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Preparation of Multisubstituted Allenes from Allylsilanes

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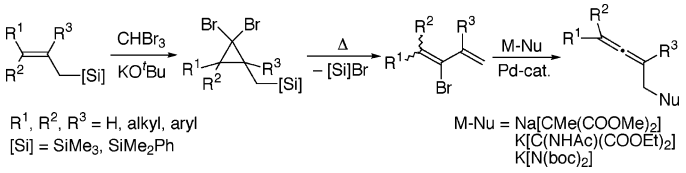
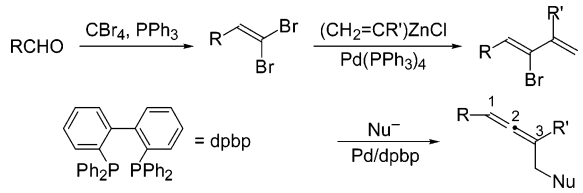


A three-step route of converting allylsilanes to functionalized allenes was developed. Thermal decomposition of 1,1-dibromo-2-(silylmethyl)cyclopropanes, which were quantitatively prepared by treatment of allylsilane derivatives with $CHBr_3$/KO^{t}Bu, afforded substituted 2-bromo-1,3-butadienes with elimination of bromosilanes. The Pd-catalyzed reaction of the bromodienes with soft nucleophiles gave the allene derivatives. Previously inaccessible tri- and tetrasubstituted allenes can be prepared by this method as well.

Introduction

Allenes have received considerable attention as important synthetic intermediates in organic synthesis.[1] Due to the cumulated propadienyl structure, allenes possess unique electronic and steric properties, and these facts make allenes attractive substrates/reagents for transition-metal-catalyzed/-mediated reactions.[2] Although many interesting transformations of allenes have been developed recently, their synthetic usefulness is clearly associated with convenient methods of preparing allenic compounds.[1,3]

SCHEME 1



Recently, we have reported a three-step conversion of a variety of aldehydes into functionalized allenes utilizing two Pd-catalyzed reactions (Scheme 1),[4] and the final step of the reaction sequence has been developed into a catalytic asymmetric reaction giving enantiomerically enriched axially chiral allenes.[5] The key compounds of the allene synthesis are 2-bromo-1,3-butadiene derivatives. Besides the allene preparation, 2-bromo-1,3-butadienes have been demonstrated as useful synthons in other organic transformations, such as Diels–Alder reactions[6] and stereoselective preparation of conjugated poly-

(1) (a) Taylor, D. R. *Chem. Rev.* **1967**, *67*, 317. (b) Rutledge, T. F. *Acetylenes and Allenes*; Reinhold: New York, 1969. (c) Patai, S. *The Chemistry of Ketenes, Allenes, and Related Compounds*; Wiley: Chichester, 1980. (d) Landor, S. R. *The Chemistry of the Allenes*; Academic Press: London, 1982. (e) Coppola, G. M.; Schuster, H. F. *Allenes in Organic Synthesis*; Wiley: New York, 1984. (f) Krause, N.; Hashmi, A. S. K. *Modern Allene Chemistry*; Wiley-VCH: Weinheim, 2004. (g) Pasto, D. J. *Tetrahedron* **1984**, *40*, 2805. (h) Marshall, J. A. *Chem. Rev.* **1996**, *96*, 31. (i) Wang, K. K. *Chem. Rev.* **1996**, *96*, 207. (j) Lu, X.; Zhang, C.; Xu, Z. *Acc. Chem. Res.* **2001**, *34*, 535. (k) Tius, M. A. *Acc. Chem. Res.* **2003**, *36*, 284. (l) Brandsma, L.; Nedolya, N. A. *Synthesis* **2004**, 735.

(2) (a) Yamamoto, Y.; Radhakrishnan, U. *Chem. Soc. Rev.* **1999**, *28*, 199. (b) Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2000**, *39*, 3590. (c) Zimmer, R.; Dinesh, C. U.; Nandanan, E.; Khan, F. A. *Chem. Rev.* **2000**, *100*, 3067. (d) Ma, S.; Li, L. *Synlett* **2001**, 1206. (e) Ma, S. In *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Ed.; Wiley-Interscience: New York, 2002; p 1491. (f) Ma, S. *Acc. Chem. Res.* **2003**, *36*, 701. (g) Ma, S. *Eur. J. Org. Chem.* **2004**, 1175.

(3) (a) Sandler, S. R.; Karo, W. *Organic Functional Group Preparations*, 2nd ed.; Academic Press: Orlando, 1986; Vol. II, p 1. (b) Sydnes, L. K. *Chem. Rev.* **2003**, *103*, 1133. (c) Brandsma, L. *Synthesis of Acetylenes, Allenes and Cumulenes*; Elsevier: Oxford, 2004. (d) Miesch, M. *Synthesis* **2004**, 746.

(4) (a) Ogasawara, M.; Ikeda, H.; Hayashi, T. *Angew. Chem., Int. Ed.* **2000**, *39*, 1042. (b) Ogasawara, M.; Ikeda, H.; Nagano, T.; Hayashi, T. *Org. Lett.* **2001**, *3*, 2615.

(5) (a) Ogasawara, M.; Ikeda, H.; Nagano, T.; Hayashi, T. *J. Am. Chem. Soc.* **2001**, *123*, 2089. (b) Ogasawara, M.; Ueyama, K.; Nagano, T.; Mizuhata, T.; Hayashi, T. *Org. Lett.* **2003**, *5*, 217.

(6) For recent examples, see: (a) Roush, W. R.; Koyama, K.; Curtin, M. L.; Moriarty, K. J. *J. Am. Chem. Soc.* **1996**, *118*, 7502. (b) Tsirk, A.; Gronowitz, S.; Hornfeldt, A. B. *Tetrahedron* **1998**, *54*, 9529. (c) Magnus, P.; Westwood, N.; Spyvee, M.; Frost, C.; Linnane, P.; Tavares, F.; Lynch, V. *Tetrahedron* **1999**, *55*, 6435. (d) Abe H.; Aoyagi, S.; Kibayashi, C. *J. Am. Chem. Soc.* **2000**, *122*, 4583.

