$	LiCl	DMF	Trace
5	$PdCl_2(MeCN)_2$	LiCl	DMF	Trace
6	$PdCl_2(PPh_3)_2$	LiCl	DMF	48
7	$Pd(PPh_3)_4$	–	DMF	41
8	$Pd(PPh_3)_4$	LiCl	DMF	99
9	$Pd(PPh_3)_4$	LiCl[c]	DMF	99
10	$Pd(PPh_3)_4$	LiCl[d]	DMF	99
11	$Pd(PPh_3)_4$	NaF	DMF	16
12	$Pd(PPh_3)_4$	CsF	DMF	26
13	$Pd(PPh_3)_4$	KBr	DMF	34
14	$Pd(PPh_3)_4$	LiBr	DMF	45
15	$Pd(PPh_3)_4$	NaCl	DMF	49
16	$Pd(PPh_3)_4$	LiCl	Toluene	0
17	$Pd(PPh_3)_4$	LiCl	CH_3CN	0
18	$Pd(PPh_3)_4$	LiCl	THF	54
19	$Pd(PPh_3)_4$	LiCl	DMA	86
20	$Pd(PPh_3)_4$	LiCl	DMSO	97

Reactions of iodobenzene (**1a**) (1.00 mmol) with *n*-tributylallenyl stannane (**2**) (1.20 mmol) were carried out at room temperature for 12 h in 3.00 mL of solvent using 5 mol% of metal-catalyst and additive (1.20 mmol).

[a] Yields were measured from crude products by the ^1H NMR integration method using mesitylene as an internal standard.

[b] 2.75 mmol of zinc was used.

[c] 2.00 mmol of LiCl was used.

[d] 3.00 mmol of LiCl was used.

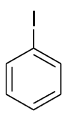
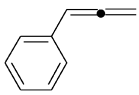
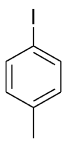
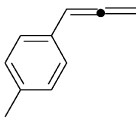
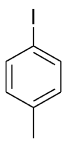
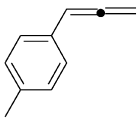
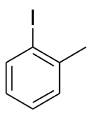
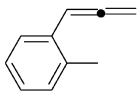
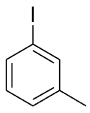
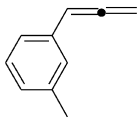
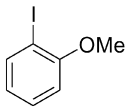
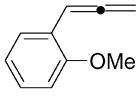
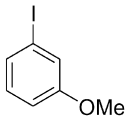
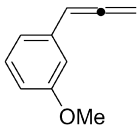
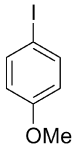
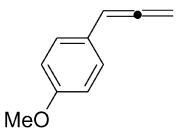
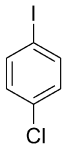
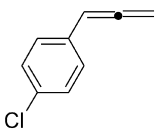
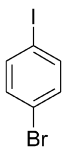
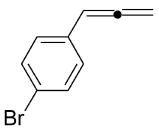
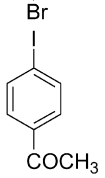
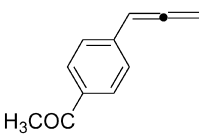
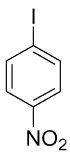
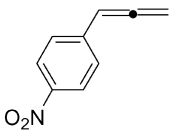
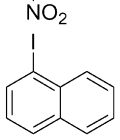
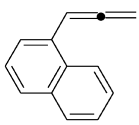
tested the reaction of iodobenzene (**1a**) with tributyl(1,2-propadienyl)stannane (**2**) under various conditions and the results are listed in Table 1. Nickel complexes $NiCl_2(PPh_3)_2$ and $Ni(dppe)Br_2$ were totally ineffective for the coupling reaction (entries 1 and 2). Phosphine–free palladium complexes such as $Pd(OAc)_2$, $Pd(dba)_2$, and $PdCl_2(CH_3CN)_2$ were also ineffective for the reaction (entries 3–5). In the presence of $PdCl_2(PPh_3)_2$, the coupling reaction gave **3a** in 48% yield (entry 6). The use of $Pd(PPh_3)_4$ without additive furnished **3a** in low yield (41%) (entry 7). The effect of various halide salts on the yield of the coupling of **1a** with **2** using $Pd(PPh_3)_4$ as catalyst is shown in entries 8–15. The highest product yield was obtained when LiCl (1.2–3 equiv.) was added (entries 8–10). Other salts NaF, CsF, KBr, LiBr and NaCl were less effective for the coupling reaction (entries 11–15). A brief examination of the influence of solvent on the yield of **3a** revealed that DMF was the solvent of choice. In toluene or CH_3CN, no reaction occurred (entries 16 and 17). The use of THF gave **3a** in 54% yield (entry 18). In addition to DMF, DMA and DMSO were also very effective affording **3a** in 86 and 97% yields, respectively (entries 19 and 20). The above results strongly suggest that the presence of both palladium–phosphine complexes and LiCl are essential for a high product yield of the coupling reaction.

