

Stereoselective Synthesis of 1,2,3,4-Tetrasubstituted Dienes from Allenates and Aldehydes: An Observation of Phosphine-Induced Chemoselectivity

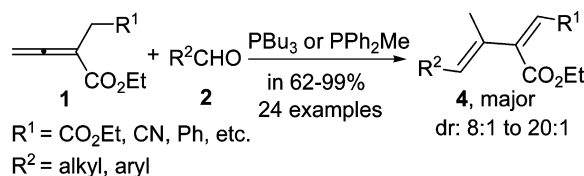
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ABSTRACT



Phosphine-mediated olefination between α -substituted allenates and aldehydes to form 1,2,3,4-tetrasubstituted 1,3-dienes is presented. High levels of chemo- and diastereoselectivity and yield are obtained for a wide scope of substrates with the choice of appropriate phosphines. This reaction evidences the capacity of phosphines in the control of reaction pathways and provides a highly efficient synthetic method for tetrasubstituted conjugated dienes.

Conjugated dienes are of great importance since they are present as substructures in a large number of naturally occurring and medicinally relevant substances¹ and also serve as versatile intermediates in many important organic transformations.² Classical procedures for the syntheses of 1,3-dienes mainly include the conventional elimination reactions from allyl bromide, allyl alcohol or dihalogenated compound,³ the P-, S-, and Si-based carbonyl olefinations,⁴ and the transition-metal-catalyzed diene formations.⁵ Despite the

effectiveness of the existing methods, the development of new strategies particularly aiming at the stereoselective synthesis of polysubstituted conjugated dienes remains challenging and highly desirable.⁶ Recently, much effort has been devoted to this area.⁷

During the past decade, chemical transformations involving allenates and a wide range of electron-poor C=C bonds

(1) (a) Glasby, J. S. *Encyclopaedia of the Terpenoids*; Wiley: Chichester, UK, 1982. (b) Devon, T. K.; Scott, A. I. *Handbook of Naturally Occurring Compounds*; Academic: New York, NY, 1972; Vol. II. (c) Pereira, A. R.; Cabezas, J. A. *J. Org. Chem.* **2005**, *70*, 2594–2597. (d) de Figueiredo, R. M.; Berner, R.; Julis, J.; Liu, T.; Turp, D.; Christmann, M. *J. Org. Chem.* **2007**, *72*, 640–642.

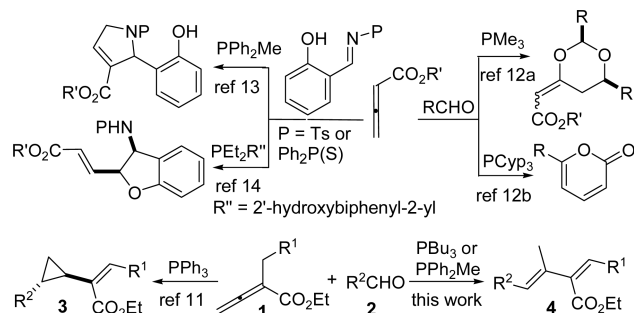
(2) (a) Rappoport, Z. *The Chemistry of Dienes and Polyenes*; John Wiley & Sons: Chichester, 1997; Vol. 1 and 2001; Vol. 2. (b) Nicolaou, K. C.; Snyder, S. S.; Montagnon, T.; Vassilikogiannakis, G. *Angew. Chem., Int. Ed.* **2002**, *41*, 1668–1698. (c) Negishi, E.-I.; Huang, Z.; Wang, G.; Mohan, S.; Wang, C.; Hattori, H. *Acc. Chem. Res.* **2008**, *41*, 1474.

(3) (a) Normant, J. F. *Modern Synthetic Methods*; Scheffold, R., Ed.; Wiley: Chichester, 1983; Vol. 3, pp 139–171. (b) Larock, R. C. *Comprehensive Organic Transformations*; VCH Publishers, Inc.: New York, 1989; pp 241–262.

