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Palladium-Catalyzed Isomerization of Methylenecyclopropanes in Acetic Acid

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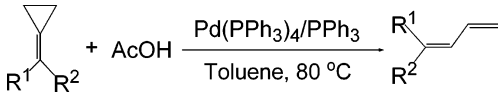

$Pd(PPh_3)_4$-catalyzed isomerization of MCPs **1** in acetic acid proceeds smoothly at 80 °C in toluene to give the corresponding 1-substituted or 1,1-disubstituted dienes **2** in good to excellent yields under mild conditions. The plausible mechanism has been disclosed on the basis of a deuterium-labeling experiment.

Introduction

Methylenecyclopropanes (MCPs) **1** are highly strained but readily accessible molecules that have served as useful building blocks in organic synthesis. MCPs **1** undergo a variety of ring-opening reactions because the relief of ring strain provides a potent thermodynamic driving force.[1] Transition metal (such as Pd, Rh, Ru, and Pt) catalyzed reactions of MCPs **1** with various reactants have attracted much attention.[2,3] In the field of Lewis acid-catalyzed ring-opening reactions of MCPs **1**, we have found that the ring of MCPs **1** can be opened by alcohols and other nucleophiles in a different, novel manner to give the corresponding homoallylic derivatives in good yields under mild conditions.[4] Previously it has been reported that platinum complex-catalyzed hydrosilylation and isomerization of 2,2-diphenyl-1-methylenecyclopropane produced the silyl compound with (2,2-diphenylcyclopropyl)methyl substituent and 1,1-diphenyl-1,3-butadiene in moderate to good yield.[5b] In this paper, we wish to report the palladium-catalyzed isomerization of a variety of MCPs **1** in acetic acid to give the corresponding 1-substituted or 1,1-disubstituted dienes **2** in good yields as a sole product.[5]

Results and Discussion

The isomerization of diphenylmethylenecyclopropane **1a** (64 mg, 0.4 mmol) was first carried out in acetic acid (48 mg, 0.8 mmol) with $Pd(PPh_3)_4$ (46 mg, 0.04 mmol) and PPh_3 (42 mg, 0.16 mmol) at 80 °C in a variety of solvents. The results are summarized in Table 1. As can be seen from Table 1, the corresponding 1,1-disubstituted diene **2a** was obtained in good to high yields in most cases (Table 1, entries 1−5). In toluene, this reaction proceeded smoothly to give **2a** in 96% within 3 h (Table 1, entry 5).

The use of 0.8 mmol of acetic acid (AcOH) in this reaction is essential to produce **2a** in high yield, because

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(1) Synthesis of MCPs: (a) Brandi, A.; Goti, A. *Chem. Rev.* **1998**, *98*, 589. (b) *Carbocyclic Three-Membered Ring Compounds* (*Houben-Weyl);* de Meijere, A., Ed.; Thieme: Stuttgart, 1996; Vol. E 17a−c. (c) For a recent review, see: Nakamura, I.; Yamamoto, Y. *Adv. Synth. Catal.* **2002**, *344*, 111.

(2) For the ring-opening of MCPs by type I (ref 4c), please see: (a) Camacho, D. H.; Nakamura, I.; Saito, S.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **1999**, *38*, 3365. (b) Camacho, D. H.; Nakamura, I.; Saito, S.; Yamamoto, Y. *J. Org. Chem*. **2001**, *66*, 270. (c) Nakamura, I.; Itagaki, H.; Yamamoto, Y. *J. Org. Chem.* **1998**, *63*, 6458. (d) Nüske, H.; Notlemeyer, M.; de Meijere, A. *Angew. Chem., Int. Ed*. **2001**, *40*, 3411. (e) Bräse, S.; de Meijere, A. *Angew. Chem., Int. Ed. Engl*. **1995**, *34*, 2545. (f) Tsukada, N.; Shibuya, A.; Nakamura, I.; Yamamoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 8123. (g) Inoue, Y.; Hibi, T.; Sataka, H.; Hashimoto, H. *Chem. Commun*. **1979**, 982. (h) Binger, P.; Germer, A. *Chem. Ber*. **1981**, *114*, 3325. (i) Nakamura, I.; Oh, B. H.; Saito, S.; Yamamoto, Y. *Angew. Chem., Int., Ed.*. **2001**, *40*, 1298. (j) Oh, B. H.; Nakamura, I.; Saito, S.; Yamamoto, Y. *Tetrahedron Lett.* **2001**, *42*, 6203. For a review of palladium in action: domino coupling and allylic substitution reactions for the efficient construction of complex organic molecules. See: (k) de Meijere, A.; Brase, S. *J. Organomet. Chem.* **1999**, *576*, 88. For the ring-opening of MCPs by type II or III (ref 4c), please see: (k) Bessmertnykh, A. G.; Blinov, K. A.; Grishin, Y. K.; Donskaya, N. A.; Tveritinova, E. V.; Yur'eva, N. M.; Beletskaya, I. P. *J. Org. Chem*. **1997**, *62*, 6069. (l) Lautens, M.; Meyer, C.; Lorenz, A. *J. Am. Chem. Soc*. **1996**, *118*, 10676. (m) Ishiyama, T.; Momota, S.; Miyaura, N. *Synlett*. **1999**, 1790. (n) Suginome, M.; Matsuda, T.; Ito, Y. *J. Am. Chem. Soc*. **2000**, *122*, 11015. (o) Chatani, N.; Takaya, H.; Hanafusa, T. *Tetrahedron Lett*. **1988**, *29*, 3979. (p) For the metal-catalyzed cocyclizations, reactions of MCPs with unsaturated carbon bonds had been extensively studied; please see the review: Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49. (q) Ohta, T.; Takaya, H. In *Comprehensive Organic Chemistry*; Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon Press: Oxford, 1991; Vol 5, p 1185. (r) Binger, P.; Schmidt, T. In *Methods of Organic Chemistry (Houben-Weyl)*; de Meijere, A., Ed.; Thieme: Stuttgart, 1997; Vol. E 17c, p 2217. (s) Binger, P.; Buch, H. M. *Top. Curr. Chem.* **1987**, *135*, 77.