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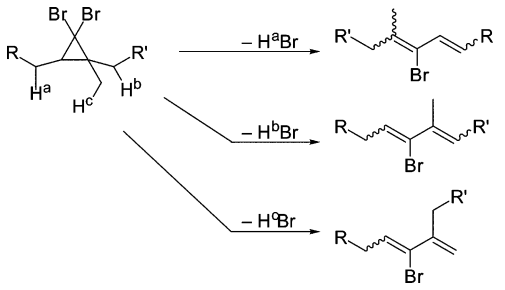
SCHEME 2



enes.[7] Most of the previously reported preparation of 2-bromo-1,3-butadienes has involved regioselective cross-coupling reactions of 1,1-dibromoolefins.[4a,7−9] However, 1,1-disubstituted bromodienes are not accessible by the route shown in Scheme 1 (vide infra). This fact restricts preparation of the corresponding 1,1-disubstituted allenes by the method shown in Scheme 1.

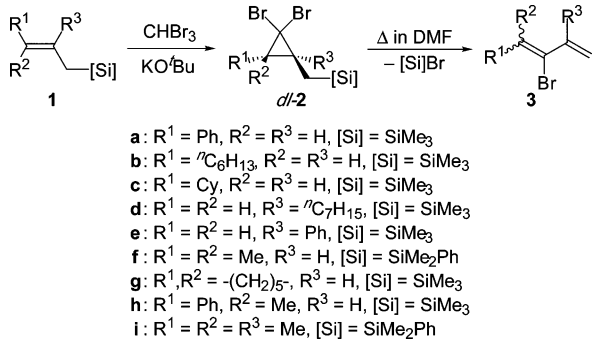
Here we report a high-yield route to the bromobutadiene derivatives from substituted allylsilanes. The route described in this paper enables us to prepare 1,1-disubstituted-2-bromo-1,3-butadienes, and thus, the multisubstituted allenes are now within our reach.

It has been known that thermolysis of *gem*-dihalocyclopropanes affords 2-halo-1,3-diene derivatives via ring-opening and 1,4-dehydrohalogenation when the compounds have hydrogen(s) in an appropriate exocyclic position.[6c,10] However, the critical problem of this method is selectivity in the thermolysis: the products were obtained as mixtures of several isomers in many cases if *gem*-dihalocyclopropanes have more than one chemically inequivalent hydrogen atoms on exocyclic α-carbons (Scheme 2). In addition, the thermolysis often requires vigorous reaction conditions (e.g., vacuum pyrolysis at ca. 500 °C),[10c] which may induce thermal rearrangement of the products. A useful strategy of solving these problems is utilizing a silyl group as a potential leaving group in the thermolysis reaction, which might increase selectivity of the reaction and enable to perform the reaction under milder conditions.[11]

Results and Discussion

Preparation of 2-Bromo-1,3-diene Derivatives from Allylsilanes. Preparation of 2-bromo-1,3-butadiene derivatives from allylsilanes[12] is summarized in Scheme 3 and Table 1. Treatment of allylsilanes **1** with an equimolar mixture of $CHBr_3$ and KO^{t}Bu (3 equiv with respect to **1**) in hexane afforded 1,1-dibromo-2-(silylmethyl)cyclopropanes **2** in nearly quantitative yields (Scheme 3).[13]

SCHEME 3



When thermolysis of dibromocyclopropane **2a** was performed under vacuum without solvent (150−180 °C, bath temperature),[11b] ring opening and 1,4-debromosilylation took place as expected and 1-phenyl-2-bromo-1,3-butadiene **3a** was obtained as a single isomer in 66% yield by vacuum distillation (Table 1, entry 1). The geometry of **3a** was determined to be (*Z*) by comparison of its ^{1}H and ^{13}C NMR spectra with those reported previously.[4a,14] GC−MS and NMR analysis of the residue of the vacuum distillation revealed that major byproducts in the thermolysis were an isomeric mixture of dehydrobromination species **4a** (Scheme 4). It was found that the undesirable dehydrobromination was nearly completely suppressed when the thermal decomposition of **2a** was carried out in DMF. The thermolysis of **2a** in DMF proceeded within 15 min at 150 °C, and **3a** was obtained in 81% isolated yield after usual workup (entry 2). For the thermolysis of the dibromocyclopropane **2** with alkyl substituents at the R^1, R^2, and/or R^3 positions (Scheme 3), the reactions at lower temperature (110 °C) generally afforded the corresponding bromodiene **3** in higher yields although the reactions took longer to reach completion.

While the bromodiene **3a** prepared from **2a** without solvent consisted of the (*Z*)-isomer only, the thermolysis of **2a** in DMF afforded **3a** as a mixture of (*Z*)- and (*E*)-isomers with a (*Z*)/(*E*) = 67/33 ratio. Analogous stereoselectivity was seen in the thermal decomposition of **2b**: while **3b** was obtained in 22% yield as a pure (*Z*)-isomer by the reaction of **2b** without solvent (entry 3), the reaction in DMF at 110 °C gave a (*Z*)/(*E*)-mixture of **3b** ((*Z*)/(*E*) = 86/14) in 86% yield (entry 4). The two isomers in **3a** and **3h** were separable by silica gel column

(7) (a) Xu, C.; Negishi, E. *Tetrahedron Lett.* **1999**, *40*, 431. (b) Zeng, X.; Hu, Q.; Qian, M.; Negishi, E. *J. Am. Chem. Soc.* **2003**, *125*, 13636. (c) Zeng, X.; Qian, M.; Hu, Q.; Negishi, E. *Angew. Chem., Int. Ed.* **2004**, *43*, 2259.

(8) (a) Roush, W. R.; Moriarty, K. J.; Brown, B. B. *Tetrahedron Lett.* **1990**, *31*, 6509. (b) Shen, W.; Wang, L. *J. Org. Chem.* **1999**, *64*, 8873.

(9) For other reports on preparation of 2-bromo-1,3-dienes, see: (a) Gronowitz, S.; Hallberg, A.; Nikitidis, G. *Tetrahedron* **1987**, *43*, 4793. (b) Alper, H.; Vasapollo, G. *Tetrahedron Lett.* **1989**, *30*, 2617. (c) Horváth, A.; Bäckvall, J.-E. *J. Org. Chem.* **2001**, *66*, 8120. (d) Ma, S.; Wang, G. *Tetrahedron Lett.* **2002**, *43*, 5723.