(4) (a) Vedejs, E.; Peterson, M. J. *Advances in Carbanion Chemistry*; Snieckus, V., Ed.; Jai Press Inc.: Greenwich, CT, 1996; Vol. 2. (b) Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863–927. (c) Ager, D. J. *Org. React.* **1990**, *38*, 1–223. (d) Blakemore, P. R. *J. Chem. Soc., Perkin Trans. 1* **2002**, 2563–2585.

(5) For leading reviews, see: (a) Ref 2c. (b) Trost, B. M.; Toste, F. D.; Pinkerton, A. B. *Chem. Rev.* **2001**, *101*, 2067. (c) Aubert, C.; Buisine, O.; Malacria, M. *Chem. Rev.* **2002**, *102*, 813. (d) Diver, S. T.; Giessert, A. J. *Chem. Rev.* **2004**, *104*, 1317. (e) Nicolaou, K. C.; Bulger, P. G.; Sarlah, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 4442. (f) Hansen, E. C.; Lee, D. *Acc. Chem. Res.* **2006**, *39*, 509.

Scheme 1. Phosphine-Induced Chemoselectivity of Allenates



or polarized C=X bonds (X = N, O) under the mediation of phosphines have been extensively studied.⁸ A number of new reactions with high synthetic potentials have emerged, including many cycloaddition reactions,⁹ olefination,¹⁰ and cyclopropanation.¹¹ Relevant investigations have revealed that the electronic and steric properties of phosphines can exert significant influence on the reaction chemoselectivity. For example, Kwon et al.¹² reported that the use of small-size phosphine catalyst PMe_3 led to the formation of dioxane products, while bulky phosphines like PCyp_3 (Cyp = cyclopentyl) produced pyrones exclusively in the phosphine-catalyzed reactions of 2,3-butadienoates with aldehydes (Scheme 1, top right). Shi and co-workers¹³ demonstrated that under the catalysis of PPh_2Me the reaction of 2,3-butadienoates with salicylic imines afforded the normal [3 + 2] cycloadducts, whereas Huang's investigations¹⁴ unveiled that the difunctional catalyst (2'-hydroxybiphenyl-2-yl)-diethylphosphine was capable of tuning the reaction to a novel [4 + 1] annulation to form dihydrobenzofurans (Scheme 1, top left).

(6) (a) Ref 2c. (b) Vasil'ev, A. A.; Sterebryakov, E. P. *Russ. Chem. Rev.* **2001**, *70*, 735. (c) Clark, D. A.; Kulkarni, A. A.; Kalbarczyk, K.; Schertzer, B.; Diver, S. T. *J. Am. Chem. Soc.* **2006**, *128*, 15632. (d) Perez, L. J.; Shimp, H. L.; Micalizio, G. C. *J. Org. Chem.* **2009**, *74*, 7211.

(7) (a) Zhang, X.; Larock, R. C. *Org. Lett.* **2003**, *5*, 2993. (b) Fu, C.; Ma, S. *Org. Lett.* **2005**, *7*, 1707. (c) Horiguchi, H.; Tsurugi, H.; Satoh, T.; Miura, M. *Adv. Synth. Catal.* **2008**, *350*, 509. (d) Aponte, J. C.; Hammond, G. B.; Xu, B. *J. Org. Chem.* **2009**, *74*, 4623. (e) Mundal, D. A.; Lutz, K. E.; Thomson, R. J. *Org. Lett.* **2009**, *11*, 465. (f) Zhang, X.; Larock, R. C. *Tetrahedron* **2010**, *66*, 4265. (g) Paih, J. L.; Bray, C. C.; Dérien, S.; Dixneuf, P. H. *J. Am. Chem. Soc.* **2010**, *132*, 7391.

(8) For recent reviews, see: (a) Lu, X.; Zhang, C.; Xu, Z. *Acc. Chem. Res.* **2001**, *34*, 535. (b) Methot, J. L.; Roush, W. R. *Adv. Synth. Catal.* **2004**, *346*, 1035. (c) Nair, V.; Menon, R. S.; Sreekanth, A. R.; Abhilash, N.; Biju, A. T. *Acc. Chem. Res.* **2006**, *39*, 520. (d) Ma, S. *Chem. Rev.* **2005**, *105*, 2829. (e) Ma, S. *Aldrichimica Acta* **2007**, *40*, 91. (f) Ye, L.-W.; Zhou, J.; Tang, Y. *Chem. Soc. Rev.* **2008**, *37*, 1140. (g) Cowen, B. J.; Miller, S. J. *Chem. Soc. Rev.* **2009**, *38*, 3102.