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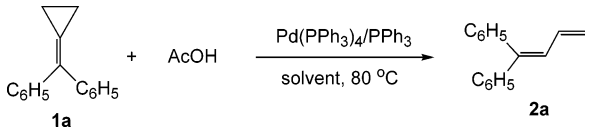
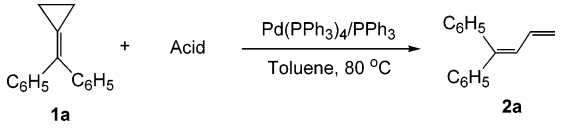
TABLE 1. Palladium-Catalyzed Isomerization of MCP 1a in a Variety of Solvents in the Presence of Acetic Acid



entry	solvent	time/h	% yield of **2a**[a]
1	dioxane	9	87
2	DCE	50	60
3	THF	12	84
4	MeCN	60	70
5	MeC_6H_5	3	96

[a] Isolated yields; **1a** (64 mg, 0.4 mmol), AcOH (48 mg, 0.8 mmol), $Pd(PPh_3)_4$ (46 mg, 0.04 mmol), PPh_3 (42 mg, 0.16 mmol).

TABLE 2. Palladium-Catalyzed Isomerization of MCP 1a in the Presence of Various Acids

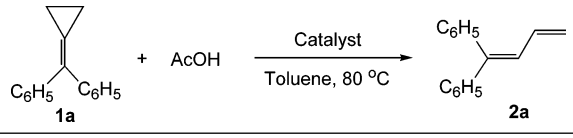


entry	acid (mmol)	$Pd(PPh_3)_4$/ mmol	time/h	% yield of **2a**[a]
1	AcOH (0.8)	0.04	3	96
2	AcOH (0.4)	0.04	3	87
3	AcOH (0.04)	0.04	24	40[b]
4	AcOH (0.8)	0.01	30	60
5	AcOH (0)	0.04	60	NR
6	*p*-$CH_3C_6H_4SO_3H$ (0.4)	0.04	50	30
7	F_3CSO_3H (0.4)	0.04	5	0
8	F_3CCO_2H (0.4)	0.04	12	NR

[a] Isolated yields; **1a** (64 mg, 0.4 mmol), $Pd(PPh_3)_4$ (46 mg, 0.04 mmol), PPh_3 (42 mg, 0.16 mmol). NR = no reaction. [b] MCP **1a** was recovered in 50% yield.

no reaction occurred in the absence of acetic acid; moreover, this reaction was sluggish in the presence of 0.04 mmol of AcOH (Table 2, entries 1−3 and 5). With 0.01 mmol of $Pd(PPh_3)_4$ and 0.8 mmol of acetic acid, this reaction was also sluggish (Table 2, entry 4). Brønsted acid TsOH is not as effective as AcOH under identical conditions (Table 2, entry 6). Other Brønsted acids, such as TfOH (CF_3SO_3H) and CF_3CO_2H did not catalyze this reaction (Table 2, entries 7 and 8).

