

Palladium-Catalyzed Synthesis of 1,3-Dienes from Allenes and Organic Halides

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A wide range of aryl and vinylic halides react with 1,1-dimethylallene (**2a**) and potassium carbonate in the presence of Pd(dba)₂ (dba = dibenzylideneacetone) in *N,N*-dimethylacetamide (DMA) at temperature 100–120 °C to give the corresponding dienes CH₂C(CH₃)CRCH₂ (**3a–o**), where R is aryl or vinylic, in good to excellent yields. Higher yields of diene products were obtained for aryl bromides than for the corresponding aryl iodides and chlorides. Under similar reaction conditions, tetramethylallene (**2b**), 1-methyl-1-phenylallene (**2c**), 1-methyl-3-phenylallene (**2d**), and 1-cyclohexylallene (**2e**) also react with aryl and vinylic halides to give diene products (**3p–w**). For **2d**, both *E* and *Z* isomers **3t** and **3u** of the diene product were observed. For **2e**, two regioisomers **3v** and **3w** were isolated with **3w** likely from alkene isomerization of **3v**. Various palladium systems were tested for the catalytic activity of diene formation. In addition to Pd(dba)₂/PPh₃, Pd(OAc)₂/PPh₃, PdCl₂(PPh₃)₂, and PdCl₂(dppe) are also very effective as catalysts for the reaction of **2a** with *p*-bromoacetophenone (**1a**) to give **3a**. Studies on the effect of solvents and bases show that DMA and K₂CO₃ are the solvent and base that give the highest yield of diene **3a**. Possible mechanisms for this catalytic diene formation are proposed.

Introduction

Palladium-catalyzed transformation of allenes into various organic substrates has continued to attract great attention due to the potential application of these methodologies in organic synthesis.¹ The pathways of these catalytic processes generally involve the addition of a palladium–carbon,² a palladium–hydride,³ or a palladium–heteroatom⁴ bond to allenes to give π -allylpalladium complexes, followed by nucleophilic attack of the

π -allylpalladium intermediates to give the final organic products.⁵ While numerous catalytic reactions involving the addition of palladium–carbon bonds to allenes (carbopalladation) as key steps are known,² there is still no method that leads to the isolation of substituted 1,3-dienes via intermolecular reaction of allenes and aryl halides. Very recently, a report by Grigg and co-workers showed that substituted 1,3-dienes were generated in situ from allenes and aryl halides in the presence of Ag₂CO₃ using palladium complexes as the catalysts.⁶ The dienes formed were trapped by dienophiles such as *N*-methylmaleimide, but no dienes were isolated by this method (vide infra). In the cyclic carbopalladation of allenes, Negishi and co-workers have observed the formation of cyclic dienes.⁷ Yamamoto et al. showed that during the hydro-palladation of allenes certain aliphatic allenes were rearranged to 1,3-dienes.⁸

Our continuing interest in the palladium-mediated allene chemistry⁹ prompted us to investigate the transformation of allenes into 1,3-dienes via eq 1 and to search for suitable conditions that can lead to the isolation of the 1,3-diene products. In this paper, we wish to report that aryl and vinylic halides, particularly the bromides, react smoothly with substituted allenes and potassium carbonate in the presence of a palladium complex to give

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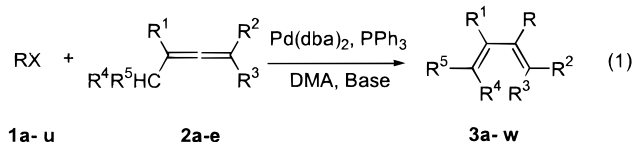
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substituted 1,3-dienes (eq 1) and for the first time that 1,3-dienes are isolated from carbopalladation of allenes.



Results and Discussion

Dienes from Reaction of 1,1-Dimethylallene with Organic Halides and Potassium Carbonate. Treatment of 1,1-dimethylallene (**2a**) with *p*-bromoacetophenone (**1a**) and potassium carbonate in *N,N*-dimethylacetamide (DMA) in the presence of 5 mol % of Pd(dba)₂ and 5 mol % of PPh₃ at 120 °C for 12 h gives diene **3a** in 94% isolated yield (Table 1, entry 1). Control experiments indicate that in the absence of either Pd(dba)₂ or potassium carbonate no diene product was observed. The yield of diene **3a** was reduced to 74%, if PPh₃ was omitted.