(10) (a) Sandler, S. R. *J. Org. Chem.* **1968**, *12*, 4537. (b) Weyerstahl, P.; Klamann, D.; Finger, D.; Fligge, M.; Nerdel, F.; Buddrus, J. *Chem. Ber.* **1968**, *101*, 1303. (c) Nerdel, F.; Hentschel, P.; Brodowski, W.; Buddrus, J. *Liebigs Ann. Chem.* **1971**, *746*, 6. (d) Molchanov, A. P.; Kostikov, R. R. *Zh. Org. Khim.* **1989**, *25*, 2533; *J. Org. Chem. USSR* **1990**, *25*, 2272. (e) Werstiuk, N. H.; Roy, C. D. *Tetrahedron Lett.*, **2001**, *42*, 3255 and references therein.

(11) For preparation of 2-halo-1,3-butadienes with similar strategy, see: (a) Seyferth, D.; Jula, T. *J. Am. Chem. Soc.* **1968**, *90*, 2938. (b) Schlosser, M.; Dahan, R.; Cottens, S. *Helv. Chim. Acta* **1984**, *67*, 284. (c) Mitani, M.; Kobayashi, Y.; Koyama, K. *J. Chem. Soc., Perkin Trans. 1* **1995**, 653. (d) Roux, M.; Santelli, M.; Parrain, J.-L. *Org. Lett.* **2000**, *2*, 1701.

(12) For preparation of allylsilanes used in this study, see: (a) Colvin, W. E. *Silicon Reagents in Organic Synthesis*; Academic Press: London, 1988; Chapter 5, pp 25−37. (b) Fleming, I.; Pearce, A. *J. Chem. Soc., Perkin Trans. 1* **1981**, 251. (c) Negishi, E.; Luo, F.-T.; Rand, C. L. *Tetrahedron Lett.* **1982**, *23*, 27. (d) Narayanan, B. A.; Bunnelle, W. H. *Tetrahedron Lett.* **1987**, *28*, 6261. (e) Okamoto, S.; Tani, K.; Sato, F.; Sharpless, K. B.; Zargarian, D. *Tetrahedron Lett.* **1993**, *34*, 2509. (f) Denmark, S. E.; Fu, J. *Org. Lett.* **2002**, *4*, 1951.

(13) (a) Creary, X.; Jiang, Z.; Butchko, M.; McLean, K. *Tetrahedron Lett.* **1996**, *37*, 579. (b) Lahrech, M.; Hacini, S.; Parrain, J.-L.; Santelli, M. *Tetrahedron Lett.* **1997**, *38*, 3395. (c) Fedorynski, M. *Chem. Rev.* **2003**, *103*, 1099.

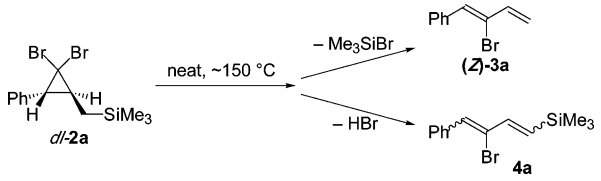
(14) Krijnen, E. S.; Zuilhof, H.; Lodder, G. *J. Org. Chem.* **1994**, *59*, 8139.

TABLE 1. Preparation of 2-Bromo-1,3-butadienes 3 from Allylsilane 1

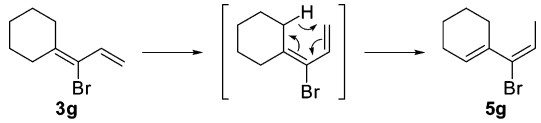
entry	allylsilane **1**	yield of **2**[a] (%)	thermolysis conditions	yield of **3**[a] (%)	(*Z*)/(*E*)[b]
1	**1a**	99 (**2a**)	neat, 150−180 °C	66 (**3a**)	100/0[c]
2	**1a**		in DMF, 150 °C, 15 min	81 (**3a**)	67/33[c]
3	**1b**	99 (**2b**)	neat, 150−180 °C	22 (**3b**)	100/0[c]
4	**1b**		in DMF, 110 °C, 4 h	86 (**3b**)	86/14[c]
5	**1c**	81 (**2c**)	in DMF, 110 °C, 4 h	94 (**3c**)	77/23[c]
6	**1d**	97 (**2d**)	in DMF, 110 °C, 4 h	82 (**3d**)	
7	**1e**	97 (**2e**)	in DMF, 150 °C, 15 min	87 (**3e**)	
8	**1f**	97 (**2f**)	in DMF, 110 °C, 4 h	79 (**3f**)	
9	**1g**	98 (**2g**)	in DMF, 110 °C, 4 h	87 (**3g**)[d]	
10	**1h**	98 (**2h**)	in DMF, 110 °C, 4 h	96 (**3h**)	91/9[e]
11	**1i**	98 (**2i**)	in DMF, 110 °C, 4 h	90 (**3i**)	

[a] Isolated yield by silica gel chromatography. [b] Determined by ^{1}H NMR analysis. [c] The geometry of the major isomers was determined by comparison of their NMR spectra with those of (*Z*)-isomers prepared by the route shown in Scheme 1 (ref 4a). [d] With ca. 8% of **5g**.[e] The geometry of the major isomer was determined by comparison of its NMR spectrum with that of the (*Z*)-isomer reported previously (ref 10d).

SCHEME 4



SCHEME 5



chromatography using hexane as an eluent; however, separation of the (*Z*)/(*E*)-isomers in **3b** and **3c** could not be achieved.

The scope of the present reaction is broad, and a wide range of substitution patterns are acceptable to the allylsilane substrates. Allylsilanes with a terminal alkenyl moiety such as **1d** and **1e** gave bromobutadienes with no substituents at both termini (entries 6 and 7). This synthetic strategy could be applicable to γ,γ-disubstituted allylsilanes, and 1,1-disubstituted-2-bromo-1,3-butadiene derivatives were prepared in excellent yields (entries 8−11). Note that diene **3g** was obtained with ca. 8% of an inseparable isomeric diene **5g** (entry 9). When the thermolysis of **2g** was performed at higher temperature (150 °C) in DMF, a mixture of **3g** and **5g** was obtained in 73% yield with a ratio of **3g**/**5g** = 83/17. Formation of **5g** could be rationalized as thermal isomerization of the initially formed **3g** under the thermolysis conditions as shown in Scheme 5.[15] Indeed, **2g** was treated in DMF for a short period (ca. 20 min), and an ^{1}H NMR analysis of the reaction mixture revealed that conversion of **2g** into **3g** was ca. 40% and no **5g** was detected.

As a leaving silyl group, not only Me_3Si- but $PhMe_2Si$- is applicable for the bromodiene synthesis (entries 8 and 11).

