DOI: 10.1002/ejoc.201100095

Phosphane-Catalyzed Umpolung Addition Reaction of Nucleophiles to Ethyl 2-Methyl-2,3-butadienoate

Xiao-Yang Guan,[a] Yin Wei,*[a] and Min Shi*[a]

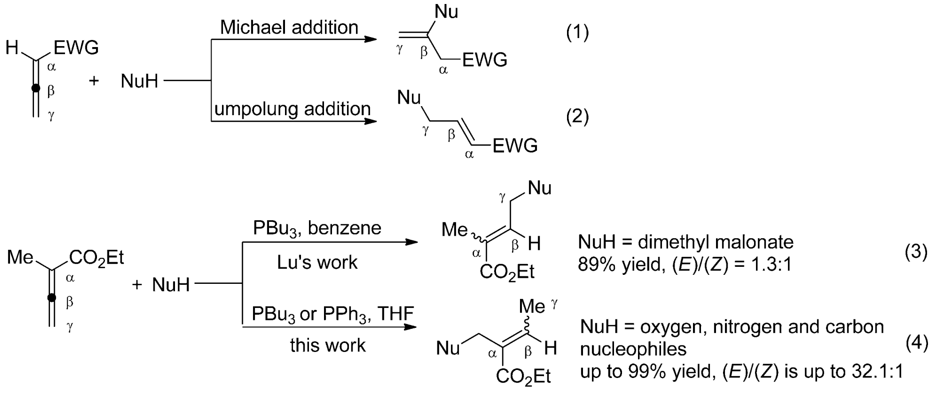
Keywords: Phosphanes / Umpolung / Addition reactions / Nucleophiles / Allenes

The phosphane-catalyzed umpolung addition of various nucleophiles to ethyl 2-methyl-2,3-butadienoate is described. Oxygen, nitrogen, and carbon nucleophiles smoothly reacted with ethyl 2-methyl-2,3-butadienoate to give the corresponding umpolung addition products in good to excellent yields by a similar reaction mechanism. For sulfur nucleophiles, the addition reactions with ethyl 2-methyl-2,3-butadienoate proceeded by a different mechanism.

Introduction

Reactivity inversion (umpolung) plays an important role in modern organic synthesis.[1] In recent years, the umpolung addition reaction between nucleophiles and 2,3-butadienoates or 2-butynoates has been developed;[2–6] for example, the nucleophilic addition of various nucleophiles to allenes bearing an electron-withdrawing group (EWG) can be divided into two categories. The first is nucleophilic addition at the α,β-double bonds to give the corresponding Michael-type adducts [Scheme 1, Equation (1)].[7] In the second, nucleophiles add inversely to the β,γ-double bonds in the presence of phosphane catalysts to give the umpolung addition products [Scheme 1, Equation (2)]. The two reactions arise from the difference in the electronic properties of the two connected carbon–carbon double bonds. The α,β-double bond is electron-deficient whereas the β,γ-double bond is relatively electron-rich.[7,8]

According to Lu and co-workers,[2a,3b] allenoates with a substituent at the α-position, such as ethyl 2-methyl-2,3-butadienoates,[9] also gave the inverse addition products with dimethyl malonate as a nucleophile in benzene in the presence of tributylphosphane (PBu_3) [Scheme 1, Equation (3)]. In contrast, under our reaction conditions, nucleophilic addition occurs at the 2-methyl group of ethyl 2-methyl-2,3-butadienoate [Scheme 1, Equation (4)]. Herein we report the details of this unexpected phosphane-catalyzed umpolung addition reaction of nucleophiles to ethyl 2-methyl-2,3-butadienoate.



Scheme 1. Different kinds of nucleophilic addition to allenoates.

Results and Discussion

Initially, the reaction of ethyl 2-methyl-2,3-butadienoate (**1**) with 4-methoxyphenol (**2a**) was conducted in the presence of PPh_3 and THF at 60 °C, which afforded an unexpected new product, **3a** [(*E*)/(*Z*) = 2.5:1], in 82% yield

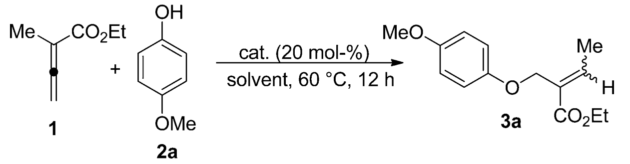
---

[a] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences,
354 Fenglin Road, Shanghai 200032, China
Fax: +86-21-64166128
E-mail: weiyin@mail.sioc.ac.cn
mshi@mail.sioc.ac.cn

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201100095.