(9) For selected examples, see: (a) Zhang, C.; Lu, X. *J. Org. Chem.* **1995**, *60*, 2906. (b) Xu, Z.; Lu, X. *Tetrahedron Lett.* **1997**, *38*, 3461. (c) Xu, S.; Zhou, L.; Ma, R.; Song, H.; He, Z. *Chem.—Eur. J.* **2009**, *15*, 8698. (d) Tran, Y. S.; Kwon, O. *J. Am. Chem. Soc.* **2007**, *129*, 12632. (e) Zhu, X.-F.; Lan, J.; Kwon, O. *J. Am. Chem. Soc.* **2003**, *125*, 4716.

(10) Xu, S.; Zhou, L.; Zeng, S.; Ma, R.; Wang, Z.; He, Z. *Org. Lett.* **2009**, *11*, 3498.

(11) Xu, S.; Zhou, L.; Ma, R.; Song, H.; He, Z. *Org. Lett.* **2010**, *12*, 544.

(12) (a) Zhu, X.-F.; Henry, C. E.; Wang, J.; Dudding, T.; Kwon, O. *Org. Lett.* **2005**, *7*, 1387. (b) Zhu, X.-F.; Schaffner, A.-P.; Li, R. C.; Kwon, O. *Org. Lett.* **2005**, *7*, 2977. (c) Creech, G. S.; Kwon, O. *Org. Lett.* **2008**, *10*, 429.

(13) Shi, Y.-L.; Shi, M. *Org. Lett.* **2005**, *7*, 3057.

(14) Meng, X.; Huang, Y.; Chen, R. *Org. Lett.* **2009**, *11*, 137.

Recently, we reported a novel PPh_3 -mediated reductive cyclopropanation between α -substituted allenates **1** and aldehydes **2** to afford highly functionalized cyclopropanes **3**, in which PPh_3 acted as both a nucleophilic trigger and a deoxygenating agent (Scheme 1, bottom left).¹¹ Further survey on this reaction revealed that the choice of phosphines had a dramatic impact on the reaction chemoselectivity, leading to a new phosphine-mediated olefination reaction to form 1,2,3,4-tetrasubstituted 1,3-dienes **4** (Scheme 1, bottom right). Herein we wish to communicate the results from such a survey.

Table 1. Survey on Conditions for Formation of **4a**^a

entry	PR ₃	solvent	time (h)	3a : yield (%) ^b	4a : yield (%) ^b , dr ^c
1	PBu ₃	CH ₂ Cl ₂	8	5	84, 20:1
2	PPhMe ₂	CH ₂ Cl ₂	48	trace	68, 20:1
3	PPh ₂ Me	CH ₂ Cl ₂	48	trace	70, 6:1
4	PTA	CH ₂ Cl ₂	54	8	66, 20:1
5	Ph ₃ P	CH ₂ Cl ₂	48	48	/
6	P(OMe) ₃	CH ₂ Cl ₂	48	/	/
7	P(NMe ₂) ₃	CH ₂ Cl ₂	48	/	/
8	PBu ₃	CH ₃ CN	23	44	31, 20:1
9	PBu ₃	1,4-dioxane	30	7	40, 20:1
10	PBu ₃	DMSO	6	25	35, 20:1
11	PBu ₃	DMF	27	55	25, 20:1
12	PBu ₃	EtOH	33	/	14, 20:1
13	PBu ₃	toluene	23	6	81, 20:1
14	PBu ₃	xylene	30	17	64, 20:1
15	PBu ₃	THF	23	15	84, 20:1
16	PBu ₃	CHCl ₃	24	3	87, 20:1
17	PBu ₃	ethyl acetate	7	17	76, 20:1
18 ^d	PBu ₃	CHCl ₃	24	10	57, 20:1
19 ^e	PBu ₃	CHCl ₃	24	3	96, 20:1

^a Typical conditions: under N₂ atmosphere and at room temperature, to a stirred solution of aldehyde **2a** (0.2 mmol) and allenate **1a** (0.3 mmol) in solvent (2 mL) was added phosphorus reagent (0.3 mmol). ^b Isolated yield based on **2a**. ^c Based on the ¹H NMR assay of crude product with (Z,E)-**4a** being the major. ^d 1.0 equiv of water was added. ^e 5 mL of solvent was used.