As shown in Table 2, various aryl iodides effectively coupled with allenylstannane **2** affording high yields of monosubstituted arylallenes. The reaction of 4-iodotoluene (**1b**) with allenylstannane **2** in the presence of $Pd(PPh_3)_4$ and LiCl at 25°C for 12 h afforded **3b** in low yield of 44% (entry 2). However, the same reaction carried out at 50°C for 24 h gave **3b** in 79% yield (entry 3). Similarly, *o*- and *m*-iodotoluene **1c**,**d** coupled effectively with **2** to furnish allenes **3c** and **3d** in 78 and 80% yields, respectively (entries 4 and 5). Aryl iodides **1e–g** with an electron-donating methoxy group at the *ortho*, *meta* and *para* positions also reacted efficiently with **2** in the presence of $Pd(PPh_3)_4$/LiCl to give arylallenes **3e–g** in 95, 92 and 96% yields, respectively (entries 6–8). An *ortho* substituent on iodoarene does not significantly affect the product yield of the catalytic reaction (entries 4 and 6). As demonstrated in entries 9 and 10, the present protocol is highly chemoselective. 4-Chloroiodobenzene (**1h**) and 4-bromoiodobenzene (**1i**) selectively coupled with allenylstannane **2** to afford 4-chlorophenylallene (**3h**) and 4-bromophenylallene (**3i**) in 93 and 92% yields, respectively (entries 9 and 10). Aryl iodides **1j** and **1k** bearing electron-withdrawing groups $-COCH_3$ and $-NO_2$, respectively, at the *para* position also reacted with allenylstannane **2** to give allenes **3j** and **3k** in 74 and 60% yields, respectively (entries 11 and 12). It is noteworthy that allenes **3h–j** are difficult to prepare by the traditional Grignard method because of incompatibility with these functional groups. The observation that both iodoarenes with an electron-donating and an electron-withdrawing substituent coupled effectively with allenylstannane indicates that the catalytic reaction is insensitive to electronic effects. As expected, a longer reaction time was required for an iodoarene bearing an electron-donating group. Finally, 1-iodonaphthalene (**1l**) also reacted successfully with allenylstannane **2** in the presence of $Pd(PPh_3)_4$/LiCl to give 1-napthylallene (**3l**) in 96% yield (entry 13).

The present protocol can be further extended to the synthesis of disubstituted allenes in high yields (Table 3). Treatment of D-allenylstannane **4a** with iodobenzene in the presence of the $Pd(PPh_3)_4$/LiCl system at ambient temperature for 12 h afforded deuterated phenylallene **5a** in good yield of 90% (entry 1). Under similar reaction conditions, reactions of 1,2-butadienyl(tributyl)stannane (**4b**) and tributyl(3-phenyl-1,2-propadienyl)stannane (**4c**) with iodobenzene furnished the corresponding 1,3-disubstiuted allenes **5b** and **5c** in 95 and 90% yields, respectively (entries 2 and 3).

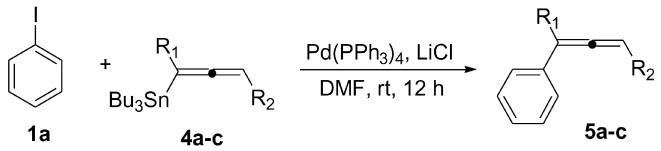
This methodology can also be applied to the synthesis of alkenylallenes (Table 4). Thus, the reaction of alkenyl iodide **6a** with allenylstannane **2** in the presence of $Pd(PPh_3)_4$ and LiCl in DMF for 40 min at room temperature afforded **7a** in a moderate yield of 55% (entry 1). The optimized reaction time is ca. 40 min. Any, further increase of the reaction time led to decomposition of the product giving only a trace of alkenylallene **7a**. Under similar optimized conditions, reactions of alkenyl iodides **6b** and **6c** with allenylstannane **2** gave the corresponding allenes **7b** and **7c** in 62 and 44% yields, respectively (entries 2 and 3). It is noteworthy that alkenylallenes find widespread applications in organic synthesis.[16]