(Table 1, Entry 1). A series of analytical measurements on compound **3a** showed that the nucleophilic addition reaction between **1** and **2a** occurs at the α-methyl group of ethyl 2-methyl-2,3-butadienoate (**1**) rather than at the γ-position of **1**. Decreasing the reaction temperature to room temperature slightly improved the stereoselectivity of the product **3a**, but the yield was sacrificed (Table 1, Entry 2). The potential of several commonly used phosphanes as catalysts was assessed in the nucleophilic addition reaction between **1** and **2a**. The results are summarized in Table 1. More nucleophilic phosphanes catalyzed this reaction to give the product **3a** with higher stereoselectivities. Of these catalysts, dimethyl(phenyl)phosphane ($PPhMe_2$) gave **3a** with the highest stereoselectivity but in a low yield (Table 1, Entry 7). PBu_3 catalyzed this reaction to give **3a** in excellent yield and with satisfactory stereoselectivity in THF (Table 1, Entry 8). The solvent effects were examined by using PBu_3 as the catalyst. *tert*-Butyl methyl ether (MTBE) was also a suitable solvent, giving **3a** in 80% yield with (*E*)/(*Z*) = 16.1:1 (Table 1, Entry 13), but the reaction did not take place effectively in acetonitrile or 1,2-dichloroethane (DCE) (Table 1, Entries 11 and 12).

Table 1. Catalyst and solvent screening for the reaction of ethyl 2-methyl-2,3-butadienoate (**1**) with 4-methoxyphenol (**2a**).[a]

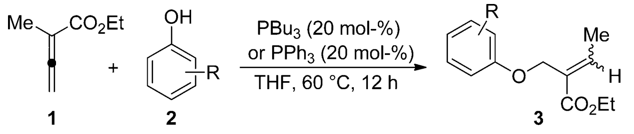


Entry	Solvent	Cat.	Yield [%][b]	(*E*)/(*Z*)[c]
1	THF	PPh_3	82	2.5:1
2[d]	THF	PPh_3	32	4.7:1
3	THF	$P(p\text{-}FC_6H_4)_3$	50	3.7:1
4	THF	$P(p\text{-}MeC_6H_4)_3$	89	4.9:1
5	THF	$P(p\text{-}MeOC_6H_4)_3$	57	1.8:1
6	THF	PPh_2Me	18	24.5:1
7	THF	$PPhMe_2$	44	32.1:1
8	THF	PBu_3	98	14.1:1
9	toluene	PBu_3	23	2.9:1
10	dioxane	PBu_3	64	8.4:1
11	CH_3CN	PBu_3	trace	–
12	DCE	PBu_3	8	11.6:1
13	MTBE	PBu_3	80	16.1:1

[a] All the reactions were performed with **1** (0.2 mmol) and **2a** (0.1 mmol) in 1.0 mL of solvent. [b] Isolated yields. [c] Determined by ^1H NMR spectroscopy. [d] At r.t.

Having identified the optimal reaction conditions, we next set out to examine the scope and limitations of this reaction by using various phenols **2** with different substituents on the benzene rings. The results are summarized in Table 2. As shown in Table 2, when phenols **2** bearing electron-donating groups at the *ortho*, *meta*, or *para* position of the benzene rings were employed, the reactions proceeded smoothly to give **3** in good to excellent yields with good stereoselectivities (Table 2, Entries 1–9). However, phenols **2** with electron-withdrawing groups on the benzene rings were not suitable substrates under the standard conditions, just giving traces of products. Therefore, it was necessary to reexamine the reaction conditions, focusing especially on the phosphane catalysts. Trimethylphosphane (PMe_3), which is a stronger nucleophilic phosphane than PBu_3, did not catalyze the reaction of **1** with phenols **2** bearing electron-withdrawing groups on the benzene rings. Analysis of the ^1H NMR spectroscopic data of the crude product showed the product derived from self-cycloaddition of **1** in the presence of the phosphane catalyst. The poor yields from the reactions of **1** with **2** having electron-withdrawing groups may be due to a rather slow reaction; meanwhile, **1** readily undergoes self-cycloaddition in the presence of strong nucleophilic phosphanes such as PBu_3 and PMe_3 (see the Supporting Information). Thus, we switched to the less nucleophilic phosphane PPh_3 as the catalyst in this reaction and found that satisfactory results could be obtained. As outlined in Table 2, phenols **2** bearing electron-withdrawing groups on the benzene rings or naphthols reacted with **1** smoothly to afford the corresponding products in good to excellent yields with acceptable stereoselectivities (Table 2, Entries 10–16).