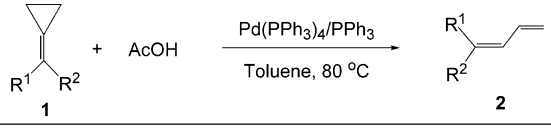
TABLE 3. Isomerization of MCP 1a with a Variety of Catalysts in the Presence of Acetic Acid

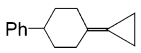


entry	catalyst	time/h	% yield of **2a**[a]
1	$Pd(PPh_3)_4$	3	96
2	$Pd(OAc)_2$	30	60[b]
3	$Pd(PPh_3)_2Cl_2$	18	NR
4	$Pd(dba)_2$	30	NR
5	$NiCl_2$(dppe)	50	NR
6	$Rh_6(CO)_{16}$	24	NR
7	$Ru_3(CO)_{12}$	24	NR

[a] Isolated yields; **1a** (64 mg, 0.4 mmol), AcOH (48 mg, 0.8 mmol), catalyst (0.04 mmol). NR = no reaction. [b] PPh_3 (42 mg, 0.16 mmol) was added.

TABLE 4. Palladium-Catalyzed Isomerization of a Variety of MCPs 1 (0.4 mmol) in Toluene in the Presence of Acetic Acid



entry	R^1	R^2		time/h	yield/[%][a] **2**
1	C_6H_5	C_6H_5	**1a**	3	**2a**, 96
2	*p*-FC_6H_4	*p*-FC_6H_4	**1b**	4	**2b**, 97
3	*p*-ClC_6H_4	*p*-ClC_6H_4	**1c**	5	**2c**, 90
4	*p*-MeC_6H_4	*p*-MeC_6H_4	**1d**	5	**2d**, 98
5	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	**1e**	5	**2e**, 77
6	Bu	Bu	**1f**	5	**2f**, 90
7	H	*p*-$MeOC_6H_4$	**1g**	5	**2g**, 86[b]
8	C_6H_5 (*o*-ClC_6H_4)	*o*-ClC_6H_4 (C_6H_5)	**1h**	5	**2h**, 89[c]
9			**1i**	5	**2i**, 98

[a] Isolated yields; AcOH (48 mg, 0.8 mmol), $Pd(PPh_3)_4$ (46 mg, 0.04 mmol), PPh_3 (42 mg, 0.16 mmol). [b] *E*-configuration. [c] Whether it is *E*- or *Z*-configuration cannot be determined.

On the other hand, only $Pd(PPh_3)_4$ catalyst can effectively catalyze this isomerization in acetic acid. Other transition metal catalysts such as $Pd(dba)_2$, $Pd(PPh_3)_2Cl_2$, $NiCl_2$(dppe), $Rh_6(CO)_{16}$, and $Ru_3(CO)_{12}$ did not catalyze this reaction under identical conditions (Table 3, entries 3−7). $Pd(OAc)_2$ is not as effective as $Pd(PPh_3)_4$ (Table 3, entries 1 and 2).

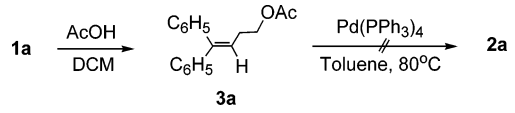
Under the optimized conditions, we next examined a variety of MCPs **1** (0.4 mmol) in this transformation. The results are summarized in Table 4 combined with result of MCP **1a**. The corresponding 1-substituted or 1,1-disubstituted dienes **2b-i** were obtained in good to high yields within 3−5 h for many types of MCPs **1** (Table 4, entries 2−9). It should be emphasized here that unsymmetrical MCPs **1g** and **1h** rearrange to the corresponding dienes **2g**,**h** with complete control of stereochemistry (**1g** as *E*-configuration and **1h** as *E*- or *Z*-configuration; see the ^1H and ^{13}C NMR spectra in the Supporting Informa-

(3) For some more recent papers related to MCPs, please see: (a) Nötzel, M. W.; Rauch, K.; Labahn, T.; de Meijere, A. *Org. Lett.* **2002**, *4*, 839. (b) Takauchi, D.; Dsakada, K. *Chem. Commun.* **2002**, 646. (c) de Meijere, A.; Leonov, A.; Heiner, T.; Noltemeyer, M.; Bes, M. T. *Eur. J. Org. Chem.* **2003**, 472. (d) Belov, V. N.; Savchenko, A. I.; Sokolov, V. V.; Straub, A.; de Meijere, A. *Eur. J. Org. Chem.* **2003**, 551. (e) de Meijere, A.; Kuchuk, I. D.; Sokolov, V. V.; Labahn, T.; Rauch, K.; Es−Sayed, M.; Krämer, T. *Eur. J. Org. Chem.* **2003**, 985. (f) Siriwardana, A. I.; Nakamura, I.; Yamamoto, Y. *Tetrahedron Lett.* **2003**, *44*, 4547. (g) Shi, M.; Shao, L.-X.; Xu, B. *Org. Lett.* **2003**, *5*, 579. (h) Shao, L.-X.; Shi, M. *Adv. Synth. Catal.* **2003**, *345*, 963. (i) Brandi, A.; Cicchi, S.; Cordero, F. M.; Goti, A. *Chem. Rev*. **2003**, *103*, 1213.