Table 2. Coupling of aryl iodides **1a**–**1l** with *n*-tributylallenyl stannane **2**

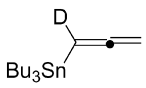
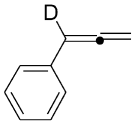
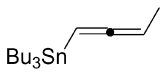
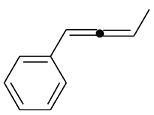
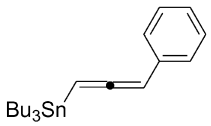
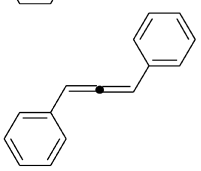
Entry	Aryl iodide		Conditions	Product		Yield (%)[a]
1		**1a**	25°C/12 h		**3a**	83(99)
2		**1b**	25°C/12 h		**3b**	44
3		**1b**	50°C/24 h		**3b**	79(82)
4		**1c**	50°C/24 h		**3c**	78(89)
5		**1d**	50°C/24 h		**3d**	80(86)
6		**1e**	50°C/24 h		**3e**	95
7		**1f**	50°C/24 h		**3f**	92(98)
8		**1g**	50°C/24 h		**3g**	96(99)
9		**1h**	25°C/12 h		**3h**	93(98)
10		**1i**	25°C/12 h		**3i**	92(99)
11		**1j**	25°C/3 h		**3j**	74(82)
12		**1k**	25°C/20 min		**3k**	60(65)
13		**1l**	25°C/12 h		**3l**	96

[a] Isolated yields; yields in parentheses were measured by ^{1}H NMR using mesitylene as an internal standard.

Table 3. Coupling of iodobenzene **1a** with substituted allenylstannanes **4a–c**



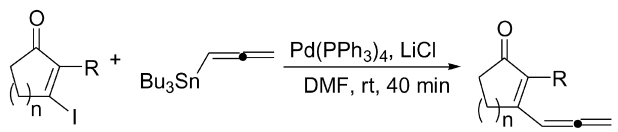
1a **4a-c** **5a-c**

Entry	Allenylstannane		Product		Yield (%)[a]
1		**4a**		**5a**[b]	90(99)
2		**4b**		**5b**	95
3		**4c**		**5c**	90(98)

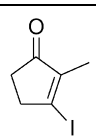
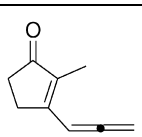
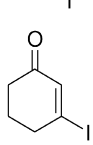
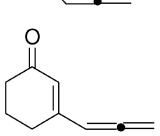
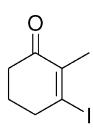
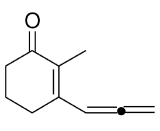
[a] Isolated yields; yields in parentheses were measured by ^{1}H NMR using mesitylene as an internal standard.
[b] 90% Deuterium purity.

The results of the present studies show a significant improvement for the synthesis of allenes compared to the previously reported method.[14] First, a wide variety of arylallenes can be conveniently prepared in good to excellent yields by the present method, whereas in the reported reaction, only limited examples of arylallenes were obtained in low yields. Second, the allene products were contaminated with tin compounds in the reported method, whereas in the present case, the allenes prepared were readily separated from tin compounds by treating the reaction mixture with saturated KF solution followed by purification on a silica gel column using *n*-pentane as eluent. Finally, the present protocol can be extended to the preparation of alkenylallenes that have not been synthesized by the reported method.

Table 4. Coupling of alkenyl iodides **6a–c** with *n*-tributylallenyl stannane **2**

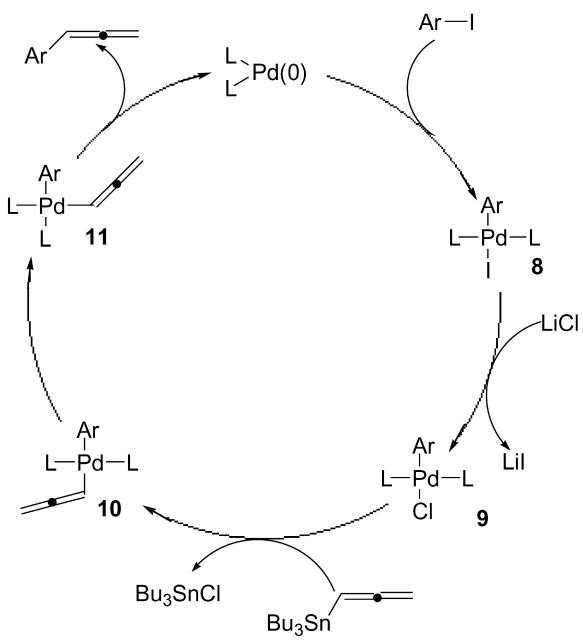


6a-c **2** **7a-c**

Entry	Alkenyl iodide		Product		Yield (%)[a]
1		**6a**		**7a**	55(62)
2		**6b**		**7b**	62(70)
3		**6c**		**7c**	44(58)

[a] Isolated yields; yields in parentheses were measured by ^{1}H NMR using mesitylene as an internal standard.