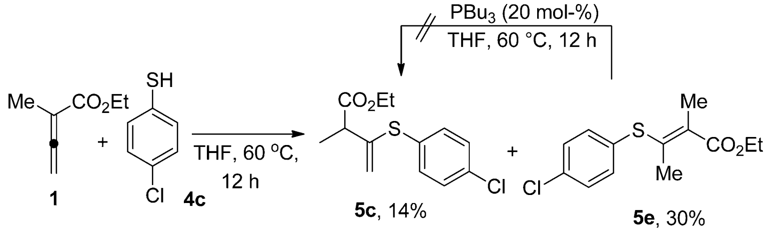
Table 2. Scope of the reactions of ethyl 2-methyl-2,3-butadienoate (**1**) with phenols **2**.[a]



Entry	R	Product	Yield [%][b]	(*E*)/(*Z*)[c]
1	4-*t*Bu	**3b**	98	16.3:1
2	$4\text{-}NH_2$	**3c**	98	18.1:1
3	$4\text{-}Ac(CH_2)_2$	**3d**	90	14.2:1
4	3-Me	**3e**	88	11.4:1
5	3-MeO	**3f**	95	11.8:1
6	2-Me	**3g**	89	9.8:1
7	2-MeO	**3h**	93	16.2:1
8	2-Bn	**3i**	94	8.0:1
9	H	**3j**	95	13.9:1
10[d]	4-Cl	**3k**	98	6.3:1
11[d]	$4\text{-}NO_2$	**3l**	82	11.1:1
12[d]	4-CN	**3m**	89	8.7:1
13[d]	3-Cl	**3n**	98	7.8:1
14[d]	2-Br	**3o**	98	8.8:1
15[d]	[e]	**3p**	97	7.4:1
16[d]	[f]	**3q**	98	5.7:1

[a] All the reactions were performed with **1** (0.4 mmol) and **2** (0.2 mmol) in 3.0 mL of THF. [b] Isolated yields. [c] Determined by ^1H NMR spectroscopy. [d] Catalyzed by 20 mol-% of PPh_3. [e] 1-Naphthol as the substrate. [f] 2-Naphthol as the substrate.

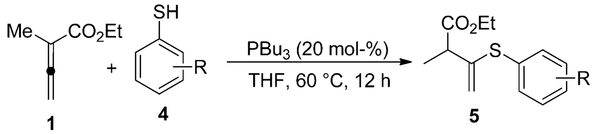
We next examined the reactions of **1** with sulfur nucleophiles in the presence of PBu_3. Under otherwise identical conditions, **1** reacted with thiophenols **4** smoothly to give the corresponding products **5** with different structures to **3** (Table 3). It is clear that product **5** is formed by nucleophilic addition of thiophenols **4** to the α,β-double bond of **1** through a Michael-type addition reaction. To clarify the reaction pathway, we performed some control experiments to further investigate the reaction mechanism (Scheme 2). Thiophenol **4c** also reacted with **1** in the absence of PBu_3



Scheme 2. Control experiments.

to give two adducts **5c** and **5e** (**5c**/**5e** = 1:2.1) in 44% total yield along with some unidentified byproducts. However, **5e** could not be transformed into **5c** under the standard reaction conditions, which suggests that PBu_3 is crucial in this reaction.