For preparation of 1,1-disubstituted 2-bromo-1,3-butadienes, reactions of 1,1-dibromo-2-phenylpropene with a (vinyl)metal reagent were also examined. When the dibromoolefin was treated with (CH_2=CH)ZnCl under conditions identical with the previous report,[4a] i.e., with 2 mol % of $Pd(PPh_3)_4$ at room temperature, no reaction was observed and the dibromoolefin was recovered in >90% yield.[16] On the other hand, under more vigorous conditions, i.e., with (CH_2=CH)MgBr using 10 mol % of $NiCl_2(PPh_3)_2$ in refluxing THF, the dibromoolefin was completely consumed; however, the product was obtained as a complex mixture and only a trace amount of bromobutadienes (*Z*)- and (*E*)-**3h** was detected in the ^{1}H NMR spectrum.[17]

TABLE 2. Palladium-Catalyzed Synthesis of Multisubstituted Allenes 7 from Bromodienes 3[a]

entry	bromodiene **3**	nucleophile **6**	*T* (°C)	yield of **7**[b] (%)
1	(*Z*)- and (*E*)-**3a**[c]	**6m**	23	91 (**7am**)
2	(*Z*)- and (*E*)-**3b**[c]	**6m**	23	87 (**7bm**)
3	(*Z*)- and (*E*)-**3c**[c]	**6m**	23	95 (**7cm**)
4	**3d**	**6m**	23	97 (**7dm**)
5	**3e**	**6m**	23	93 (**7em**)[d]
6	**3f**	**6m**	23	70 (**7fm**)[e]
7	**3g**	**6m**	23	94 (**7gm**)
8	**3g**	**6n**	40	96 (**7gn**)
9	**3g**	**6o**	40	92 (**7go**)
10	(*Z*)-**3h**	**6m**	23	92 (**7hm**)
11	(*E*)-**3h**	**6m**	23	96 (**7hm**)
12	(*Z*)-**3h**	**6n**	40	87 (**7hn**)
13	(*Z*)-**3h**	**6o**	40	92 (**7ho**)
14	**3i**	**6m**	23	91 (**7im**)

[a] Reaction was carried out with **3** (1.0 mmol) and **6** (1.1 mmol) in THF in the presence of the catalyst (2 mol %) generated from [PdCl(π-allyl)]$_2$ and dpbp. [b] Isolated yield by silica gel chromatography. [c] As a (*Z*)- and (*E*)-mixture. [d] Taken from ref 4a. [e] The relatively low yield could be ascribed to high volatility of the product. The GC analysis of the crude reaction mixture showed a nearly quantitative yield of **7fm**.

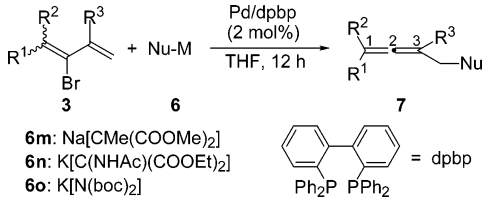
Palladium-Catalyzed Reactions of 2-Bromo-1,3-dienes with Nucleophiles. The bromodienes **3** obtained here are excellent substrates for the Pd-catalyzed allene synthesis.[4,5] The results of the Pd-catalyzed reaction are summarized in Table 2 and Scheme 6. As reported previously,[4a] 1-monosubstituted 2-bromo-1,3-butadienes (**3a**−**c**) and terminally unsubstituted 3-hydrocarbyl-2-bromo-1,3-butadienes (**3d**,**e**) reacted with a soft nucleophile Na[CMe(COOMe)$_2$] (**6m**) in THF in the presence

(15) (a) Frey, H. M.; Walsh, R. *Chem. Rev.* **1969**, *69*, 103. (b) Curry, M. J.; Stevens, I. D. R. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1756.

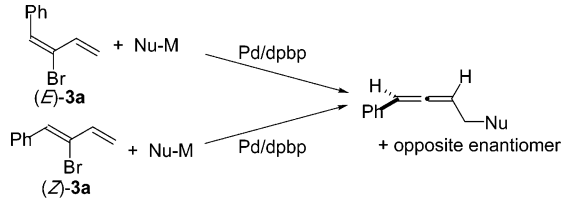
(16) Stoichiometric reactions of 1,1-dibromo-2-phenylpropene with $Pd(PPh_3)_4$ were reported; see: Ma, S.; Xu, B.; Ni, B. *J. Org. Chem.* **2000**, *65*, 8532.

(17) Reaction of 1,1-dibromo-2-phenylpropene with a Grignard reagent in the presence of a Ni catalyst was reported; see: Okamoto, Y.; Yoshikawa, Y.; Hayashi, T. *J. Organomet. Chem.* **1989**, *359*, 143.

SCHEME 6



SCHEME 7



of 2 mol % of a Pd catalyst generated in situ from [PdCl(π-allyl)]$_2$ and dpbp[18] to give the corresponding allenes in excellent yields (Table 2, entries 1−5).

The bromodiene **3a** was used for the Pd-catalyzed reaction as a mixture of the (*Z*)- and (*E*)-isomers, and the allene **7am** was obtained as the sole product in 91% yield (entry 1). During the transformation of **3a** into **7am**, the geometrical isomeric information in **3a** was lost because of the perpendicular structure of the allenic C=C=C moiety in **7am**, and thus, the isostructural allene was obtained from both (*Z*)- and (*E*)-**3a** (Scheme 7). Similarly, **3b** and **3c**, which were obtained as the (*Z*)/(*E*)-mixtures, could be used for the allene synthesis without separating the isomers.

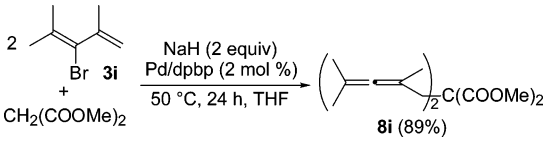
The 1,1-disubstituted 2-bromo-1,3-dienes **3f**−**h** are as reactive as the 1-monosubstituted bromodienes for the Pd-catalyzed reaction. With these bromodienes, 1,1-disubstituted allenes, which were not accessible by the previous method,[4a] were prepared in excellent yields (entries 6−13). The two geometrical isomers of **3h** were easily separated by silica gel chromatography, and both (*Z*)- and (*E*)-**3h** displayed nearly identical reactivity toward the Pd-catalyzed reaction with **6m** (entries 10 and 11). Other soft nucleophiles, such as **6n** and a *N*-nucleophile **6o**, are applicable for preparation of 1,1-disubstituted allenes as well (entries 8, 9, 12, and 13).