Based on known palladium chemistry, we propose a mechanism to account for the formation of products (Scheme 2). The first step is the oxidative addition of Ar–I to Pd(0) to form organopalladium (II) iodide **8**.



Scheme 2.

Exchange of Cl^- with the coordinated iodide in **8** affords organopalladium (II) chloride **9**. Transmetalation of allenylstannane with **9** gives η^1-allenylpalladium intermediate **10** and Bu_3SnCl. Further isomerization of **10** to the corresponding cis isomer **11** followed by reductive elimination affords the desired allene product and regenerates the Pd(0) catalyst.

While the exact reason for the remarkable additive effect of LiCl is not clear, it is likely that the chloride ion undergoes halide exchange with the coordinated iodide in the oxidative addition product **8** to give organopalladium chloride **9** prior to the transmetalation step.[17] The chloro complex **9** facilitates the transmetalation with allenylstannane by the formation of stable Bu_3SnCl. The presence of Bu_3SnCl is supported by the ^{119}Sn NMR studies of the reaction mixture of allenylstannane **2** with iodobenzene in the presence of 5 mol% of $Pd(PPh_3)_4$ and 1.2 equiv. of LiCl. The ^{119}Sn NMR spectrum of this reaction mixture shows a strong signal at δ 158.25 ppm corresponding to the ^{119}Sn resonance of Bu_3SnCl. The assignment is based on the ^{119}Sn NMR data of an authentic sample of Bu_3SnCl.

In conclusion, we have developed an improved procedure for the palladium-catalyzed coupling of allenylstannanes with organic iodides and demonstrated that this methodology is a simple and efficient method for the preparation of various monosubstituted arylallenes, disubstituted allenes, and alkenylallenes. This coupling reaction is highly chemoselective and compatible with a wide range of functional groups. Further application of these allenes in organic synthesis and detailed mechanistic studies are in progress.

3. Experimental

3.1. General

Melting points are uncorrected. All reactions were conducted under a nitrogen atmosphere on a dual-manifold Schlenk line unless otherwise mentioned and in oven-dried glasswares. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ using TMS as an internal standard on a Varian 400 NMR instrument at 400 and 100.4 MHz, respectively. ^{119}Sn NMR spectra were recorded in $CDCl_3$ using Me_4Sn as an external standard on a Varian 500 NMR instrument. IR spectra were recorded on a BOMEM MB-100 instrument. High resolution mass spectra were recorded on a Jeol JMS-HX 110 instrument and low mass spectra were recorded on a GC-MS Thermo Finnigan instrument. All solvents were dried according to known methods and distilled prior to use.[18] Starting materials allenylstannanes **2** and **4a–c** were synthesized according to the literature procedures.[19] $NiCl_2(PPh_3)_2$,[20] Ni(dppe)Br_2,[20] $Pd(PPh_3)_4$,[20] $PdCl_2(PPh_3)_2$[21] and $Pd(dba)_2$[22] were prepared by reported procedures. Other reagents were commercially available and used as purchased.

3.2. General procedure for the coupling of allenylstannanes with aryl iodides or alkenyl iodides

A 25-mL round-bottom flask containing $Pd(PPh_3)_4$ (0.050 mmol), LiCl (1.20 mmol) and DMF (3.00 mL) was purged with nitrogen gas several times. To the flask were then added aryl iodide or alkenyl iodide (1.00 mmol) and allenylstannane (1.20 mmol). The reaction mixture was stirred at a specified temperature and for a specified period as shown in Tables 1–3. The reaction mixture was then treated with 10 mL of saturated KF solution and allowed to stir for 30 min at ambient temperature, filtered through Celite and silica gel, and eluted with 50 mL of ether. The organic layer was washed with water, dried ($MgSO_4$) and concentrated in vacuo. The residue was purified on a silica gel column using *n*-pentane as eluent to give the desired allene product.