Under similar conditions, a vast number of aryl bromides including *o*-bromoacetophenone, *p*- and *m*-bromotoluene, *p*-bromochlorobenzene, *p*- and *o*-bromonitrobenzene, *p*- and *o*-bromobenzonitrile, *p*-bromoanisole, ethyl *o*-bromobenzoate, 9-bromoanthracene, and 1,4-dibromobenzene (**1b–m**) react with 1,1-dimethylallene (**2a**) and potassium carbonate to afford the corresponding dienes (**3b–m**) in good to excellent yields. Table 1 shows the reaction conditions and the product yields of these reactions (Table 1, entries 2–13). Aryl bromides with either an electron-withdrawing substituent or an electron-donating group react smoothly with 1,1-dimethylallene (**2a**) to yield 1,3-diene derivatives. However, fine-tuning of the reaction conditions is required for each aryl halide employed in order to achieve high yield. For example, the reaction of *p*-bromoanisole (**1j**) with 1,1-dimethylallene (**2a**) using 5 mol % Pd(dba)₂/PPh₃ as the catalyst requires 120 °C and 24 h in DMA to afford the best yield (90%) (Table 1, entry 10), but for *p*-bromonitrobenzene (**1f**) and *p*-bromobenzonitrile (**1h**) the yields of the corresponding dienes are higher at 100 °C than at 120 °C (Table 1, entries 6 and 8). All these diene products show four characteristic ¹H NMR singlets in the region δ 4.8–5.6 ppm for the terminal olefinic protons. The mass and ¹³C NMR spectra of these compounds are also in agreement with the proposed diene structures.

Aryl iodides also react with 1,1-dimethylallene (**2a**) and potassium carbonate to give the corresponding diene derivatives. The yields of these reactions are also listed in Table 1 (Table 1, entries 14 and 15). The results show that aryl iodides give lower yields of the diene derivatives than the corresponding aryl bromides at 120 °C. This is surprising in view of the fact that, for most palladium-catalyzed reactions, aryl iodides are generally more reactive and give higher product yields than the corresponding aryl bromides. Attempts to optimize the reaction conditions for aryl iodides by varying the reaction temperature, base, and solvent did not significantly improve the yields of dienes. The reason for the observed higher yields of diene products for aryl bromides than for aryl iodides is not clear.

Unlike aryl bromides and aryl iodides, most aryl chlorides react very slowly with 1,1-dimethylallene (**2a**) and potassium carbonate in the presence of Pd(dba)₂/PPh₃ to give trace amounts of the diene products. As

expected, the reaction of *p*-bromochlorobenzene (**1e**) with 1,1-dimethylallene (**2a**) gave only 1-chloro-4-(2-methyl-1-methyleneallyl)benzene (**3e**) (Table 1, entry 5). There is no corresponding 1-bromo-4-(2-methyl-1-methyleneallyl)benzene product observed, indicating that only the C–Br bond in *p*-bromochlorobenzene (**1e**) undergoes oxidative addition to the palladium center. The yields of diene products increase for aryl chlorides possessing an electron-withdrawing substituent. For example, 4-chloroacetophenone (**1p**) and 1-chloro-4-nitrobenzene (**1q**) react with 1,1-dimethylallene (**2a**) to give the corresponding 1,3-dienes in 21 and 29% yields, respectively (Table 1, entries 16 and 17). These results may be understood on the basis of the fact that an electron-withdrawing group on an aryl halide generally enhances the rate of oxidative addition of this substrate to the palladium center.¹⁰

Under similar reaction conditions, vinylic bromides including α -bromostyrene (**1s**) and 3-bromo-5,5-dimethyl-2-cyclohexen-1-one (**1t**) react with 1,1-dimethylallene (**2a**) and potassium carbonate to give cross trienes **3n** and **3o** in 82 and 67% yields, respectively (Table 1, entries 19 and 20). To the best of our knowledge, few of these unusual cross trienes are known in the literature.¹¹ The Diels–Alder cycloaddition of these trienes with dienophiles should be interesting. Investigation in this direction is in progress.

Reaction of Other Allenes with Organic Halides and Potassium Carbonate. Several substituted allenes including tetramethylallene (**2b**), 1-methyl-1-phenylallene (**2c**), 1-methyl-3-phenylallene (**2d**), and 1-cyclohexylallene (**2e**) were also investigated for the reactions with aryl and vinylic halides and potassium carbonate. Thus, in the presence of 5 mol % Pd(dba)₂, **2b** reacts with *p*-bromoacetophenone (**1a**), α -bromostyrene (**1s**), or 3-bromo-5,5-dimethyl-2-cyclohexen-1-one (**1t**) and potassium carbonate to give the corresponding dienes **3p–r** in 38–77% yields (Table 1, entries 21–23); the reaction of **2c** with **1a** and **1u** affords 2,3-disubstituted dienes **3s** and **3n** in 42 and 45% yields, respectively. Two isomers **3t** and **3u** were isolated in 53% combined yield from the reaction of **2d** with **1t** (Table 1, entry 26). The stereochemistry of these isomers was established on the basis of the NOE experimental results of these products. Isomer **3t** exhibits ¹H NMR signals at 6.61 and 2.45 ppm for olefin proton H_a and methylene protons H_b, respectively. Irradiation at H_b led to increase of the intensity of H_a by 2.8%. In contrast, irradiation at methylene protons H_d of **3u** showed essentially no change of the intensity of H_c (Scheme 1). These NOE results indicate that **3t** has the *E* structure, while **3u** is a *Z* isomer.