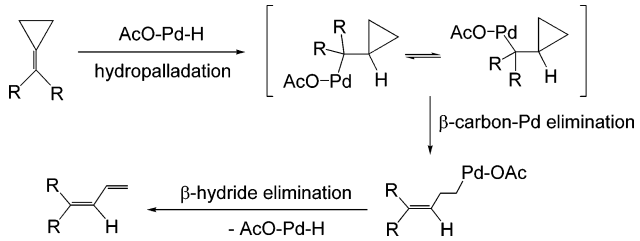
(4) (a) Shi, M.; Xu, B. *Org. Lett.* **2002**, *4*, 2145. (b) Shi, M.; Chen, Y.; Xu, B. Tang, J. *Tetrahedron Lett.* **2002**, *43*, 8019. (c) Xu, B.; Shi, M. *Org. Lett.* **2003**, 5, 1415. (d) Huang, J.-W.; Shi, M. *Synlett* **2004**, 2343. (e) Nakamura, I.; Kamada, M.; Yamamoto, Y. *Tetrahedron Lett.* **2004**, *45*, 2903.

(5) For the preparation of 1-substituted or 1,1-disubstituted dienes. See: (a) Wang, K.-T.; Hung, Y.-Y. *Tetrahedron Lett*. **2003**, *44*, 8033 and references therein. (b) Itazaki, M.; Nishihara, Y.; Osakada, K. *J. Org. Chem.* **2002**, *67*, 6889. (c) Mashima, K.; Sakai, N.; Takaya, H. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2475. (d) Nakamura, I.; Siriwardana, A.; Saito, S.; Yamamoto, Y. *J. Org. Chem*. **2002**, *67*, 3445. (e) Bessmertnykh, A. G.; Blinov, K. A.; Grishin, Y. K.; Donskaya, N. A.; Tveritinova, E. V.; Beletskaya, I. P. *Russ. J. Org. Chem.* **1998**, *34*, 799.

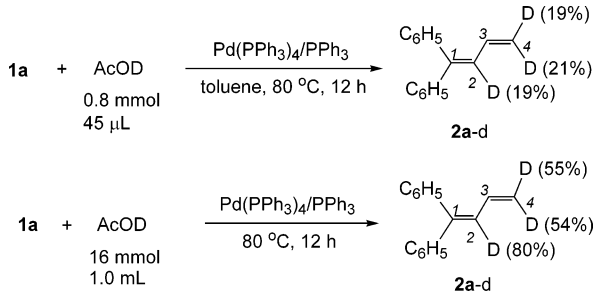
SCHEME 1. Control Experiment



SCHEME 2. A Plausible Mechanism



SCHEME 3. Reaction of MCP 1a (64 mg, 0.4 mmol) in AcOD



tion) (Table 4, entries 8 and 9). Their structures are determined by spectroscopic data, microanalyses, and HRMS.

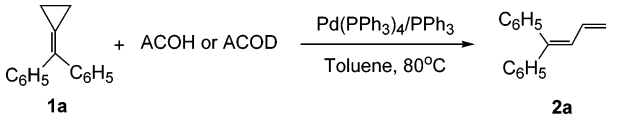
The control experiment indicated that **2a** is not derived from the β-hydride elimination of **3a**, a Brønsted acid AcOH-catalyzed ring-opened product of **1a**, in the presence of Pd(0) catalyst (Scheme 1).[4a]

The mechanism of this effective Pd(0)-catalyzed transformation of MCPs **1** has not been unequivocally established, but one plausible explanation is proposed in Scheme 2 on the basis of the previous investigations.[1c,2k,5b] To clarify the mechanism of this isomerization, the reaction of **1a** (0.4 mmol) in deuterated acetic acid, AcOD (D content 99%), was carried out under identical conditions (Scheme 3). The preliminary isotopic effect has been observed ($k_H/k_D \approx 8.4$ at initial stage) and the results are summarized in Table 5 (entries 1−5) (Figure SI-1 in the Supporting Information). This result suggests that the ring-opening isomerization directly involves with the proton of acetic acid, as shown in Scheme 2.