Products **3a–l**, **5a–c**, and **7a–c** were obtained according to this procedure. Product yields of these reactions are listed in Tables 1–3. All new compounds gave satisfactory spectral data and NMR data of known compounds were in good agreement with the literature report.

3.2.1. 1-(1,2-Propadienyl)benzene (3a).[23] Colorless oil; ^1H NMR: δ 7.45–7.42 (m, 4H), 7.35–7.32 (m, 1H), 6.31 (t, J=6.8 Hz, 1H), 5.28 (d, J=6.4 Hz, 2H); ^{13}C NMR: δ 209.72, 133.82, 128.53, 126.81, 126.62, 93.92, 78.65; HRMS calcd for C_9H_8 116.0626, found 116.0656.

3.2.2. 1-Methyl-4-(1,2-propadienyl)benzene (3b).[24] Colorless oil; ^1H NMR: δ 7.31 (d, J=8.8 Hz, 2H), 7.22 (d, J=8.8 Hz, 2H), 6.26 (t, J=6.4 Hz, 1H), 5.23 (d, J=6.8 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR: δ 209.53, 136.44, 130.80, 129.24, 126.52, 93.70, 78.47, 21.00; MS (*m*/*z*): 130 (M^+).

3.2.3. 1-Methyl-2-(1,2-propadienyl)benzene (3c).[25] Colorless oil; ^1H NMR: δ 7.37 (d, J=7.2 Hz, 1H), 7.14–7.08 (m, 3H), 6.33 (t, J=6.8 Hz, 1H), 5.09 (d, J=6.4 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR: δ 210.89, 134.84, 132.08, 130.40, 127.14, 126.76, 126.09, 91.11, 77.86, 19.74; MS (*m*/*z*): 130 (M^+).

3.2.4. 1-Methyl-3-(1,2-propadienyl)benzene (3d).[24] Colorless oil; ^1H NMR: δ 7.17 (t, J=8.0 Hz, 1H), 7.10–7.06 (m, 2H), 6.99 (d, J=7.2 Hz, 1H), 6.11 (t, J=6.4 Hz, 1H), 5.11 (t, J=7.2 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR: δ 209.73, 138.08, 133.69, 128.41, 127.65, 127.27, 123.80, 93.89, 78.53, 21.25; MS (*m*/*z*): 130 (M^+).

3.2.5. 1-Methyloxy-2-(1,2-propadienyl)benzene (3e).[26] Colorless oil; ^1H NMR: δ 7.37 (d, J=8.0 Hz, 1H), 7.16 (t, J=8.0 Hz, 1H), 6.90 (t, J=7.6 Hz, 1H), 6.84 (d, J=8.0 Hz, 1H), 6.55 (t, J=6.8 Hz, 1H), 5.08 (t, J=7.2 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR: δ 210.17, 155.86, 127.92, 127.72, 125.78, 120.76, 110.93, 87.78, 77.93, 55.55; MS (*m*/*z*): 146 (M^+).

3.2.6. 1-Methyloxy-3-(1,2-propadienyl)benzene (3f). Colorless oil; ^1H NMR: δ 7.23 (t, J=7.2 Hz, 1H), 6.88 (d, J=7.6 Hz, 1H), 6.85 (s, 1H), 6.75 (d, J=7.2 Hz, 1H), 6.14 (t, J=6.8 Hz, 1H), 5.15 (d, J=6.4 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR: δ 209.85, 159.91, 135.39, 129.54, 119.37, 112.76, 111.86, 93.95, 78.80, 55.18; HRMS calcd for $C_{10}H_{10}O$ 146.0732, found 146.0740.

3.2.7. 1-Methyloxy-4-(1,2-propadienyl)benzene (3g).[27] Colorless oil; ^1H NMR: δ 7.25 (d, J=8.8 Hz, 2H), 6.88

(d, J=8.8 Hz, 2H), 6.16 (t, J=6.8 Hz, 1H), 5.15 (d, J=6.8 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR: δ 209.31, 158.66, 127.69, 126.04, 114.07, 93.29, 78.65, 55.17; MS (m/z): 146 (M^+).

3.2.8. 1-Chloro-4-(1,2-propadienyl)benzene (3h).[28] Colorless oil; ^{1}H NMR: δ 7.26 (d, J=8.8 Hz, 2H), 7.20 (d, J=8.4 Hz, 2H), 6.11 (t, J=6.4 Hz, 1H), 5.14 (d, J=6.8 Hz, 2H); ^{13}C NMR: δ 209.81, 132.46, 128.73, 127.85, 93.11, 79.14; MS (m/z): 150 (M^+).