Even persubstituted allenes could be made by the route developed in this study. Allylsilane **1i**, which possesses a persubstituted alkenyl moiety, was converted into 1,1,3-trisubstituted 2-bromo-1,3-butadiene **3i**. Treatment of **3i** with **6m** under the Pd catalysis afforded the persubstituted allene **7im** in 91% yield (entry 14). The Pd-catalyzed reaction of **3i** with 0.5 equiv of dimethyl malonate in the presence of equimolar NaH gave a persubstituted bis-allene **8i** in 89% yield (Scheme 8).

Conclusions

In summary, we have developed a general and efficient new method for the conversion of allylsilane derivatives to functionalized allenes. Using allylsilanes with proper substituents at proper positions, a variety of multisubstituted allenes can be made. The intermediates of the process, 2-bromo-1,3-butadienes, have been demonstrated as useful synthons in many organic transformations, and our method also provides a novel route to these bromodiene derivatives as well. Allylsilanes have been established as versatile synthetic intermediates, and their preparation methods have been well-developed. This fact, combined with the high yield of the present process, should enhance the synthetic usefulness of our method.

SCHEME 8



Experimental Section

Preparation of Dibromosilylmethylcyclopropanes 2. The yields are described in Table 1. To a suspension of allylsilane **1** (10 mmol) and KO^{t}Bu (3.4 g, 30 mmol) in dry hexane (20 mL) was slowly added bromoform (7.6 g, 30 mmol) at 0 °C. The mixture was stirred for 1 h at 0 °C and an additional 1 h at room temperature. The mixture was then filtered through Celite, and the filtrate was washed with saturated NaCl solution. The aqueous phase was extracted with ether, and the combined organic layer was dried over $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography on silica gel (with hexane) to give the dibromocyclopropane **2** as colorless oil. These compounds were >95% pure (by ^{1}H NMR) and used for the next step without further purification. Because of their thermal instability, the products were characterized by NMR measurements, and HRMS and EA analyses were not performed. The ^{1}H and ^{13}C{^{1}H} NMR data of the dibromocyclopropanes are listed below.

***trans*-1,1-Dibromo-2-phenyl-3-(trimethylsilylmethyl)-cyclopropane (2a).** ^{1}H NMR ($CDCl_3$): δ 0.09 (s, 9H), 0.77 (dd, J = 9.4 and 14.7 Hz, 1H), 1.31 (dd, J = 5.3 and 14.7 Hz, 1H), 1.87 (ddd, J = 5.3, 8.5, and 9.4 Hz, 1H), 2.38 (d, J = 8.5 Hz, 1H), 7.19−7.28 (m, 2H), 7.29−7.32 (m, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ −1.3, 20.4, 32.5, 41.4, 42.8, 127.4, 128.2, 128.5, 136.5.

***trans*-1,1-Dibromo-2-hexyl-3-(trimethylsilylmethyl)cyclopropane (2b).** ^{1}H NMR ($CDCl_3$): δ 0.11 (s, 9H), 0.61−0.68 (m, 1H), 0.90−1.08 (m, 6H), 1.34−1.59 (m, 10H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ −0.8, 14.6, 20.7, 23.1, 28.7, 29.5, 32.2, 33.3, 34.3, 38.8, 42.5.

***trans*-1,1-Dibromo-2-cyclohexyl-3-(trimethylsilylmethyl)cyclopropane (2c).** ^{1}H NMR ($CDCl_3$): δ 0.12 (s, 9H), 0.70 (dd, J = 7.3 and 14.9 Hz, 1H), 0.81−0.85 (m, 1H), 0.99 (dd, J = 6.9 and 14.9 Hz, 1H), 1.09−1.31(m, 7H), 1.68−1.76 (m, 4H), 2.08−2.10 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ −0.3, 21.5, 26.4, 26.9, 27.1, 32.5, 32.9, 33.6, 42.2, 43.3 44.8.

1,1-Dibromo-2-heptyl-2-(trimethylsilylmethyl)cyclopropane (2d). ^{1}H NMR ($CDCl_3$): δ 0.06 (s, 9H), 0.82−0.93-(m, 4H), 1.14−1.65 (m, 15H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 0.0, 14.4, 22.9, 23.7, 26.6, 29.5, 29.8, 32.1, 32.7, 35.8, 38.2, 42.7.

1,1-Dibromo-2-phenyl-2-(trimethylsilylmethyl)cyclopropane (2e). ^{1}H NMR ($CDCl_3$): δ 0.07 (s, 9H), 1.41 (d, J = 14.5 Hz, 1H), 1.99 (d, J = 7.7 Hz, 1H), 2.03 (d, J = 14.5 Hz, 1H), 2.56 (d, J = 7.7 Hz, 1H), 7.57−7.68 (m, 5H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ −1.3, 29.5, 33.4, 37.8, 39.9, 127.3, 128.3, 128.9, 141.4.

1,1-Dibromo-2,2-dimethyl-3-[(phenyldimethylsilyl)methyl]cyclopropane (2f). ^{1}H NMR ($CDCl_3$): δ 0.38 (s, 3H), 0.39 (s, 3H), 0.77 (dd, J = 7.6 and 15.1 Hz, 1H), 0.99 (dd, J = 6.7 and 15.1 Hz, 1H), 1,02 (s, 3H), 1.25 (dd, J = 6.7 and 7.6 Hz, 1H), 1.29 (s, 3H), 7.35−7.38 (m, 3H), 7.52−7.54 (m, 2H).

(18) dpbp=2,2′-bis(diphenylphosphino)-1,1′-biphenyl. See: Ogasawara, M.; Yoshida, K.; Hayashi, T. *Organometallics* **2000**, *19*, 1567 and references cited therein.

$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ −2.6, −2.3, 15.1, 19.9, 27.8, 28.8, 37.2, 51.6, 128.3, 129.7, 134.0, 138.7.

1,1-Dibromo-2,2-(1,5-pentanediyl)-3-(trimethylsilylmethyl)cyclopropane (2g). ^1H NMR ($CDCl_3$): δ 0.04 (s, 9H), 0.54 (dd, J = 6.4 and 15.0 Hz, 1H), 0.64 (dd, J = 7.8 and 15.0 Hz, 1H), 1.13 (dd, J = 6.4 and 7.8 Hz, 1H), 1.33−1.60 (m, 10H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ −1.3, 14.0, 24.5, 25.0, 25.9, 30.0, 33.4, 36.9, 37.5, 50.8.