On the basis of ^{1}H NMR spectroscopic data, we confirmed that, besides the olefinic proton at C_2 (D content 19%), deuterium incorporation also occurred at the olefinic protons of C_4 in 0.8 mmol (45 μL) of AcOD (D content 19% and 21%, respectively) in the isomerization of **1a** (0.4 mmol) for 12 h (Figures SI-2 and SI-3 in the Supporting Information). In 1.0 mL of AcOD, deuterium incorporation occurred at the olefinic proton of C_2 (D content 80%) and at the olefinic protons of C_4 (D content 55% and 54%, respectively) for 12 h (Figure SI-4 in the Supporting Information) (Scheme 3).[6] During a prolonged reaction time (2 days), the D contents at C_2 and C_4 of **2a** did not change in each case. This result suggests that no additional H/D exchange occurs at longer times. In addition, the control experiment confirmed that deuterium incorporation at the olefinic protons of C_4 is derived from the scrambling of **2a** (0.2 mmol) with AcOD catalyzed by Pd(0) catalyst (Scheme 4, Figures SI-5 and SI-6, and control experiment in Figure SI-7) via a Pd(0)-catalyzed AcOD addition and elimination process. It should be noted that, with AcOD (0.4 mmol or 1.0 mL), upon scrambling of **2a** (0.2 mmol) catalyzed by Pd(0) catalyst via a Pd(0)-catalyzed AcOD addition and elimination process, deuterium incorporation occurred only at the olefinic protons of C_4 (Scheme 4 and Figures SI-5 and SI-6 in Supporting Information) rather than at C_2. Therefore, the incorporation of D at C_2 in Scheme 3 points toward an intermolecular source of H/D during the isomerization of **1a**, namely derived from the addition of AcO−Pd−D to **1a** rather than the H/D scrambling of **2a** (0.2 mmol) catalyzed by Pd(0) catalyst.

The increase in D at C_2 when a large excess of AcOD is used presumably reflects the fact that there is more D available to compete with the H eliminated as the reaction proceeds. Therefore, the D content of 19% at C_2 in 0.8 mmol of AcOD is due to the generation of AcO−Pd−H species during the reaction, which can initiate the same isomerization in a kinetically favored way to give the normal diene **2a** even in AcOD (Scheme 2),[7] and minor quantities of AcOH (around 1% according to the 99% D content of AcOD) present in the deuterated AcOD, in addition to its higher reactivity (k_H/k_D between 8 and 9 at initial stage), can also be responsible for the low D% at C_2. Moreover, the H coming from the D scrambling of olefinic protons at C_4 can also be contributing to the

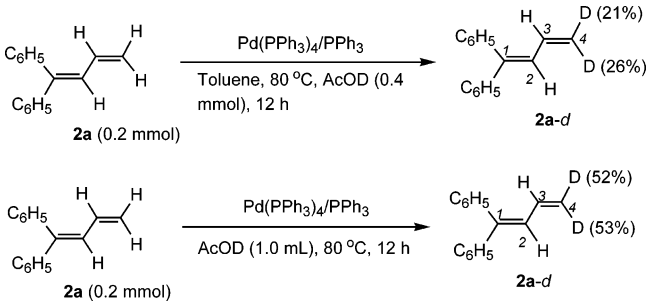
TABLE 5. Palladium-Catalyzed Isomerization of MCP 1a (0.4 mmol) in the Presence of AcOH or AcOD vs Reaction Time[a]



		2a/mol %	
entry	time/min	with AcOH	with AcOD
1	0	0	0
2	10	1.375	0.415
3	45	8.33	1.062
4	60	19.289	1.628
5	120	77.011	38.102

[a] Acid (48 mg, 0.8 mmol), $Pd(PPh_3)_4$ (46 mg, 0.04 mmol), PPh_3 (42 mg, 0.16 mmol).

SCHEME 4. Deuterium Scrambling at Olefinic Protons of C_4



(6) The D content is also corroborated by mass spectrometry (see the Supporting Information).

formation of AcOH in the 1.0 mL of AcOD, which can then produce the normal diene **2a**. These results also indicate that this reaction indeed proceeds through a β-hydride elimination, as shown in Scheme 2.

Overall, the initial step of this reaction should indeed proceed through the hydropalladation of the olefinic moiety of **1** via the hydridopalladium species as shown in Scheme 2.[7]

With this reaction mechanism (Scheme 2), it is conceivable that the β-carbon−Pd elimination takes place to give a thermodynamically stable intermediate. This is why for unsymmetrical MCPs **1**, the dienes **2** are formed exclusively with complete control of stereochemistry.