Table 3. Scope of the reactions of ethyl 2-methyl-2,3-butadienoate (**1**) with thiophenols **4**.[a]

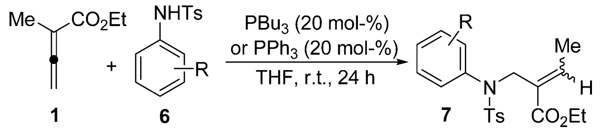


Entry	R	Yield [%][b]
1	H	**5a**, 94
2	4-Me	**5b**, 58
3	4-Cl	**5c**, 76
4	2,4-Cl_2	**5d**, 81

[a] All the reactions were performed with **1** (0.4 mmol) and **4** (0.2 mmol) in 3.0 mL of THF. [b] Isolated yields.

We also examined the reactions of **1** with nitrogen nucleophiles **6** in the presence of PBu_3. The results are summarized in Table 4. Tosyl-protected anilines with electron-donating groups at the *ortho*, *meta*, or *para* position of the aniline benzene ring underwent the nucleophilic addition reaction in the presence of PBu_3 at room temperature instead of 60 °C to give the corresponding products **7** in moderate to good yields with high stereoselectivities (Table 4, Entries 1–6). We also confirmed that products **7** could decompose to the starting materials at 60 °C in the presence of PBu_3. However, Ts-protected anilines with electron-withdrawing groups did not react with **1** in the presence of PBu_3, similarly to the reaction of **1** with phenols bearing electron-withdrawing groups. PPh_3 was able to solve this substrate limitation again to afford the products **7** from the reaction between Ts-protected anilines bearing either electron-donating or -withdrawing groups and **1** in excellent yields at room temperature, although the reaction rates were relatively low and the stereoselectivities poor (Table 4, Entries 7–10).

Table 4. Scope of the reactions of ethyl 2-methyl-2,3-butadienoate (**1**) with Ts-protected anilines **6**.[a]

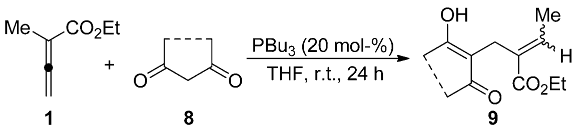


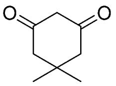
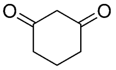
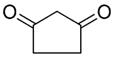
Entry	R	Product	Yield [%][b]	(*E*)/(*Z*)[c]
1	H	**7a**	79	10.5:1
2	4-MeO	**7b**	81	10.5:1
3	4-Me	**7c**	71	11.8:1
4	3-Me	**7d**	62	12.5:1
5	2-Me	**7e**	47	8.0:1
6	3,5-$(MeO)_2$	**7f**	35	15.4:1
7[d]	H	**7a**	99	1.6:1
8[d]	2-Me	**7e**	98	1.4:1
9[d]	3,5-$(MeO)_2$	**7f**	98	1.6:1
10[d]	4-Cl	**7g**	98	1.8:1

[a] All the reactions were performed with **1** (0.4 mmol) and **6** (0.2 mmol) in 3.0 mL of THF. [b] Isolated yields. [c] Determined by ^1H NMR spectroscopy. [d] Catalyzed by 20 mol-% of PPh_3 for 72 h.

Some carbon nucleophiles were also examined in this reaction. The results of these experiments are shown in Table 5. As can be seen from Table 5, cyclic 1,3-diones **8** also reacted with **1** smoothly to give the corresponding adducts **9** with enolization of one of the carbonyl groups in high yields with good stereoselectivities (Table 5). Dimethyl malonate was also examined in this reaction. However, the desired product was not formed in THF under the standard conditions.

Table 5. Scope of the reactions of ethyl 2-methyl-2,3-butadienoate (**1**) with cyclic 1,3-diones **8**.[a]



Entry[a]	**8**	Yield (%)[b]	(*E*)/(*Z*)[c]
1		**9a**, 81	12.7:1
2		**9b**, 76	11.2:1
3[d]		**9c**, 90	7.8:1

[a] All the reactions were performed with **1** (0.4 mmol) and **8** (0.2 mmol) in 3.0 mL of THF. [b] Isolated yields. [c] Determined by ^1H NMR spectroscopy. [d] At 60 °C.