The reaction of allene **2e** with **1a** affords two isomers **3v** and **3w** in 28 and 31% yields, respectively (Table 1, entry 27). Product **3w** is likely from alkene isomerization of **3v**. The stereochemistry of **3w** is also based on the NOE technique. In the ¹H NMR spectrum, compound **3w** exhibits signals at 2.16 and 2.19 ppm for methylene (H_d) and methyl protons and at 5.74, 6.23, and 7.47 ppm for olefin and aromatic protons H_a, H_b, and H_c, respectively. Irradiation at H_b led to an increase of the intensity of H_c by 10.3% and of H_a by 2.3%. Irradiation at H_a also led to an increase of the intensities of the methylene protons and

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Table 1. Results of Palladium-Catalyzed Diene Formations from Allenes and Organic Halides^a

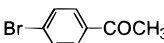

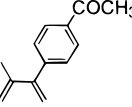
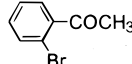
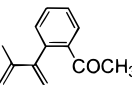
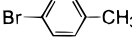

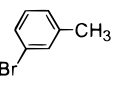
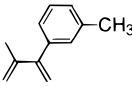
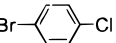



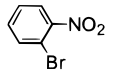

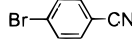

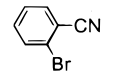

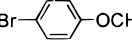

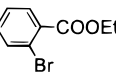

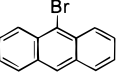


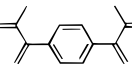
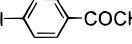
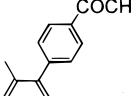
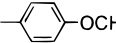

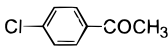
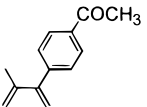
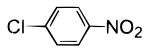
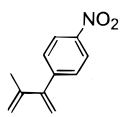
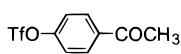
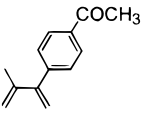


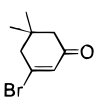
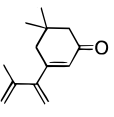
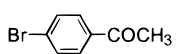

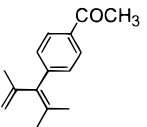
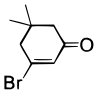
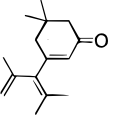


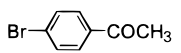
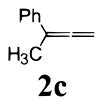
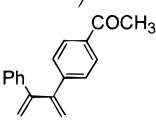


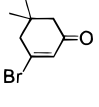
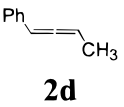
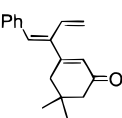
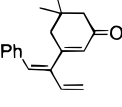
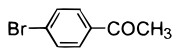
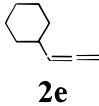
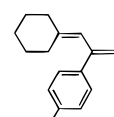
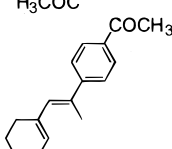
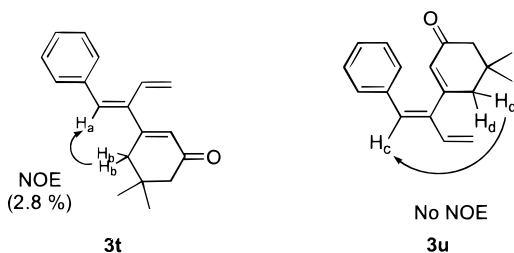
entry	RX	Allene	T (°C)	Time (h)	Product	Yield (%) ^b
1	 1a	 2a	120	12	 3a	94
2	 1b	2a	100	24	 3b	65
3	 1c	2a	120	12	 3c	82
4	 1d	2a	120	12	 3d	84
5	 1e	2a	100	12	 3e	91
6	 1f	2a	100	12	 3f	90
7	 1g	2a	100	12	 3g	64
8	 1h	2a	100	12	 3h	94
9	 1i	2a	100	12	 3i	82
10	 1j	2a	120	24	 3j	90
11	 1k	2a	100	24	 3k	75
12	 1l	2a	120	12	 3l	89
13	 1m	2a	120	12	 3m	65
14	 1n	2a	120	12	 3a	60
15	 1o	2a	120	12	 3j	60

Table 1. (Continued)

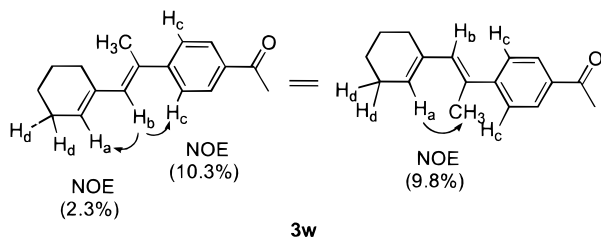
entry	RX	Allene	T (°C)	Time (h)	Product	Yield (%) ^b
16	 1p	2a	120	12	 3a	21
17	 1q	2a	120	12	 3f	29
18	 1r	2a	120	12	 3a	52
19	 1s	2a	120	12	 3n	82
20	 1t	2a	120	12	 3o	67
21	 1a	 2b	120	12	 3p	60
22	 1t	2b	120	12	 3q	38
23	 1s	2b	120	12	 3r	77
24	 1a	 2c	120	12	 3s	42
25	 1u	2c	120	12	 3n	45
26	 1t	 2d	120	12	 3t	28
					 3u	25
27	 1a	 2e	120	12	 3v	28
					 3w	31

^a All reactions were carried out using allene (2.00 mmol), aryl or vinylic bromide (1.00 mmol), Pd(dba)₂ (0.0500 mmol), PPh₃ (0.0500 mmol), K₂CO₃ (2.00 mmol), and DMA (1.0 mL). ^b Isolated yields.