Conclusion

We disclosed an effective $Pd(PPh_3)_4$-catalyzed isomerization of MCPs **1** in acetic acid to give the corresponding 1-substituted or 1,1-disubstituted dienes **2** under mild conditions. These reactions completed at 80 °C in toluene within 3−5 h to give the dienes **2** in good to excellent yields. On the basis of a deuterium labeling experiment, we found that this reaction process is involved with the hydropalladation of the olefinic moiety of **1** by AcO−Pd−H, as shown in Scheme 2. Efforts are underway to elucidate the mechanistic details of this reaction and to disclose its scope and limitations. Work along this line is currently in progress.

Experimental Section

General Procedure for the Palladium-Catalyzed Isomerization of MCPs 1 in the Presence of Acetic Acid. A mixture of MCP **1** (0.4 mmol), $Pd(PPh_3)_4$ (0.04 mmol), AcOH (0.8 mmol), and toluene (2.0 mL) was stirred for 5 h at 80 °C. The solvent was removed under reduced pressure and the residue was purified by a silica gel column chromatography using petroleum ether as eluent to give the product.

1,1-Diphenyl-1,3-butadiene (2a). This compound was obtained as a colorless liquid (79 mg, 96%). This is a known compound and its ^{1}H NMR spectroscopic data are consistent with those reported (see: Itazaki, M.; Nishihara, Y.; Osakada, K. *J. Org. Chem.* **2002**, *67*, 6889−6895). IR (KBr): ν = 700, 731, 765, 775, 904, 996, 1030, 1069, 1349, 1445, 1494, 1590, 1608, 2852, 2925, 3026, 3056, 3080 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 5.13 (dd, J = 2.4, 10.2 Hz, 1H, CH_2), 5.40 (dd, J = 1.5, 16.5 Hz, 1H, CH_2), 6.44 (ddd, J = 16.5, 10.2, 10.8 Hz, 1H, CH), 6.70 (d, J = 10.8 Hz, 1H, CH), 7.24−7.41 (m, 10H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 118.6, 127.3, 127.45, 127.54, 128.1, 128.2, 128.5, 130.4, 134.9, 139.6, 142.0, 143.1. MS (EI) *m/z*: 77 [(M − 129)$^+$, 9.36], 91 [(M − 115)$^+$, 29.83], 128 [(M − 78)$^+$, 24.99], 165 [(M − 41)$^+$, 14.08], 178 [(M − 28)$^+$, 10.64], 191 [(M − 15)$^+$, 25.80], 206 (M$^+$, 100). HRMS (MALDI): calcd for $C_{16}H_{15}$ (M$^+$ + 1) requires 207.1168, found 207.1175.

1,1-Bis(4-fluorophenyl)-1,3-butadiene (2b). This compound was obtained as a colorless liquid (94 mg, 97%). IR (KBr): ν = 539, 584, 733, 801, 836, 910, 997, 1014, 1096, 1158, 1232, 1347, 1422, 1508, 1602, 2853, 2924, 3044 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 5.15 (dd, J = 1.8, 10.2 Hz, 1H, CH_2), 5.40 (dd, J = 2.1, 17.1 Hz, 1H, CH_2), 6.40 (ddd, J = 17.1, 11.4, 10.2 Hz, 1H, CH), 6.63 (d, J = 11.4 Hz, 1H, CH), 6.92−7.24 (m, 8H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 115.1 (d, J_{C-F} = 21.2 Hz), 115.2 (d, J_{C-F} = 21.2 Hz), 119.0, 128.6 (d, J_{C-F} = 1.5 Hz), 129.1 (d, J_{C-F} = 8.0 Hz), 132.0 (d, J_{C-F} = 8.0 Hz), 134.5, 135.3 (d, J_{C-F} = 3.5 Hz), 138.1(d, J_{C-F} = 3.5 Hz), 140.9, 162.2 (d, J_{C-F} = 245.0 Hz), 162.4 (d, J_{C-F} = 245.0 Hz). MS (EI) *m/z*: 109 [(M − 133)$^+$, 8.51], 146 [(M − 96)$^+$, 7.69], 204 [(M − 38)$^+$, 24.54], 221 [(M − 21)$^+$, 14.45], 227 [(M − 15)$^+$, 15.41], 242 (M$^+$, 100). HRMS (EI): calcd for $C_{16}H_{12}F_2$ requires 242.0907, found 242.0919.