Initial investigation showed that employing more nucleophilic PBu₃ instead of PPh₃ in the reaction of allenate **1a** and benzaldehyde (**2a**) in CH₂Cl₂ at room temperature led to the formation of diene **4a** in 84% yield and excellent diastereoselectivity (dr 20:1), along with only a small amount of cyclopropane **3a** (5% yield) (Table 1, entry 1). Several other nucleophilic phosphorus reagents were also examined. Ph₂PMe, PhPMe₂, and 1,3,5-triaza-7-phosphaadamantane (PTA)¹⁵ also readily produced the diene **4a**, but in lower yields or diastereoselectivity compared with PBu₃ (entries 2–4). PPh₃ only gave cyclopropane **3a** in 48% yield under similar conditions (entry 5), while P(OMe)₃ and P(NMe₂)₃ failed to mediate either cyclopropanation or olefination reaction (entries 6, 7). With the choice of PBu₃ as the

(15) An air-stable and water-soluble phosphine, often used as a nucleophilic trialkylphosphine. See ref 10 and references cited therein.

phosphine agent, further survey on conditions indicated such polar solvents as CH₃CN, 1,4-dioxane, DMSO, DMF, and ethanol were detrimental to the olefination reaction with regard to yield and chemoselectivity (entries 8–12). Among other tested solvents (entries 13–17), CHCl₃ emerged as the best, giving diene **4a** in 87% yield and excellent stereoselectivity (entry 16). Addition of water as a protic additive resulted in substantial decrease in both yield and chemoselectivity (entry 18). To our surprise, a relatively dilute reactant concentration was found to be good for the olefination, which gave **4a** in almost quantitative yield when run at 0.04 M concentration of **2a** (entry 19). Thus, the optimal conditions for the olefination were established.

Table 2. Synthesis of **4** from Allenates **1** and Aldehydes **2**^a

R¹: CO₂Et (**1a**), CN (**1b**), Ph (**1c**), *E*-styryl (**1d**)

entry	1	R ² in 2	time (h)	3 (%) ^b	4 (%) ^b , dr ^c
1	1a	C ₆ H ₅	24	3a , 3	4a , 96, 20:1
2	1a	4-CH ₃ C ₆ H ₄	24	3b , 3	4b , 85, 20:1
3	1a	4-CH ₃ OC ₆ H ₄	24	\	4c , 87, 20:1
4	1a	2-CH ₃ OC ₆ H ₄	23	3c , 99	\
5	1a	2-OHC ₆ H ₄	1	\	4d , 72, 20:1
6	1a	3-Br-4-CH ₃ OC ₆ H ₃	4	\	4e , 88, 20:1
7	1a	4-ClC ₆ H ₄	24	3d , 9	4f , 90, 20:1
8	1a	3-ClC ₆ H ₄	24	3e , 12	4g , 62, 9:1
9	1a	2-ClC ₆ H ₄	24	3f , 83	\
10	1a	4-IC ₆ H ₄	3	3g , 13	4h , 69, 12:1
11	1a	3-BrC ₆ H ₄	1	3h , 14	4i , 72, 10:1
12	1a	4-FC ₆ H ₄	2.5	3i , 8	4j , 84, 11:1
13 ^d	1a	4-NO ₂ C ₆ H ₄	1	3j , 2	4k , 63, 8:1
14 ^d	1a	3-NO ₂ C ₆ H ₄	1.2	\	4l , 79, 12:1
15 ^d	1a	4-CF ₃ C ₆ H ₄	6	3k , 4	4m , 95, 20:1
16 ^d	1a	3-CF ₃ C ₆ H ₄	6	\	4n , 96, 20:1
17 ^d	1a	2-CF ₃ C ₆ H ₄	4	3l , 51	\
18	1a	2-furyl	4	\	4o , 88, 20:1
19	1a	2-thiofuryl	1	\	4p , 85, 20:1
20	1a	<i>E</i> -styryl	24	\	4q , 80, 20:1
21	1a	C ₂ H ₅	40	\	4r , 98, 20:1
22	1a	<i>n</i> -C ₃ H ₇	24	\	4s , 99, 20:1
23	1a	<i>iso</i> -C ₄ H ₉	24	\	4t , 97, 20:1
24	1a	<i>n</i> -C ₅ H ₁₁	24	\	4u , 87, 20:1
25 ^{d,e}	1b	C ₆ H ₅	24	\	4v , 63, 12:1
26	1c	C ₆ H ₅	24	\	4w , 91, 17:1
27	1d	C ₆ H ₅	4	\	4x , 79, 20:1