Scheme 1



Scheme 2

Table 2. Effect of Catalysts and Ligand on the Yield of **3a**^a

entry	Pd catalyst	PPh ₃ (equiv) ^b	yield ^b (%)
1	Pd(PPh ₃) ₄		44
2	Pd(dba) ₂		74
3	Pd(dba) ₂	1	98
4	Pd(dba) ₂	2	82
5	Pd(dba) ₂	4	50
6	Pd(dba) ₂	6	33
7	PdCl ₂ (PPh ₃) ₂		79
8	PdCl ₂ (dppf)		89
9	Pd(OAc) ₂		55
10	Pd(OAc) ₂	1	94
11	Pd(OAc) ₂	2	91
12	PdCl ₂		33
13	PdCl ₂	1	74
14	PdCl ₂	2	67
15	PdCl ₂ (CH ₃ CN) ₂		41
16	PdCl ₂ (CH ₃ CN) ₂	1	52

^a All reactions were carried out using 1,1-dimethylallene (2.00 mmol), 4-bromoacetophenone (1.00 mmol), 5 mol % of Pd catalyst (0.0500 mmol), K₂CO₃ (2.00 mmol), and DMA (1.0 mL) at 120 °C; reaction time: 12 h. ^b Yields were determined by ¹H NMR.

H_b by 9.8% and 3.6%, respectively (Scheme 2). These NOE results clearly show that isomer **3w** is an *E* product. The corresponding *Z* isomer was not observed in the reaction.

Effect of Reaction Conditions on the Yield of Diene Product. The present palladium-catalyzed 1,3-diene formations from allenenes and aryl halides are greatly sensitive to the reaction temperature, solvent, base, and amount of phosphine used. The results for the reaction of *p*-CH₃COC₆H₄X (X = Br, I, Cl, OTf) with 1,1-dimethylallene (**2a**) using various palladium systems under different conditions are shown in Tables 2 and 3. When potassium carbonate was used as the base, a suitable temperature range for the catalytic reaction was 100–120 °C. At reaction temperatures below 70 °C, the rate of 1,3-diene formation was slow and a low yield of the diene product was obtained (Table 3, entries 15 and 16). Several solvents, DMF, DMA, DMSO, and toluene, were employed in the catalytic reactions at 120 °C with DMA giving the highest yield of product (Table 3, entries 1 and 5–7). Addition of 1 or 2 equiv of PPh₃ to the reaction solution using Pd(dba)₂ as the catalyst greatly increases the product yield. However, a further increase of the amount of PPh₃ reduces the yield (Table 2, entries 1–6).

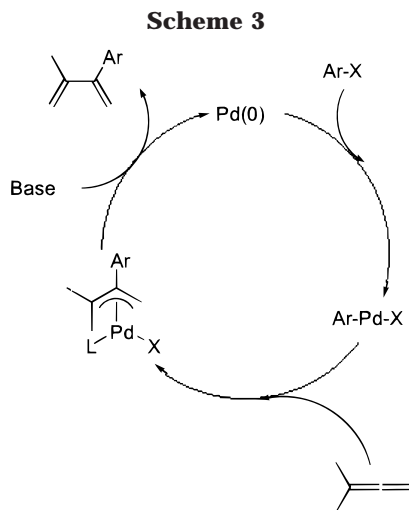
Table 3. Effect of Solvent, Temperature, and Base on the Yield of Diene **3a**^a

entry	X	solvent	T (°C)	base (equiv)	yield ^b (%)
1	Br	DMA	120	K ₂ CO ₃ (2)	94 (98) ^c
2	Br	DMA	100	K ₂ CO ₃ (2)	90
3	Br	DMA	120	K ₂ CO ₃ (3)	85
4	Br	DMA	120	K ₂ CO ₃ (4)	65
5	Br	DMF	120	K ₂ CO ₃ (2)	68
6	Br	DMSO	120	K ₂ CO ₃ (2)	60
7	Br	Toluene	120	K ₂ CO ₃ (2)	55 ^c
8	Br	DMA	120	Na ₂ CO ₃ (2)	47
9	Br	DMA	120	NaHCO ₃ (2)	16 ^c
10	Br	DMA	120	NaOAc (2)	79 ^c
11	Br	DMA	120	LiOAc (2)	48
12	Br	DMA	120	Li ₂ CO ₃ (2)	23 ^c
13	Br	DMA	120	CS ₂ CO ₃ (2)	47 ^c
14	Br	DMA	120	Ag ₂ CO ₃ (2)	
15	Br	DMA	70	K ₂ CO ₃ (2)	23
16	Br	DMA	rt	K ₂ CO ₃ (2)	
17	I	DMA	120	K ₂ CO ₃ (2)	60
18	I	DMA	70	K ₂ CO ₃ (2)	30 ^c
19 ^d	I	CH ₃ CN	80	NET ₃ (2)	
20	I	DMF	rt	KOH (2)	52
21	I	DMA	rt	KOH (2)	28
22	Br	DMA	rt	KOH (2)	41
23 ^d	I	DMA	rt	K ₂ CO ₃ (2)	
24 ^d	I	Toluene	80	DMAP (2)	
25	Cl	DMA	120	K ₂ CO ₃ (2)	21 ^c
26	OTf	DMA	120	K ₂ CO ₃ (2)	52