1,1-Bis(4-chlorophenyl)-1,3-butadiene (2c). This compound was obtained as a colorless liquid (99 mg, 90%). IR (KBr): ν = 521, 606, 702, 765, 830, 911, 995, 1014, 1091, 1397, 1419, 1492, 1588, 2844, 2924, 3031, 3074 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 5.18 (m, 1H, CH_2), 5.42 (m, 1H, CH_2), 6.38 (m, 1H, CH), 6.67 (d, J = 10.8 Hz, 1H, CH), 7.11−7.37 (m, 8H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 119.8, 128.4, 128.5, 128.7, 129.2, 131.6, 133.5, 133.6, 134.3, 137.5, 140.1, 140.6. MS (EI) *m/z*: 101 [(M − 173)$^+$, 28.00], 125 [(M − 149)$^+$, 18.42], 163 [(M − 111)$^+$, 6.86], 204 [(M − 70)$^+$, 94.8], 239 [(M − 35)$^+$, 100.00], 274 (M$^+$, 37.88). HRMS (EI): calcd for $C_{16}H_{12}Cl_2$ requires 274.0316, found 274.0301.

1,1-Bis(4-methylphenyl)-1,3-butadiene (2d). This compound was obtained as a colorless liquid (92 mg, 98%). IR (KBr): ν = 540, 588, 611, 882, 901, 997, 1024, 1106, 1180, 1346, 1416, 1446, 1512, 1612, 2855, 2922, 3021, 3082 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.41 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 5.17 (dd, J = 2.4, 10.5 Hz, 1H, CH_2), 5.44 (dd, J = 1.8, 16.5 Hz, 1H, CH_2), 6.56 (ddd, J = 16.5, 10.8, 10.5 Hz, 1H, CH), 6.76 (d, J = 10.8 Hz, 1H, CH), 7.15−7.28 (m, 8H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 21.1, 21.2, 117.7, 127.50, 127.53, 128.80, 128.83, 130.3, 135.1, 136.8, 136.9, 137.2, 139.5, 143.0. MS (EI) *m/z*: 91 [(M − 143)$^+$, 10.02], 105 [(M − 129)$^+$, 21.99], 142 [(M − 92)$^+$, 11.15], 178 [(M − 56)$^+$, 6.76], 204 [(M − 30)$^+$, 27.84], 219 [(M − 15)$^+$, 85.00], 234 (M$^+$, 100.00). HRMS (MALDI): calcd for $C_{18}H_{19}$ (M$^+$ + 1) requires 235.1481, found 235.1480.

1,1-Bis(4-methoxyphenyl)-1,3-butadiene (2e). This compound was obtained as a colorless liquid (82 mg, 77%). IR (KBr): ν = 555, 593, 611, 806, 832, 901, 1035, 1173, 1246, 1286, 1350, 1463, 1511, 1605, 2835, 2931, 2954, 2999, 3037 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 3.78 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 5.06 (dd, J = 1.8, 9.9 Hz, 1H, CH_2), 5.32 (dd, J = 1.8, 16.8 Hz, 1H, CH_2), 6.47 (ddd, J = 16.8, 11.4, 9.9 Hz, 1H, CH), 6.59 (d, J = 11.4 Hz, 1H, CH), 6.80−7.22 (m, 8H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 55.19, 55.21, 113.45, 113.50, 117.2, 126.7, 128.8, 131.6, 132.1, 135.0, 135.2, 142.4, 158.9, 159.2. MS (EI) *m/z*: 84 [(M − 182)$^+$, 13.97], 115 [(M − 151)$^+$, 16.10], 121 [(M − 145)$^+$, 43.23], 178 [(M − 88)$^+$, 12.68], 235 [(M − 31)$^+$, 55.05], 251 [(M − 15)$^+$, 19.92], 266 (M$^+$, 100.00). HRMS (MALDI): calcd for $C_{18}H_{19}O_2$ (M$^+$ + 1) requires 267.1380, found 267.1363.

1,1-Dibutyl-1,3-butadiene (2f). This compound was obtained as a colorless liquid (60 mg, 90%). IR (KBr): ν = 748, 895, 962, 986, 1377, 1463, 2857, 2925, 2956, 3040 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.91 (t, 6H, CH_3), 1.28−1.45 (m, 8H, CH_2), 2.02−2.18 (m, 4H, CH_2), 4.96 (dd, J = 2.1, 10.2 Hz, 1H, CH_2), 5.08 (dd, J = 1.5, 16.5 Hz, 1H, CH_2), 5.84 (d, J = 11.4 Hz, 1H, CH), 6.59 (ddd, J = 16.5, 11.4, 10.2 Hz 1H, CH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 14.01, 14.02, 22.6, 22.8, 29.7, 30.3, 31.0, 36.9, 114.4, 125.2, 133.3, 144.5. MS (EI) *m/z*: 91 [(M − 75)$^+$, 100.0], 115 [(M − 51)$^+$, 32.90], 129 [(M − 37)$^+$, 64.93], 143 [(M − 23)$^+$, 96.94], 166 (M$^+$, 1.54). HRMS (EI): calcd for $C_{16}H_{15}$ requires 166.1721, found 166.1753.