***trans*-1,1-Dibromo-2-methyl-2-phenyl-3-(trimethylsilylmethyl)cyclopropane (2h).** ^1H NMR ($CDCl_3$): δ 0.15 (s, 9H), 0.75 (dd, J = 7.0 and 15.1 Hz, 1H), 0.88 (dd, J = 7.4 and 15.1 Hz, 1H), 1.42 (s, 3H), 1.95 (dd, J = 7.0 and 7.4 Hz, 1H), 7.22−7.26 (m, 3H), 7.31−7.34 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ −1.2, 15.0, 21.9, 35.0, 37.7, 48.0, 127.0, 128.3, 128.4, 144.6.

1,1-Dibromo-2,2,3-trimethyl-3-[(phenyldimethylsilyl)methyl]cyclopropane (2i). ^1H NMR ($CDCl_3$): δ 0.41 (s, 3H), 0.42 (s, 3H), 1.16 (d, J = 14.5 Hz, 1H), 1.17 (s, 3H), 1.20 (s, 3H), 1.24 (s, 3H), 1.25 (d, J = 14.5 Hz, 1H), 7.22−7.36 (m, 3H), 7.53−7.56 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ −1.5, −1.5, 21.7, 21.9, 22.5, 23.1, 30.3, 32.3, 61.1, 127.8, 129.0, 133.5, 139.6.

Preparation of Bromodienes 3. The reaction conditions and results are described in Table 1. Dibromocyclopropane **2** (4.0 mmol) was dissolved in DMF (30 mL), and the solution was heated to 110 °C for 4 h (or 150 °C for 15 min) with stirring. Then the solution was poured onto ice−water and the mixture was extracted with hexane four times. The combined hexane solution was washed with water twice and dried over $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography on silica gel (with hexane) or by vacuum-transfer to give the bromodiene **3** as colorless oil. The bromodienes (*Z*)-**3a**,[4a,14] **3e**,[4a] and **3i**[6c] were characterized by comparison of their spectroscopic data with those reported previously. The characterization data of the other bromodienes are listed below.

(*E*)-2-Bromo-1-phenyl-1,3-butadiene (*E*-3a). ^1H NMR ($CDCl_3$): δ 5.35 (d, J = 10.6 Hz, 1H), 5.72 (d, J = 16.2 Hz, 1H), 6.69 (dd, J = 10.6 and 16.2 Hz, 1H), 7.10 (s, 1H), 7.14−7.28 (m, 5H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 122.3, 125.1, 127.8, 128.4, 128.9, 131.4, 134.5, 136.0. EI-HRMS: calcd for $C_{10}H_9Br$ 207.9887, found 207.9893.

(*Z*/*E*)-3-Bromo-1,3-decadiene (*Z*/*E*-3b). ^1H NMR ($CDCl_3$): δ 0.88−0.92 (m, 3H of *Z*/*E*-isomers), 1.31−1.48 (m, 8H of *Z*/*E*-isomers), 2.23 (td, J = 6.8 and 7.9 Hz, 2H of *E*-isomer), 2.32 (dt, J = 7.1 and 7.6 Hz, 2H of *Z*-isomer), 5.16 (d, J = 10.4 Hz, 1H of *Z*-isomer), 5.31 (d, J = 10.6 Hz, 1H of *E*-isomer), 5.54 (d, J = 16.3 Hz, 1H of *Z*-isomer), 5.63 (d, J = 16.1 Hz, 1H of *E*-isomer), 5.99 (t, J = 7.1 Hz, 1H of *Z*-isomer), 6.09 (t, J = 7.9 Hz, 1H of *E*-isomer), 6.31 (dd, J = 10.4 and 16.3 Hz, 1H of *Z*-isomer), 6.58 (dd, J = 10.6 and 16.3 Hz, 1H of *E*-isomer). $^{13}C\{^1H\}$ NMR for (*Z*)-isomer ($CDCl_3$): δ 14.1, 22.6, 28.3, 28.9, 31.5, 31.6, 117.0, 125.8, 135.3, 135.9. $^{13}C\{^1H\}$ NMR for (*E*)-isomer ($CDCl_3$): δ 14.1, 22.7, 28.8, 29.1, 29.6, 31.6, 120.1, 122.0, 129.9, 136.3. EI-HRMS: calcd for $C_{10}H_{17}Br$ 216.0513, found 216.0500.

(*Z*/*E*)-2-Bromo-1-cyclohexyl-1,3-butadiene (*Z*/*E*-3c). ^1H NMR ($CDCl_3$): δ 1.04−1.41 (m, 6H of *Z*/*E*-isomers), 1.63−2.05 (m, 4H of *Z*/*E*-isomers), 2.45−2.63 (m, 1H of *Z*/*E*-isomers), 5.16 (d, J = 10.2 Hz, 1H of *Z*-isomer), 5.30 (d, J = 10.5 Hz, 1H of *E*-isomer), 5.52 (d, J = 16.5 Hz, 1H of *Z*-isomer), 5.61 (d, J = 16.2 Hz, 1H of *E*-isomers), 5.80 (d, J = 8.7 Hz, 1H of *Z*-isomer), 5.95 (d, J = 9.9 Hz, 1H of *E*-isomer), 6.28 (dd, J = 10.2 and 16.5 Hz, 1H of *Z*-isomer), 6.58 (dd, J = 10.5 and 16.2 Hz, 1H of *E*-isomer). $^{13}C\{^1H\}$ NMR for (*Z*)-isomer ($CDCl_3$): δ 25.5, 25.9, 31.7, 40.4, 117.1, 123.8, 135.9, 140.0. $^{13}C\{^1H\}$ NMR for (*E*)-isomer ($CDCl_3$): δ 25.6, 25.7, 32.7, 38.9, 120.0, 120.9, 130.0, 141.5. EI-HRMS: calcd for $C_{10}H_{15}Br$ 214.0357, found 214.0349.

2-Bromo-3-heptyl-1,3-butadiene (3d). ^1H NMR ($CDCl_3$): δ 0.88 (t, J = 6.8 Hz, 3H), 1.27−1.34 (m, 8H), 1.41−1.47 (m, 2H), 2.31 (dt, J = 1.6 and 7.8 Hz, 2H), 5.15 (s, 1H), 5.51 (s, 1H), 5.65 (s, 1H), 5.87 (d, J = 1.6 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.1, 22.6, 28.3, 29.1, 29.3, 31.8, 33.5, 117.5, 118.4, 132.5, 145.5. EI-HRMS: calcd for $C_{11}H_{19}Br$ 230.0670, found 230.0677.