3.2.9. 1-Bromo-4-(1,2-propadienyl)benzene (3i). Colorless oil; ^{1}H NMR: δ 7.41 (d, J=7.6 Hz, 2H), 7.14 (d, J=8.8 Hz, 2H), 6.10 (t, J=6.8 Hz, 1H), 5.14 (d, J=6.4 Hz, 2H); ^{13}C NMR: δ 209.75, 132.88, 131.62, 128.15, 120.46, 93.15, 79.21; HRMS calcd for C_9H_7Br 193.9731, found 193.9726.

3.2.10. 1-(4-(1,2-Propadienyl)phenyl)-1-ethanone (3j). Colorless oil; ^{1}H NMR: δ 7.84 (d, J=8.4 Hz, 2H), 7.31 (d, J=8.4 Hz, 2H), 6.15 (t, J=6.8 Hz, 1H), 5.16 (d, J=6.8 Hz, 2H), 2.53 (s, 3H); ^{13}C NMR: δ 210.63, 197.29, 139.13, 135.43, 128.66, 126.58, 93.46, 79.11, 26.37; HRMS calcd for $C_{11}H_{10}O$ 158.0732, found 158.0729.

3.2.11. 1-Nitro-4-(1,2-propadienyl)benzene (3k).[29] Colorless solid, mp 63°C; ^{1}H NMR: δ 8.10 (d, J=8.8 Hz, 2H), 7.37 (d, J=8.8 Hz, 2H), 6.19 (t, J=6.4 Hz, 1H), 5.23 (d, J=6.4 Hz, 2H); ^{13}C NMR: δ 211.11, 146.37, 141.31, 126.99, 123.88, 92.99, 79.67; MS (m/z): 161 (M^+).

3.2.12. 1-(1,2-Propadienyl)naphthalene (3l). Colorless oil; ^{1}H NMR: δ 8.19 (d, J=8.0 Hz, 1H), 7.84 (d, J=7.2 Hz, 1H), 7.73 (d, J=8.4 Hz, 1H), 7.58 (d, J=6.8 Hz, 1H), 7.52–7.41 (m, 3H), 6.85 (t, J=6.8 Hz, 1H), 5.19 (d, J=6.8 Hz, 2H); ^{13}C NMR: δ 211.06, 133.95, 130.81, 130.15, 128.66, 127.46, 126.00, 125.69, 125.62, 125.33, 123.51, 90.44, 77.76; HRMS calcd for $C_{13}H_{10}$ 166.0783, found 166.0771MS.

3.2.13. 1-(1-Deuterio-1,2-propadienyl)benzene (5a). Colorless oil; ^{1}H NMR: δ 7.33–7.23 (m, 5H), 5.17 (s, 1H); ^{13}C NMR: δ 209.78, 133.83, 128.58, 126.84, 126.64, 93.92, 93.69, 93.45, 78.82; HRMS calcd for C_9H_7D 117.0688, found 117.0692.

3.2.14. 1-(1,2-Butadienyl)benzene (5b).[13c] Colorless oil; ^{1}H NMR: δ 7.36–7.21 (m, 5H), 6.16 (m, 1H), 5.60 (m, 1H), 1.86–1.83 (m, 3H); ^{13}C NMR: δ 205.99, 135.02, 128.50, 126.62, 93.98, 89.52, 14.03; HRMS calcd for $C_{10}H_{10}$ 130.07833, found 130.0746.

3.2.15. 1-(3-Phenyl-1,2-propadienyl)benzene (5c).[30] Colorless solid, mp 53°C; ^{1}H NMR: δ 7.36–7.21 (m, 10H), 6.58 (m, 2H); ^{13}C NMR: δ 207.79, 133.60, 128.73, 127.31, 126.99, 98.42; HRMS calcd for $C_{15}H_{12}$ 192.0939, found 192.0933.

3.2.16. 2-Methyl-3-(1,2-propadienyl)-2-cyclopenten-1-one (7a). Yellow oil; IR (neat) 1928, 1668, 1614, 809 cm^{-1}; ^{1}H NMR: δ 6.29 (t, J=6.4 Hz, 1H), 5.12 (d, J=6.4 Hz, 2H), 2.51 (m, 2H), 2.34 (m, 2H), 1.71 (s, 3H); ^{13}C NMR: δ 212.68, 208.94, 161.74, 136.06, 89.96, 78.24, 33.67, 26.67, 7.97; HRMS calcd for $C_9H_{10}O$ 134.0732, found 134.0728.