^a All reactions were carried out using 1,1-dimethylallene (**2a**) (2.00 mmol), *p*-CH₃COC₆H₄X (1.00 mmol, X = Br, I, Cl or OTf), Pd(dba)₂ (0.0500 mmol), PPh₃ (0.0500 mmol), base (2.00 mmol), and solvent (1.0 mL) at 120 °C, 12 h. ^b Isolated yield. ^c Yields determined by ¹H NMR. ^d 24 h.

In addition to the Pd(dba)₂/PPh₃ system, PdCl₂(dppf) and Pd(OAc)₂/PPh₃ are also effective for the diene formation (Table 2, entries 8 and 9–11). Several bases including Na₂CO₃, NaHCO₃, NaOAc, LiOAc, Li₂CO₃, CS₂CO₃, Ag₂CO₃, NET₃ (triethylamine), and DMAP (4-(dimethylamino)pyridine) were tested (Table 3, entries 8–14, 19, and 24). All but Ag₂CO₃, NET₃, and DMAP show certain activities. Among the bases used, K₂CO₃ gives the highest yield of diene **3a**. It is interesting to note that Ag₂CO₃, which did not give the expected diene under the present reaction conditions, was used by Grigg and co-workers in the in situ generation of diene from allenenes and aryl iodides for Diels–Alder reaction.⁷ It is not clear why we were unable to isolate the diene product under the reaction conditions. A possible reason is that the diene produced is further transformed into unknown products under the reaction conditions. The activity of strong base, KOH, was also tested. Although this base gives a poor yield of diene **3a** at temperatures above 100 °C, it shows substantial activity for the reaction of *p*-iodoacetophenone (**1n**) and *p*-bromoacetophenone (**1a**) with **2a** at room temperature (Table 3, entries 20–22). At this temperature, K₂CO₃ exhibits no activity toward the diene formation reaction.

Proposed Mechanism. Based on the known palladium chemistry and our observations during these present studies, we propose a catalytic cycle shown in Scheme 3 to account for the present catalytic diene formation reaction (eq 1). The initial step likely involves oxidative addition of aryl halide to palladium(0) to give an arylpalladium(II) species. Coordination of allene followed by insertion of the coordinated allene into the Pd–aryl bond affords a π -allylpalladium species. Deprotonation at the α -carbon of the π -allylpalladium intermediate by a base produces the final diene product and regenerates the palladium(0) species. Oxidative addition of



organic halide to palladium(0) species¹² and insertion of allene to palladium(II)–aryl bond to give a π -allylpalladium species^{5a,13} were demonstrated in many palladium-mediated reactions. Deprotonation of a substituted π -allylmethyl complex to yield the corresponding 1,3-diene species was also reported previously.¹⁴

Alternatively, the π -allylpalladium species is converted to a Pd- σ -allyl via coordination of an extra ligand.¹⁵ This Pd-allyl species then undergoes β -hydrogen elimination to give the diene product and a palladium–hydride species. Deprotonation of the palladium–hydride with a base regenerates the palladium(0) species. In view of the fact that diene formation depends greatly on the base and the use of a strong base decreases drastically the temperature required for the reaction to proceed (Table 3, entries 20–22), the mechanism via deprotonation pathway appears more favorable than that via β -hydrogen elimination. The former is expected to depend greatly on the base used, and the latter is likely independent of the base.

Conclusion

We have demonstrated that it is possible to design a catalytic reaction based on carbopalladation of allenes, deprotonation of the resulting π -allylpalladium(II) intermediate, and careful selection of suitable reaction conditions to transfer allenes into substituted 1,3-butadienes. A series of new 1,3-butadiene derivatives can thus be synthesized.

Experimental Section

General Methods. All reactions were run under a nitrogen atmosphere, unless otherwise mentioned, in oven-dried glassware. All solvents were dried according to known methods and

distilled prior to use. Pd(PPh₃)₄,¹⁶ PdCl₂(PPh₃)₂,¹⁷ PdCl₂(dppe),¹⁶ PdCl₂(CH₃CN)₂,¹⁶ Pd(dba)₂,¹⁸ 1,1-dimethylallene,¹⁹ 1-methyl-1-phenylallene,²⁰ 1-methyl-3-phenylallene,²¹ cyclohexylallene,²¹ and 3-bromo-5,5-dimethyl-2-cyclohexen-1-one²² were prepared by procedures previously reported. Other reagents were commercially available and used as purchased.