Other allenoates, such as ethyl 2-ethyl-2,3-butadienoate, ethyl 2-benzyl-2,3-butadienoate, and ethyl 2-methyl-2,3-pentadienoate, were also examined in this interesting phosphane-catalyzed umpolung addition reaction. However, none of the desired products were formed under the standard reaction conditions with nucleophiles that are suitable for ethyl 2-methyl-2,3-butadienoate.

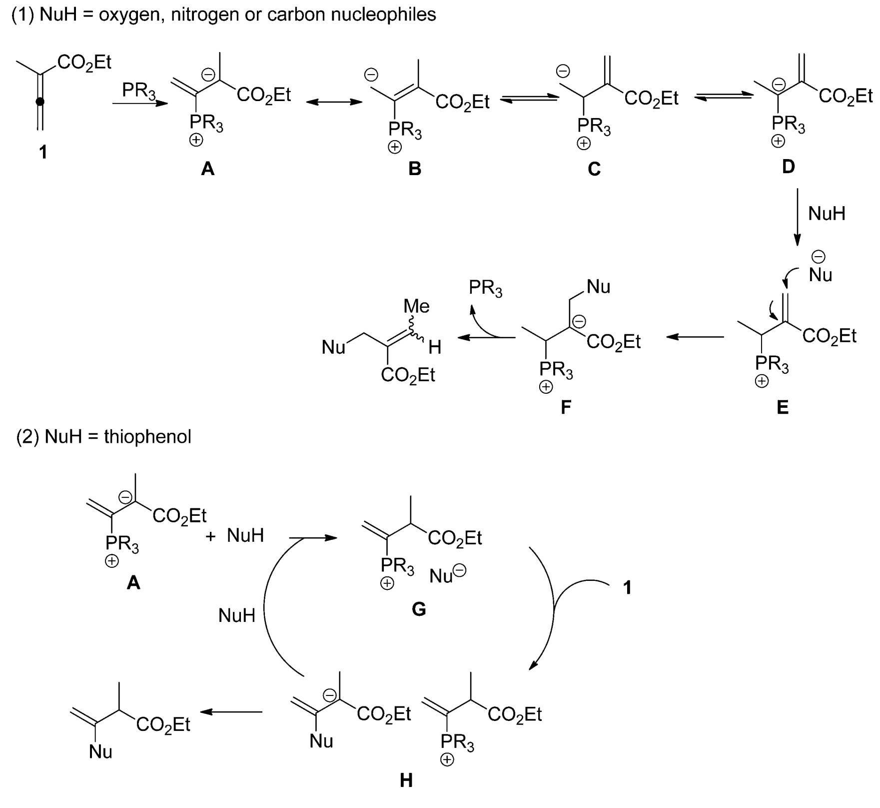
On the basis of the above results and previous reports in the literature,[3b,9t,10] a plausible mechanism for the phosphane-catalyzed umpolung addition reactions between ethyl 2-methyl-2,3-butadienoate (**1**) and different kinds of nucleophiles is proposed (Scheme 3). With oxygen, nitrogen, or carbon nucleophiles, PBu_3 or PPh_3 as nucleophilic initiator reacts with ethyl 2-methyl-2,3-butadienoate to produce the zwitterionic intermediate **A**, which can isomerize to intermediate **B**. Intermediate **B** can be further transformed into intermediate **D**, presumably via intermediate **C** by stepwise proton transfers. Intermediate **D** can deprotonate the pronucleophile employed to generate intermediate **E** and the corresponding nucleophilic anion. The nucleophilic anion undergoes subsequent addition to intermediate **E** to afford intermediate **F**. Subsequent elimination of the phosphane from **F** furnishes the corresponding product and regenerates the phosphane catalyst. With sulfur nucleophiles, the reaction proceeds in a different way. The zwitterionic intermediate **A** deprotonates the nucleophile to form the ion pair **G**. The nucleophilic anion in **G** then undergoes a subsequent conjugate addition to the α,β-double bond of **1** to afford the other ion pair **H**. Protonation of the anion partner in **H** results in the formation of the corresponding product and regenerates the ion pair **G** to complete the catalytic cycle. The reason for the difference between our results and those of Lu and co-workers is presumably due to the nucleophiles employed and solvent polarity. Different nucleophiles and solvents can lead to different results. In polar solvents such as THF (our work), intermediate **A** is inclined to be transformed into intermediate **D**. However, in nonpolar solvents such as benzene (Lu and co-workers), intermediate **A** predominately exists in the reaction system (Scheme 3).