***E*-1-(Buta-1,3-dienyl)-4-methoxybenzene (2g).** This compound was obtained as a colorless solid (55 mg, 86%). This is a known compound and its ^{1}H NMR spectroscopic data are consistent with those reported (see: Baudin, J. B.; Hareau, G.; Julia, S. A.; Ruel, O. *Bull. Soc. Chim. Fr.* **1993**, 856−878). mp: 43−44 °C. IR (KBr): ν = 644, 823, 869, 901, 954, 1007, 1033, 1176, 1253, 1294, 1453, 1509, 1601, 2837, 2955, 3010

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cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 3.82$ (s, 3H, CH_3), 5.12 (dd, $J = 1.2$, 9.6 Hz, 1H, CH_2), 5.29 (dd, $J = 2.1$, 17.3 Hz, 1H, CH_2), 6.43−6.56 (m, 2H, CH), 6.64−6.73 (m, 1H, CH), 6.84−6.89 (m, 2H, ArH), 7.33−7.38 (m, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): $\delta = 55.2$, 114.0, 116.4, 127.6, 129.9, 132.4, 137.3, 159.2. MS (EI) *m/z*: 91 [$(M - 69)^+$, 24.78], 115 [$(M - 45)^+$, 47.92], 129 [$(M - 31)^+$, 38.82], 144 [$(M - 16)^+$, 40.63], 160 (M^+, 100). HRMS (MALDI): calcd for $C_{11}H_{13}O$ ($M^+ + 1$) requires 161.0961, found 161.0964.

***E*- or *Z*-1,1-Phenyl(2-chlorophenyl)-1,3-butadiene (2h).** This compound was obtained as a colorless liquid (86 mg, 89%). IR (KBr): $\nu = 639$, 693, 750, 763, 907, 988, 1054, 1342, 1446, 1486, 1586, 1616, 2911, 2963, 3022, 3044, 3089 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 5.13−5.17$ (m, 1H, CH_2), 5.40−5.46 (m, 1H, CH_2), 6.07−6.20 (m, 1H, CH), 6.87 (d, $J = 8.1$ Hz, 1H, CH), 7.21−7.48 (m, 9H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): $\delta = 119.3$, 126.3, 126.7, 127.6, 128.4, 128.9, 129.3, 129.8, 132.1, 134.0, 134.4, 138.1, 139.8, 140.0. MS (EI) *m/z*: 101 [$(M - 139)^+$, 27.61], 125 [$(M - 115)^+$, 26.8], 165 [$(M - 75)^+$, 13.27], 205 [$(M - 35)^+$, 100.0], 240 (M^+, 92.47). HRMS (EI): calcd for $C_{16}H_{13}Cl$ requires 240.0706, found 240.0725.

(4-Allylidenecyclohexyl)benzene (2i). This compound was obtained as a colorless liquid (78 mg, 98%). IR (KBr): $\nu = 699$, 755, 840, 963, 1024, 1239, 1434, 1452, 1493, 1597, 2836, 2914, 3026 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 1.77−1.91$ (m, 4H, CH_2), 2.26−2.49 (m, 4H, CH_2), 2.80−2.85 (m, 1H, CH), 5.62−5.76 (m, 2H), 6.16 (m, 1H), 7.23−7.38 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): $\delta = 18.2$, 25.2, 29.7, 33.9, 40.3, 121.8, 125.97, 125.98, 126.8, 128.3, 134.1, 135.5, 146.9. MS (EI) *m/z*: 79 [$(M - 119)^+$, 100.0], 94 [$(M - 104)^+$, 30.68], 104 [$(M - 94)^+$, 35.2], 156 [$(M - 42)^+$, 9.41], 169 [$(M - 29)^+$, 8.12], 198 (M^+, 67.38). HRMS (MALDI): calcd for $C_{15}H_{19}{}^{+1}$ requires 199.1481, found 199.1486.

Acetic Acid 4,4-Diphenylbut-3-enyl Ester (3a). This compound was obtained as a colorless liquid. ^1H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 2.04$ (s, 3H, CH_3), 2.26−2.49 (m, 2H, CH_2), 4.13 (t, $J = 6.6$ Hz, 2H, OCH_2), 6.06 (t, $J = 7.2$ Hz, 1H, CH), 7.16−7.40 (m, 10H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): $\delta = 20.9$, 29.2, 63.8, 124.3, 127.06, 127.08, 127.2, 128.0, 128.2, 129.6, 139.6, 142.2, 144.1, 170.9.

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Supporting Information Available: ^1H and ^{13}C NMR spectra of dienes **2** and deuterium labeling products. This material is available free of charge via the Internet at http://pubs.acs.org.

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