General Procedure for the Synthesis of 1,3-Diene Derivatives from Organic Halides (1) and Allene (2). A 25-mL round-bottom flask containing Pd(dba)₂ (0.0287 g, 0.0500 mmol), PPh₃ (0.0131 g, 0.0500 mmol), organic halide (1.00 mmol), and potassium carbonate (0.282 g, 2.00 mmol) was purged with nitrogen gas several times. To the flask were then added DMA (1 mL) and allene (2.00 mmol). The reaction mixture was heated with stirring at 100 or 120 °C for 12–24 h. The solution changed color from purple red to black in 2 h and maintained at the same color during the reaction. As the reaction approached completion, the black precipitate of palladium metal surrounding the wall of the flask appeared gradually. At the end of the reaction, the solution was filtered through Celite and silica gel using CH₂Cl₂ as eluent. The filtrate was concentrated, and the residue was separated on a silica gel column using hexane and ethyl acetate as eluent to give the desired product **3**.

Compounds **3a–w** were prepared according to this method. Product yields of these reactions are listed in Table 1, while important spectral data of these diene compounds are shown below or listed in the Supporting Information.

1-[4-(2-Methyl-1-methylenallyl)phenyl]-1-ethanone (3a). The reaction mixture was chromatographed using a mixture of ethyl acetate/hexane (1:50) as eluent to yield a light yellow liquid: ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, J = 8.4 Hz, 2 H), 7.35 (d, J = 8.4 Hz, 2 H), 5.35 (s, 1 H), 5.15 (s, 1 H), 5.10 (s, 1 H), 4.79 (s, 1 H), 2.58 (s, 3 H), 1.98 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 197.72 (s), 150.10 (s), 146.51 (s), 143.02 (s), 135.93 (s), 128.77 (d), 128.01 (d), 117.28 (t), 115.01 (t), 26.56 (q), 21.04 (q); IR (neat) 2955, 1684, 1266, 902 cm⁻¹; HRMS calcd for C₁₃H₁₄O 186.1045, found 186.1053.

1-[2-(2-Methyl-1-methylenallyl)phenyl]-1-ethanone (3b). The reaction mixture was chromatographed using a mixture of ethyl acetate/hexane (1:50) as eluent to yield a pale yellow liquid: ¹H NMR (400 MHz, CDCl₃) δ 7.56–7.17 (m, 4 H), 5.41 (s, 1 H), 5.06 (s, 2 H), 4.59 (s, 1 H), 2.38 (s, 3 H), 2.02 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 202.70 (s), 149.81 (s), 143.50 (s), 140.48 (s), 139.98 (s), 130.17 (d), 130.59 (d), 127.78 (d), 127.31 (d), 117.53 (t), 115.64 (t), 29.42 (q), 20.54 (q); IR (neat) 2959, 1689, 1244, 900, 764 cm⁻¹; HRMS calcd for C₁₃H₁₄O 186.1045, found 186.1050.

1-Methyl-3-(2-methyl-1-methylenallyl)benzene (3d). The reaction mixture was chromatographed using hexane as eluent to yield a light yellow liquid: ¹H NMR (400 MHz, CDCl₃) δ 7.20 (m, 1 H), 7.12–7.06 (m, 3 H), 5.28 (d, J = 1.6 Hz, 1 H), 5.11 (d, J = 1.6 Hz, 1 H), 5.09 (d, J = 1.6 Hz, 1 H), 4.87 (d, J = 1.6 Hz, 1 H), 2.34 (s, 3 H), 1.99 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 151.14 (s), 143.69 (s), 141.49 (s), 137.39 (s), 129.27 (d), 127.85 (d), 127.74 (d), 125.68 (d), 116.86 (t), 113.71 (t), 21.38 (q), 21.17 (q); IR (neat) 2944, 1591, 887 cm⁻¹; HRMS calcd for C₁₂H₁₄ 158.1096, found 158.1096.

1-Chloro-4-(2-methyl-1-methylenallyl)benzene (3e). The reaction mixture was chromatographed using hexane as eluent to yield a colorless liquid: ¹H NMR (400 MHz, CDCl₃) δ 7.28 (d, J = 8.6 Hz, 2 H), 7.20 (d, J = 8.6 Hz, 2 H), 5.30 (s,

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1 H), 5.11 (s, 2 H), 4.82 (s, 1 H), 1.98 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.94 (s), 143.34 (s), 139.97 (s), 133.02 (s), 129.90 (d), 128.06 (d), 117.08 (t), 114.33 (t), 21.07 (q); IR (neat) 2889, 1488, 1093, 831 cm^{-1} ; HRMS calcd for $\text{C}_{11}\text{H}_{11}\text{Cl}$ 178.0550, found 178.0558.