Conclusion

We have developed a novel phosphane-catalyzed umpolung addition reaction for oxygen, nitrogen, and carbon nucleophiles with ethyl 2-methyl-2,3-butadienoate in which nucleophiles attack the 2-methyl group of ethyl 2-methyl-2,3-butadienoate. These addition reactions afforded the corresponding adducts in good to excellent yields with good to high stereoselectivities. As for sulfur nucleophiles, they added to the β-carbon atom of allenoates to give different adducts. Research is in progress to elucidate further mechanistic details of these reactions and to explore the scope and limitations of allenoates.

Experimental Section

General: ^1H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively. MS and HRMS was performed by using the ESI method. The organic solvents were dried by standard methods if it was necessary. Satisfactory CHN microanalyses were obtained with an analyzer. Commercially obtained reagents were used without further purification. All the reactions were monitored by



Scheme 3. Plausible mechanism for the phosphane-catalyzed umpolung addition of nucleophiles to ethyl 2-methyl-2,3-butadienoate.

TLC using silica gel coated plates. Flash column chromatography was carried out by using silica gel at increased pressure.

General Procedure for the PBu_3-Catalyzed Reaction of Ethyl 2-Methyl-2,3-butadienoate (1) with Phenols 2: Ethyl 2-methyl-2,3-butadienoate (**1**; 50 mg, 0.4 mmol), phenols (0.2 mmol), and PBu_3 (8 mg, 0.04 mmol) were stirred in THF (3.0 mL) under argon in a 10 mL Schlenk tube. After stirring the reaction mixture at 60 °C for 12 h, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography (SiO_2; EtOAc/petroleum ether, 1:30) to yield the corresponding product **3**.

Compound (*E*)-3a: Colorless oil (23 mg, 92% yield, 0.1 mmol scale). ^1H NMR ($CDCl_3$, 300 MHz, TMS): $\delta = 1.29$ (t, $J = 7.2$ Hz, 3 H, CH_3), 1.93 (d, $J = 7.5$ Hz, 3 H, CH_3), 3.77 (s, 3 H, OCH_3), 4.22 (q, $J = 7.2$ Hz, 2 H, OCH_2), 4.73 (s, 2 H, OCH_2), 6.80–6.85 (m, 2 H, Ar), 6.88–6.92 (m, 2 H, Ar), 7.19 (q, $J = 7.5$ Hz, 1 H, =CH) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): $\delta = 14.2$, 14.7, 55.7, 60.7, 62.6, 114.5, 116.1, 129.2, 144.2, 152.9, 154.0, 166.7 ppm. IR (CH_2Cl_2): $\tilde{\nu} = 2982$, 2939, 2907, 2834, 1710, 1506, 1282, 1222, 1139, 1036, 1012, 824, 732 cm^{-1}. MS (EI): *m*/*z* (%) = 250 (13.6) $[M]^+$, 124 (100.0), 123 (25.9), 109 (25.3), 95 (8.4), 53 (8.1), 205 (6.9), 54 (6.7), 41 (4.7). HRMS (EI): calcd. for $C_{14}H_{18}O_4$ $[M]^+$ 250.1205; found 250.1206.

Supporting Information (see footnote on the first page of this article): Spectroscopic data of all new compounds shown in Tables 1–5, detailed descriptions of experimental procedures.

Acknowledgments

We thank the Shanghai Municipal Committee of Science and Technology (08dj1400100-2), the National Basic Research Program of China (973-2010CB833302), and the National Natural Science Foundation of China for financial support (21072206, 20872162, 20672127, 20821002, 20732008, and 20702059).