3.2.17. 3-(1,2-Propadienyl)-2-cyclohexen-1-one (7b). Yellow oil; IR (neat) 1930, 1670, 1611, 802 ccm^{-1}; ^{1}H NMR: δ 5.89 (t, J=6.4 Hz, 1H), 5.82 (s, 1H), 5.06 (d, J=6.4 Hz, 2H), 2.32–2.28 (m, 4H), 1.95–1.88 (m, 2H); ^{13}C NMR: δ 212.19, 199.15, 155.70, 125.69, 95.93, 78.82, 37.27, 25.99, 22.12; HRMS calcd for $C_9H_{10}O$ 134.0732, found 134.0728.

3.2.18. 2-Methyl-3-(1,2-propadienyl)-2-cyclohexen-1-one (7c). Yellow oil; IR (neat) 1928, 1658, 1599, 813 cm^{-1}; ^{1}H NMR: δ 6.29 (t, J=6.4 Hz, 1H), 5.07 (d, J=6.8 Hz, 2H), 2.40–2.36 (m, 4H), 1.94–1.86 (m, 2H), 1.81 (s, 3H); ^{13}C NMR: δ 212.39, 198.48, 147.70, 130.55, 93.23, 78.13, 37.55, 27.06, 21.80, 10.29; HRMS calcd for $C_{10}H_{12}O$ 148.0888, found 148.0889.

Acknowledgements

We thank the National Science Council of the Republic of China (NSC 91-2113-M-007-053) for support of this research.

References

1. For reviews, see: Brandsma, L.; Verkruijsse, H. D. *Synthesis of Acetylenes, Allenes and Cummulenes*; Elsevier: New York, 1981.
2. For reviews, see: (a) Marshall, J. A. *Chem. Rev.* **1996**, *96*, 31. (b) Yamamoto, Y.; Radhakrishnanan, U. *Chem. Soc. Rev.* **1999**, *28*, 199. (c) Zimmer, R.; Dinesh, C. U.; Nandanam, E.; Khan, F. A. *Chem. Rev.* **2000**, *100*, 3067. (d) Marshall, J. A. *Chem. Rev.* **2000**, *100*, 3163.
3. (a) Yang, F.-Y.; Cheng, C.-H. *J. Am. Chem. Soc.* **2001**, *123*, 761. (b) Jeganmohan, M.; Shanmugasundaram, M.; Chang, K.-J.; Cheng, C.-H. *Chem. Commun.* **2002**, 2552. (c) Onozawa, S.-y.; Hatanaka, Y.; Tanaka, M. *Chem. Commun.* **1999**, 1863. (d) Suginome, M.; Ohmori, Y.; Ito, Y. *Synlett* **1999**, 1567.
4. (a) Wu, M.-Y.; Yang, F.-Y.; Cheng, C.-H. *J. Org. Chem.* **1999**, *64*, 2471. (b) Yang, F.-Y.; Wu, M.-Y.; Cheng, C.-H. *J. Am. Chem. Soc.* **2000**, *122*, 7122. (c) Huang, T.-H.; Chang, H.-M.; Wu, M.-Y.; Cheng, C.-H. *J. Org. Chem.* **2002**, *67*, 99. (d) Tsuji, J.; Shimizu, I. *Chem. Lett.* **1984**, 233. (e) Chaptal, N.; Colovray-Gotteland, V.; Grandjean, C.; Cazes, B.; Gore, J. *Tetrahedron Lett.* **1991**, *32*, 1795.
5. (a) Chang, H.-M.; Cheng, C.-H. *Org. Lett.* **2000**, *2*, 3439. (b) Anwar, U.; Grigg, R.; Rasparini, M.; Savic, V.; Sridharan, V. *Chem. Commun.* **2000**, 645.
6. (a) Shanmugasundaram, M.; Wu, M.-S.; Cheng, C.-H. *Org. Lett.* **2001**, *3*, 4233. (b) Shanmugasundaram, M.; Wu, M.-S.; Jeganmohan, M.; Huang, C.-W.; Cheng, C.-H. *J. Org. Chem.* **2002**, *67*, 7724.
7. (a) Alexakis, A.; Marek, I.; Mangeney, P.; Normant, J. F. *J. Am. Chem. Soc.* **1990**, *112*, 8042. (b) Alexakis, A.; Marek, II.; Mangeney, P.; Normant, J. F. *Tetrahedron* **1991**, *47*, 1677. (c) Nantz, M. H.; Bender, D. M.; Janaki, S. *Synthesis* **1993**, 577. (d) Myers, A. G.; Zheng, B. *J. Am. Chem. Soc.* **1996**, *118*, 4492.