3-Bromo-4-methyl-1,3-pentadiene (3f).[19] ^1H NMR ($CDCl_3$): δ 1.95 (s, 3H), 2.03 (s, 3H), 5.18 (d, J = 10.8 Hz, 1H), 5.53 (d, J = 15.9 Hz, 1H), 6.50 (dd, J = 10.8 and 15.9 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 21.1, 26.4, 117.8, 119.8, 131.6, 135.9. EI-HRMS: calcd for C_6H_9Br 159.9888, found 159.9883.

2-Bromo-1,1-(1,5-pentanediyl)-1,3-butadiene (3g). ^1H NMR ($CDCl_3$): δ 1.54 (m, 6H), 2.46−2.57 (m, 4H), 5.22 (d, J = 10.8 Hz, 1H), 5.60 (d, J = 15.9 Hz, 1H), 6.74 (dd, J = 10.8 and 15.9 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 26.4, 27.4, 27.8, 31.9, 36.5, 117.3, 118.6, 131.1, 143.6. EI-HRMS: calcd for $C_9H_{13}Br$ 200.0200, found 200.0192.

(*Z*)-3-Bromo-4-phenyl-1,3-pentadiene (*Z*-3h). ^1H NMR ($CDCl_3$): δ 2.34 (s, 3H), 5.08 (d, J = 10.5 Hz, 1H), 5.56 (d, J = 15.9 Hz, 1H), 6.32 (dd, 10.5 and 15.9 Hz, 1H), 7.15−7.38 (m, 5H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 21.3, 119.3, 126.5, 128.0, 128.1, 128.9, 129.5, 136.5, 141.8. EI-HRMS: calcd for $C_{11}H_{11}Br$ 222.0044, found 222.0042.

(*E*)-3-Bromo-4-phenyl-1,3-pentadiene (*E*-3h). ^1H NMR ($CDCl_3$): δ 2.24 (s, 3H), 5.39 (d, J = 10.5 Hz, 1H), 5.74 (d, J = 15.6 Hz, 1H), 6.80 (dd, 10.5 and 15.6 Hz, 1H), 7.19−7.40 (m, 5H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 22.2, 120.2, 120.3, 127.2, 127.7, 128.1, 131.8, 139.6, 144.7. EI-HRMS: calcd for $C_{11}H_{11}Br$ 222.0044, found 222.0044.

1-Bromo-1-(1-cyclohexenyl)propene (5g). This compound was an inseparable minor product and characterized by ^1H and $^{13}C\{1H\}$ NMR only. ^1H NMR ($CDCl_3$): δ 1.59 (m, 4H), 1.87 (d, J = 6.6 Hz, 3H), 2.18−2.19 (m, 2H), 2.23−2.26 (m, 2H), 5.97 (q, J = 6.6 Hz, 1H), 6.24 (m, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 17.7, 22.1, 22.8, 25.7, 27.0, 121.8, 129.2, 130.4, 134.5.

Palladium-Catalyzed Synthesis of Allenes 7. The reaction was conducted according to a reported procedure.[4a] The reaction conditions and results are described in Table 2. A mixture of $[PdCl(\pi\text{-allyl})]_2$ (1.8 mg, 10 μmol/Pd), dpbp (5.7 mg, 11 mmol), and **3** (0.50 mmol) was dissolved in THF (5 mL), and the solution was added to the nucleophile **6** (0.55 mmol) by cannula transfer under nitrogen. The mixture was stirred at appropriate temperature for 12 h, then filtered through a short pad of SiO_2 to remove precipitated inorganic salts. The silica gel pad was washed with a small amount of Et_2O three times and the combined solution was evaporated to dryness under reduced pressure. The yellow residue was chromatographed on silica gel to give the allene **7**. The allenes **7am** and **7em** were characterized by comparison of their spectroscopic data with those reported previously.[4a] The characterization data of the other allenic products are listed below.

Dimethyl 2-Methyl-2-(2,3-decadienyl)propan-1,3-dioate (7bm). ^1H NMR ($CDCl_3$): δ 0.88 (t, J = 6.8 Hz, 3H), 1.27−1.40 (m, 8H), 1.44 (s, 3H), 1.92−1.98 (m, 2H), 2.50 (m, 2H), 4.90−5.00 (m, 1H), 5.04−5.11 (m, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.0, 19.7, 22.5, 28.7, 28.7, 29.8, 31.6, 35.9, 52.37, 52.40, 53.9, 84.9, 90.9, 172.18, 172.24, 205.9. Anal. Calcd for $C_{16}H_{26}O_4$: C, 68.06; H, 9.28. Found: C, 67.77; H, 9.19.

Dimethyl 2-Methyl-2-(4-cyclohexyl-2,3-butadienyl)propan-1,3-dioate (7cm). ^1H NMR ($CDCl_3$): δ 1.04−1.32 (m, 6H), 1.44 (s, 3H), 1.61−1.73 (m, 4H), 1.90−1.95 (m, 1H), 2.51−2.63 (m, 2H), 3.72 (s, 6H), 4.92−5.00 (m, 1H), 5.04−5.09 (m, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 19.8, 25.9, 26.1, 32.96, 32.99, 36.2, 37.1, 52.4, 52.5, 53.8, 85.9, 96.9, 172.27, 172.31, 204.7. Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.54; H, 8.63. Found: C, 68.40; H, 8.61.

Dimethyl 2-Methyl-2-(2-heptyl-2,3-butadienyl)propan-1,3-dioate (7dm). ^1H NMR ($CDCl_3$): δ 0.88 (t, J = 6.6 Hz, 3H), 1.26−1.44 (m, 10H), 1.48 (s, 3H), 1.83−1.90 (m, 2H), 2.58 (t, J = 2.7 Hz, 2H), 3.70 (s, 6H), 4.62−4.66 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.1, 19.8, 22.6, 27.4, 29.12, 29.14, 31.8, 33.3,

(19) Nilsen, N. O.; Skattebøl, L.; Baird, M. S.; Buxton, S. R.; Slowey, P. D. *Tetrahedron Lett.* **1984**, *25*, 2887.