1,4-Di-(2-methyl-1-methyleneallyl)benzene (3m). The reaction mixture was chromatographed using hexane eluent to yield a colorless liquid: ^1H NMR (400 MHz, CDCl_3) δ 7.29 (s, 4 H), 5.34 (d, $J = 1.2$ Hz, 2 H), 5.20 (d, $J = 1.2$ Hz, 2 H), 5.15 (d, $J = 1.2$ Hz, 2 H), 4.96 (d, $J = 1.2$ Hz, 2 H), 2.04 (s, 6 H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.83 (s), 143.65 (s), 140.33 (s), 128.09 (d), 116.86 (t), 113.73 (t), 21.24 (q); IR (neat) 3092, 2951, 1591, 899 cm^{-1} ; HRMS calcd for $\text{C}_{16}\text{H}_{18}$ 210.1409, found 210.1404.

1-(3-Methyl-1,2-dimethylene-3-butenyl)benzene (3n). The reaction mixture was chromatographed using hexane as eluent to yield a pale yellow liquid: ^1H NMR (400 MHz, CDCl_3) δ 7.43–7.20 (m, 5 H), 5.50 (d, $J = 1.4$ Hz, 1 H), 5.37 (d, $J = 1.4$ Hz, 1 H), 5.25 (d, $J = 1.4$ Hz, 1 H), 5.20 (d, $J = 1.4$ Hz, 1 H), 4.98 (s, 1 H), 4.93 (s, 1 H), 1.96 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.57 (s), 149.63 (s), 141.91 (s), 140.27 (s), 128.17 (d), 127.46 (d), 126.41 (d), 117.01 (t), 115.21 (t), 114.52 (t), 20.64 (q); IR (neat) 2925, 1662, 1042, 702 cm^{-1} ; HRMS calcd for $\text{C}_{13}\text{H}_{14}$ 170.1096, found 170.1084.

5,5-Dimethyl-3-(2-methyl-1-methyleneallyl)-2-cyclohexen-1-one (3o). The reaction mixture was chromatographed using a mixture of ethyl acetate/hexane (1:50) as eluent to yield a yellow liquid: ^1H NMR (400 MHz, CDCl_3) δ 5.98 (s, 1 H), 5.20 (s, 1 H), 5.16 (s, 1H), 5.04 (s, 1 H), 4.88 (s, 1 H), 2.33 (s, 2 H), 2.24 (s, 2 H), 1.86 (s, 3 H), 1.04 (s, 3 H), 1.02 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.34 (s), 158.90 (s), 151.12 (s), 142.14 (s), 126.37 (d), 116.19 (t), 114.72 (t), 51.10 (t), 42.60 (t), 33.75 (s), 28.23 (q), 21.62 (q); IR (neat) 2949, 1686, 1370, 906 cm^{-1} ; HRMS calcd for $\text{C}_{13}\text{H}_{18}\text{O}$ 190.1358, found 190.1358.

1-[4-(1-Isopropenyl-2-methyl-1-propenyl)phenyl]-1-ethanone (3p). The reaction mixture was chromatographed using a mixture of ethyl acetate/hexane (1:50) as eluent to yield a light yellow liquid: ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, $J = 8.4$ Hz, 2 H), 7.25 (d, $J = 8.4$ Hz, 2 H), 5.06 (d, $J = 2.6$ Hz, 1 H), 4.86 (d, $J = 2.6$ Hz, 1 H), 2.57 (s, 3 H), 1.86 (s, 3 H), 1.63 (s, 3 H), 1.61 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.74 (s), 146.64 (s), 145.42 (s), 138.17 (s), 135.09 (s), 130.03 (s), 129.43 (d), 127.97 (d), 115.01 (t), 26.48 (q), 22.59 (q), 22.09 (q), 21.66 (q); IR (neat) 3077, 2919, 1683, 1268, 834, 600 cm^{-1} ; HRMS calcd for $\text{C}_{15}\text{H}_{18}\text{O}$ 214.1358, found 214.1365.

1-[4-(1-Methylene-2-phenylallyl)phenyl]-1-ethanone (3s). The reaction mixture was chromatographed using a mixture of ethyl acetate/hexane (1:50) as eluent to yield a yellow liquid: ^1H NMR (400 MHz, CDCl_3) δ 7.84 (d, $J = 8.4$ Hz, 2 H), 7.46 (d, $J = 8.4$ Hz, 2 H), 7.39–7.34 (m, 2 H), 7.29–7.21 (m, 3 H), 5.64 (d, $J = 1.2$ Hz, 1 H), 5.58 (d, $J = 1.2$ Hz, 1 H), 5.44 (d, $J = 1.2$ Hz, 1 H), 5.34 (d, $J = 1.2$ Hz, 1 H), 2.54 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.54 (s), 149.13 (s), 148.88 (s), 144.69 (s), 139.54 (s), 135.97 (s), 128.28 (d), 128.21 (d), 127.65 (d), 127.52 (d), 127.28 (d), 118.01 (t), 116.65 (t), 26.48 (q); IR (neat) 3055, 1682, 1266, 847 cm^{-1} ; HRMS calcd for $\text{C}_{18}\text{H}_{16}\text{O}$ 248.1202, found 248.1205.