8. Tanaka, K.; Otsubo, K.; Fuji, K. *Synlett* **1995**, 933.
9. Doering, W. E.; LaFlamme, P. M. *Tetrahedron* **1958**, *2*, 75.
10. Brummond, K. M.; Dingess, E. A.; Kent, J. L. *J. Org. Chem.* **1996**, *61*, 6096.
11. Ogasawara, M.; Ikeda, H.; Hayashi, T. *Angew. Chem. Int. Ed.* **2000**, *39*, 1042.
12. Delouvrie, B.; Lacote, E.; Fensterbank, L.; Malacria, M. *Tetrahedron Lett.* **1999**, *40*, 3565.
13. (a) Mizuno, M.; Fujii, K.; Tomioka, K. *Angew. Chem. Int. Ed.* **1998**, *37*, 515. (b) Nagaoka, Y.; Tomioka, K. *Org. Lett.* **1999**, *1*, 1467. (c) Inoue, H.; Tsubouchi, H.; Nagaoka, Y.; Tomioka, K. *Tetrahedron* **2002**, *58*, 83.
14. Aidhen, I. S.; Braslau, R. *Synth. Commun.* **1993**, *24*, 789.
15. Badone, D.; Cardamone, R.; Guzzi, U. *Tetrahedron Lett.* **1994**, *35*, 5477.
16. (a) Mandai, T.; Suzuki, S.; Ikawa, A.; Murakami, T.; Kawada, M.; Tsuji, J. *Tetrahedron Lett.* **1991**, *32*, 7687. (b) Murakami, M.; Itami, K.; Ito, Y. *Angew. Chem. Int. Ed.* **1995**, *34*, 2691. (c) Kerr, C. E.; Eaton, B. E.; Kaduk, J. A. *Organometallics* **1995**, *14*, 269. (d) Murakami, M.; Ubukata, M.; Itami, K.; Ito, Y. *Angew. Chem. Int. Ed.* **1998**, *37*, 2248.
17. (a) Stang, P. J.; Kowalski, M. H.; Schiavelli, M. D.; Longford, D. *J. Am. Chem. Soc.* **1989**, *111*, 3347. (b) Hoshino, M.; Degenkolb, P.; Curran, D. P. *J. Org. Chem.* **1997**, *62*, 8341.
18. Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; 3rd ed. Pergamon: New York, 1988.
19. (a) Tanaka, H.; Hai, A. K. M. A.; Ogawa, H.; Torii, S. *Synlett* **1993**, 835. (b) Marshall, J. A.; Wang, X. *J. Org. Chem.* **1992**, *57*, 1242.
20. Colquhoun, H. M.; Halton, J.; Thompson, D. J.; Twigg, M. V. *New Pathways for Organic Synthesis—Practical Applications of Transition Metals*; Plenum: New York, 1988.
21. Heck, R. F. *Palladium Reagents in Organic Syntheses*; Academic: New York, 1978.
22. Takahashi, Y.; Ito, T.; Sakai, S.; Ishii, Y. *J. Chem. Soc., Chem. Commun.* **1970**, 1065.
23. Tsuji, J.; Sugiura, T.; Minami, I. *Synthesis* **1987**, 603.
24. Okuyama, Y.; Izawa, K.; Fueno, T. *J. Am. Chem. Soc.* **1973**, *95*, 6749.
25. Eichinger, P. C. H.; Bowie, J. H. *J. Chem. Soc., Perkin Trans. 2* **1988**, 497.
26. Jung, M. E.; Hagenah, J. A. *J. Org. Chem.* **1987**, *52*, 1889.
27. Mouries, V.; Delouvrie, B.; Lacote, E.; Fensterbank, L.; Malacria, M. *Eur. J. Org. Chem.* **2002**, 1776.
28. Ruitenberg, K.; Kleijn, H.; Meijer, J.; Oostveen, E. A.; Vermeer, P. *J. Organomet. Chem.* **1982**, *224*, 399.
29. Rafizadeh, K.; Yates, K. *J. Org. Chem.* **1984**, *49*, 1500.
30. Ohno, H.; Miyamura, K.; Tanaka, T.; Oishi, S.; Toda, A.; Takemoto, Y.; Fujii, N.; Ibuka, T. *J. Org. Chem.* **2002**, *67*, 1359.