---

[1] For reviews of umpolung reactions, see: a) D. Seebach, *Angew. Chem.* **1969**, *81*, 690–700; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 639–649; b) D. Seebach, *Synthesis* **1969**, 17–36; c) D. Seebach, *Angew. Chem.* **1979**, *91*, 259–278; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 239–258; d) T. A. Hase, *Umpoled Synthons*, Wiley, New York, **1987**; e) H. Stetter, H. Kuhlmann, *Org. React.* **1991**, *40*, 407–496; f) D. Enders, J. P. Shilvock, *Chem. Soc. Rev.* **2000**, *29*, 359–373; g) D. Enders, T. Balensiefer, *Acc. Chem. Res.* **2004**, *37*, 534–541; h) J. S. Johnson, *Angew. Chem.* **2004**, *116*, 1348–1350; *Angew. Chem. Int. Ed.* **2004**, *43*, 1326–1328; i) A. B. Smith, C. M. Adams, *Acc. Chem. Res.* **2004**, *37*, 365–377; j) C. Kison, N. Meyer, T. Opatz, *Angew. Chem.* **2005**, *117*, 5807–5809; *Angew. Chem. Int. Ed.* **2005**, *44*, 5662–5664; k) C. Burstein, S. Tschan, X. Xie, F. Glorius, *Synthesis* **2006**, 2418–2439; l) R. Brehme, D. Enders, R. Fernandez, J. M. Lassaletta, *Eur. J. Org. Chem.* **2007**, 5629–5660; m) J. S. Dickstein, M. C. Kozlowski, *Chem. Soc. Rev.* **2008**, *37*, 1166–1173; n) K. D. Moeller, *Synlett* **2009**, 1208–1218.

[2] For reviews on the reactions of allenes and allenoates, see: a) X. Lu, C. Zhang, Z. Xu, *Acc. Chem. Res.* **2001**, *34*, 535–544; b) S. Ma, *Acc. Chem. Res.* **2003**, *36*, 701–712; c) S. Ma, *Chem. Rev.* **2005**, *105*, 2829–2871; d) B. J. Cowen, S. J. Miller, *Chem. Soc. Rev.* **2009**, *38*, 3102–3116.

[3] For some examples using carbon nucleophiles, see: a) B. M. Trost, C.-J. Li, *J. Am. Chem. Soc.* **1994**, *116*, 3167–3168; b) C. Zhang, X. Lu, *Synlett* **1995**, 645–646; c) Z. Chen, G. Zhu, Q. Jiang, D. Xiao, P. Cao, X. Zhang, *J. Org. Chem.* **1998**, *63*, 5631–5635; d) S. W. Smith, G. C. Fu, *J. Am. Chem. Soc.* **2009**, *131*, 14231–14233; e) R. Sinisi, J.-W. Sun, G. C. Fu, *Proc. Natl. Acad. Sci. USA* **2010**, *107*, 20652–20654.

[4] For some examples using nitrogen nucleophiles, see: a) B. M. Trost, G. R. Dake, *J. Org. Chem.* **1997**, *62*, 5670–5671; b) B. M. Trost, G. R. Dake, *J. Am. Chem. Soc.* **1997**, *119*, 7595–7596; c) B. Liu, R. Davis, B. Joshi, D. W. Reynolds, *J. Org. Chem.* **2002**, *67*, 4595–4598; d) C. Lu, X. Lu, *Org. Lett.* **2002**, *4*, 4677–4679; e) V. Sriramurthy, G. A. Barcan, O. Kwon, *J. Am. Chem. Soc.* **2007**, *129*, 12928–12929; f) V. Sriramurthy, O. Kwon, *Org. Lett.* **2010**, *12*, 1084–1087.

[5] For some examples using oxygen nucleophiles, see: a) B. M. Trost, C.-J. Li, *J. Am. Chem. Soc.* **1994**, *116*, 10819–10820; b) C. Alvarez-Ibarra, A. G. Csaky, C. G. de la Oliva, *Tetrahedron Lett.* **1999**, *40*, 8465–8467; c) S. Gabillet, D. Lecerclé, O. Loreau, S. Dézard, J.-M. Gomis, F. Taran, *Synthesis* **2007**, 515–522; d) Y. K. Chung, G. C. Fu, *Angew. Chem.* **2009**, *121*, 2259–2261; *Angew. Chem. Int. Ed.* **2009**, *48*, 2225–2227.