5,5-Dimethyl-3-[1-(E)-1-phenylmethylidene]allyl]-2-cyclohexen-1-one (3t). The reaction mixture was chromatographed using a mixture of ethyl acetate/hexane (1:50) as eluent to yield a yellow liquid: ^1H NMR (400 MHz, CDCl_3) δ 7.34–7.32 (m, 5 H), 6.69–6.63 (m, 1 H), 6.61, (s, 1 H), 6.17 (t, $J = 1.6$ Hz, 1 H), 5.40–5.36 (m, 1 H), 5.29–5.23 (m, 1 H), 2.44 (d, $J = 1.6$ Hz, 2 H), 2.29 (s, 2 H), 1.09 (s, 6 H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.12 (s), 160.19 (s), 140.48 (s), 136.14 (s), 132.56 (d), 130.39 (d), 129.81 (d), 128.19 (d), 127.80 (d), 127.01 (d), 120.18 (t), 51.24 (t), 42.97 (t), 33.93 (s), 28.22 (q); IR (neat) 2949, 1685, 1278, 700 cm^{-1} ; HRMS calcd for $\text{C}_{18}\text{H}_{20}\text{O}$ 252.1515, found 252.1521.

5,5-Dimethyl-3-[1-(Z)-1-phenylmethylidene]allyl]-2-cyclohexen-1-one (3u). The reaction mixture was chromatographed using 1:50 a mixture of ethyl acetate/hexane (1:50) as eluent to yield a yellow liquid: ^1H NMR (400 MHz, CDCl_3) δ 7.35–7.17 (m, 5 H), 6.51–6.42 (m, 2 H), 6.05 (t, $J = 2$ Hz, 1 H), 5.20–5.13 (m, 2 H), 2.28 (s, 2 H), 2.19 (d, $J = 2$ Hz, 2 H), 1.00 (s, 6 H); ^{13}C NMR (100 MHz, CDCl_3) δ 199.27 (s), 158.19 (s), 140.13 (s), 138.51 (d), 135.90 (s), 130.60 (d), 129.72 (d), 128.72 (d), 128.37 (d), 127.74 (d), 115.46 (t), 51.01 (t), 42.98 (t), 33.41 (s), 28.48 (q); IR (neat) 2944, 1667, 756 cm^{-1} ; HRMS calcd for $\text{C}_{18}\text{H}_{20}\text{O}$ 252.1515, found 252.1521.

1-[4-[1-(Cyclohexylidene)methyl]vinyl]phenyl]-1-ethanone (3v). The reaction mixture was chromatographed using a mixture of ethyl acetate/hexane (1:100) as eluent to yield a light yellow liquid: ^1H NMR (400 MHz, CDCl_3) δ 7.89 (d, $J = 8.4$ Hz, 2 H), 7.49 (d, $J = 8.4$ Hz, 2 H), 5.87 (s, 1 H), 5.56 (s, 1 H), 5.15 (s, 1H), 2.58 (s, 3 H), 2.23 (t, $J = 5.6$ Hz, 2 H), 2.14 (t, $J = 5.6$ Hz, 2 H), 1.68–1.51 (m, 4 H), 1.50–1.40 (m, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.65 (s), 146.07 (s), 145.55 (s), 144.11 (s), 135.93 (s), 128.50 (d), 126.62 (d), 121.01 (d), 116.14 (t), 37.44 (t), 30.03 (t), 28.69 (t), 27.86 (t), 26.58 (q), 26.55 (t); IR (neat) 2943, 1684 cm^{-1} ; HRMS calcd for $\text{C}_{17}\text{H}_{20}\text{O}$ 240.1515, found 240.1512.

1-[4-(E)-2-(1-cyclohexenyl)-1-methyl-1-ethenyl]phenyl]-1-ethanone (3w). The reaction mixture was chromatographed using a mixture of ethyl acetate/hexane (1:100) as eluent to yield a light yellow liquid: ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, $J = 8$ Hz, 2 H), 7.46 (d, $J = 8$ Hz, 2 H), 6.23 (s, 1 H), 5.74 (s, 1 H), 2.56 (s, 3 H), 2.21–2.13 (m, 7 H), 1.71–1.56 (m, 4 H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.56 (s), 149.32 (s), 135.42 (s), 135.17 (s), 133.00 (s), 132.73 (d), 128.63 (d), 128.30 (d), 125.79 (d), 29.16 (t), 26.46 (q), 25.68 (t), 22.86 (t), 22.04 (t), 17.34 (q); IR (neat) 2933, 1681, 1268, 738 cm^{-1} ; HRMS calcd for $\text{C}_{17}\text{H}_{20}\text{O}$ 240.1515, found 240.1512.

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Supporting Information Available: ^1H NMR spectra of compounds **3a–w** and spectral data for compounds **3c,f–1,q–r**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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