37.4, 52.4, 53.5, 76.3, 98.4, 172.5, 206.6. Anal. Calcd for $C_{17}H_{28}O_4$: C, 68.89; H, 9.52. Found: C, 68.73; H, 9.50.

Dimethyl 2-Methyl-2-(4-methyl-2,3-pentadienyl)propan-1,3-dioate (7fm). ^{1}H NMR ($CDCl_3$): δ 1.41 (s, 3H), 1.62 (d, J = 2.7 Hz, 6H), 2.50 (d, J = 7.5 Hz, 2H), 3.69 (s, 6H), 4.79 (m, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 19.6, 20.5, 36.1, 52.5, 53.8, 82.9, 95.1, 172.4, 203.8. Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.67; H, 8.18.

Dimethyl 2-Methyl-2-[4,4-(1,5-pentanediyl)-2,3-butadienyl]propan-1,3-dioate (7gm). ^{1}H NMR ($CDCl_3$): δ 1.44 (s, 3H), 1.44−1.61 (m, 6H), 2.04−2.08 (m, 4H), 2.54 (d, J = 7.5 Hz, 2H), 3.72 (s, 6H), 4.80−4.85 (m, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 19.5, 26.0, 27.1, 31.4, 36.3, 52.4, 53.8, 82.7, 102.1, 172.3, 200.5. Anal. Calcd for $C_{15}H_{22}O_4$: C, 67.64; H, 8.33. Found: C, 67.80; H, 8.26.

Diethyl 2-Acetamido-2-[4,4-(1,5-pentanediyl)-2,3-butadienyl]propane-1,3-dioate (7gn). ^{1}H NMR ($CDCl_3$): δ 1.26 (t, J = 7.2 Hz, 6H), 1,46−1.57(m, 6H), 2.02−2.06 (m, 7H), 2.98 (d, J = 7.5 Hz, 2H), 4.16−4.32 (m, 4H), 4.69−4.75 (m, 1H), 6.82 (br, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.0, 23.0, 25.9, 27.1, 31.4, 33.0, 62.5, 66.5, 81.6, 102.4, 167.7, 168.7, 200.6. Anal. Calcd for $C_{18}H_{27}NO_5$: C, 64.07; H, 8.07; N, 4.15. Found: C, 64.09; H, 8.26; N, 4.05.

Di-*tert*-butyl *N*-[4,4-(1,5-Pentanediyl)-2,3-butadienyl]-iminodicarboxylate (7go). ^{1}H NMR ($CDCl_3$): δ 1.50 (s, 18H), 1.54−1.62 (m, 6H), 2.09 (m 4H), 4.18 (d, J = 2.7 Hz, 2H), 5.01−5.06 (m, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 26.0, 27.3, 28.1, 31.4, 45.5, 82.0, 85.9, 104.8, 152.2, 198.1. Anal. Calcd for $C_{19}H_{31}NO_4$: C, 67.63; H, 9.26; N, 4.15. Found: C, 67.57; H, 9.20; N, 4.14.

Dimethyl 2-Methyl-2-(4-phenyl-2,3-pentadienyl)propan-1,3-dioate (7hm). ^{1}H NMR ($CDCl_3$): δ 1.50 (s, 3H), 2.07 (d, J = 3.0 Hz, 3H), 2.69 (d, J = 7.8 Hz, 2H), 3.69 (s, 6H), 5.33 (qt, J = 3.0 and 7.8 Hz, 1H), 7.17−7.38 (m, 5H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 17.1, 19.9, 35.8, 52.5 (2C), 53.7, 87.2, 100.6, 125.7, 126.6, 128.2, 136.8, 172.2 (2C), 205.9. Anal. Calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.26; H, 7.07.

Diethyl 2-Acetamido-2-(4-phenyl-2,3-pentadienyl)propane-1,3-dioate (7hn). ^{1}H NMR ($CDCl_3$): δ 1.20 (t, J = 7.2 Hz, 3H), 1.25 (t, J = 7.2 Hz, 3H), 1.86 (s, 3H), 2.05 (d, J = 2.7 Hz, 3H), 3.14 (d, J = 7.5 Hz, 2H), 4.09−4.31 (m, 4H), 5.20−5.26 (m, 1H), 6.77 (br, 1H), 7.18−7.37 (m, 5H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.9, 14.0, 17.0, 22.8, 32.4, 62.59, 62.63, 66.3, 86.0, 101.0, 125.7, 126.8, 128.3, 136.8, 167.5 (2C), 169.0, 206.1. Anal. Calcd for $C_{20}H_{25}NO_5$: C, 66.83; H, 7.01; N, 3.90. Found: C, 66.99; H, 7.01; N, 3.70.

Di-*tert*-butyl *N*-(4-Phenyl-2,3-pentadienyl)iminodicarboxylate (7ho). ^{1}H NMR ($CDCl_3$): δ 1.45 (s, 18H), 2.09 (d, J = 2.7 Hz, 2H), 4.26 (d, J = 5.7 Hz, 3H), 5.53 (qt, J = 2.7 and 5.7 Hz, 1H), 7.15−7.41 (m, 5H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 17.0, 28.0, 44.9, 82.3, 90.1, 102.8, 125.9, 126.7, 128.1, 136.7, 152.2, 204.2. Anal. Calcd for $C_{21}H_{29}NO_4$: C, 70.17; H, 8.13; N, 4.15. Found: C, 70.11; H, 8.18; N, 3.83.

Dimethyl 2-Methyl-2-(2,4-dimethyl-2,3-pentadienyl)-propan-1,3-dioate (7im). ^{1}H NMR ($CDCl_3$): δ 1.46 (s, 3H), 1.60 (s, 6H), 1.61 (s, 3H), 2.56 (s, 2H), 3.70 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 19.5, 20.6, 20.8, 39.6, 52.4, 53.2, 91.8, 95.3, 172.5, 199.6. Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 65.12; H, 8.21.

Dimethyl 2,2-Bis(2,4-dimethyl-2,3-pentadienyl)propan-1,3-dioate (8i). ^{1}H NMR ($CDCl_3$): δ 1.60 (s, 12H), 1.61 (s, 6H), 2.69 (s, 4H), 3.67 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 20.8, 21.1, 35.5, 52.4, 56.7, 92.2, 95.2, 171.4, 199.8. Anal. Calcd for $C_{19}H_{28}O_4$: C, 71.22; H, 8.81. Found: C, 71.20; H, 8.87.

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Supporting Information Available: ^{1}H- and ^{13}C NMR spectra for all of the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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