[6] For some examples using sulfur nucleophiles, see: a) S. Cabiddu, E. Cadoni, E. Ciuffarin, C. Fattuoni, C. Floris, *J. Heterocycl. Chem.* **1991**, *28*, 1573–1580; b) S. Cabiddu, C. Fattuoni, M. Lucarini, G. F. Pedulli, *Tetrahedron* **1994**, *50*, 4001–4008; c) S. Gabillet, D. Lecerclé, O. Loreau, M. Carboni, S. Dézard, J.-M. Gomis, F. Taran, *Org. Lett.* **2007**, *9*, 3925–3927; d) J.-W. Sun, G. C. Fu, *J. Am. Chem. Soc.* **2010**, *132*, 4568–4569.

[7] a) S. R. Landor, *The Chemistry of Allene* (Ed.: S. R. Landor), Academic Press, New York, **1982**, vol. 2, pp. 361–397; b) X. Huang, R.-W. Shen, *Synthesis* **2006**, 2731–2737.

[8] A. Padwa, P. E. Yeske, *J. Org. Chem.* **1991**, *56*, 6386–6390.

[9] For some examples of the reactions of ethyl 2-methyl-2,3-butadienoates, see: a) M. E. Jung, N. Nishimura, *J. Am. Chem. Soc.* **1999**, *121*, 3529–3530; b) K. Kumar, A. Kapur, M. P. S. Ishar, *Org. Lett.* **2000**, *2*, 787–789; c) S. Ma, H. Xie, G. Wang, J. Zhang, Z. Shi, *Synthesis* **2001**, 713–730; d) M. E. Jung, N. Nishimura, *Org. Lett.* **2001**, *3*, 2113–2115; e) X. Zhu, J. Lan, O. Kwon, *J. Am. Chem. Soc.* **2003**, *125*, 4716–4717; f) S. Ma, N. Jiao, L. Ye, *Chem. Eur. J.* **2003**, *9*, 6049–6056; g) M. P. S. Ishar, A. Kapur, T. Raj, N. K. Girdhar, A. Kaur, *Synthesis* **2004**, 775–778; h) S. Ma, H. Xie, *Tetrahedron* **2005**, *61*, 251–258; i) M. E. Jung, N. Nishimura, A. R. Novack, *J. Am. Chem. Soc.* **2005**, *127*, 11206–11207; j) R. P. Wurtz, G. C. Fu, *J. Am. Chem. Soc.* **2005**, *127*, 12234–12235; k) G.-L. Zhao, Y.-L. Shi, M. Shi, *Org. Lett.* **2005**, *7*, 4527–4530; l) M. E. Jung, A. R. Novack, *Tetrahedron Lett.* **2005**, *46*, 8237–8240; m) M. Shi, L.-Z. Dai, Y.-L. Shi, G.-L. Zhao, *Adv. Synth. Catal.* **2006**, *348*, 967–972; n) X. Huang, R. Shen, T. Zhang, *J. Org. Chem.* **2007**, *72*, 1534–1537; o) S. Castellano, H. D. G. Fiji, S. S. Kinderman, M. Watanade, P. de Leon, F. Tamanoi, O. Kwon, *J. Am. Chem. Soc.* **2007**, *129*, 5843–5845; p) L.-Z. Dai, Y.-L. Shi, G.-L. Zhao, M. Shi, *Chem. Eur. J.* **2007**, *13*, 3701–3706; q) Y. S. Tran, O. Kwon, *J. Am. Chem. Soc.* **2007**, *129*, 12632–12633; r) X. Huang, F. Sha, *J. Org. Chem.* **2008**, *73*, 1173–1175; s) B. Chen, Z. Lu, G. Chai, C. Fu, S. Ma, *J. Org. Chem.* **2008**, *73*, 9486–9489; t) Y. Liang, S. Liu, Z. Yu, *Synlett* **2009**, 905–909; u) J. Yu, L. He, X.-H. Chen, J. Song, W.-J. Chen, L.-Z. Gong, *Org. Lett.* **2009**, *11*, 4946–4949.

[10] a) Z.-R. He, X.-F. Tang, Z.-J. He, *Phosphorus Sulfur Silicon Relat. Elem.* **2008**, *183*, 1518–1525; b) S.-L. Xu, W. Zou, G.-P. Wu, H.-B. Song, Z.-J. He, *Org. Lett.* **2010**, *12*, 3556–3559; c) I. C. Stewart, R. G. Bergman, F. D. Toste, *J. Am. Chem. Soc.* **2003**, *125*, 8696–8697.

Received: January 22, 2011