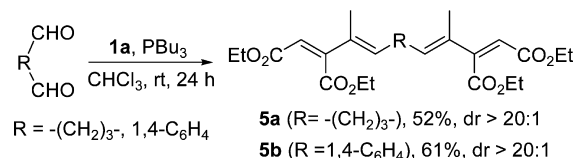
^a For details, see Supporting Information. ^b Isolated yield based on **2**. ^c Based on the ¹H NMR assay of crude product. ^d PPh₂Me was used instead of PBu₃. ^e 2.0 equiv of both **1b** and phosphine was used.

Under the optimized conditions, the substrate scope of this olefination was examined (Table 2). A variety of aldehydes **2** were explored with the allenolate **1a**. Except some *o*-substituted ones, aromatic aldehydes with electron-donating or -withdrawing groups readily gave dienes **4** in fair to excellent yields with good to high levels of diastereoselectivity (entries 1–17). *o*-Substituted benzaldehydes exclusively afforded cyclopropanation products **3** in 51–99%

yields (entries 4, 9, 17) with an exception of salicylaldehyde, which underwent the olefination to give the corresponding diene **4d** in 72% yield (entry 5).¹⁶ Relatively electron-rich benzaldehydes exhibited better chemoselectivity for the olefination, predominantly affording the dienes **4** in good to excellent yields (entries 1–3, 5–6). Halo-benzaldehydes produced the corresponding dienes **4** as the major associated with the cyclopropanation products as the minor (entries 7, 8, 10–12). For the more reactive benzaldehydes bearing electron-withdrawing substituents, their olefinations with the allenolate **1a** were better mediated with the less nucleophilic phosphine PPh₂Me, readily giving the dienes in fair to excellent yields (entries 13–16). Heteroaromatic aldehydes like furylaldehyde or thiofurylaldehyde also proved effective in the olefination with **1a**, giving the dienes **4o** and **4p** in good yields (entries 18, 19).

An α,β -unsaturated aldehyde such as (*E*)-cinnamaldehyde was also effective, giving (*Z,E,E*)-triene **4q** in 80% yield (Table 2, entry 20). Aliphatic aldehydes, in sharp contrast with their failure in the reported cyclopropanation,¹¹ worked well in the PBu₃-mediated olefination with allenolate **1a**, providing the corresponding dienes **4** in excellent yields with high chemo- and stereoselectivities (entries 21–24). Notably, dialdehydes like glutaraldehyde and terephthalaldehyde readily incorporated with two molecules of the allenolate **1a**, forming tetraenes **5a** and **5b**, respectively, in moderate yield and high stereoselectivity (Scheme 2).

Scheme 2. Synthesis of Tetraenes **5** from Dialdehydes and **1a**



Several structurally similar α -substituted allenates **1** (R¹ = CN, **1b**; Ph, **1c**; *E*-styryl, **1d**; *n*-Pr, **1e**; H, **1f**) were also investigated in the olefination with benzaldehyde. The allenates **1b**, **1c**, and **1d** all exhibited reactivity similar to that of **1a** and readily underwent the olefination under the mediation of PBu₃ or PPh₂Me, giving the corresponding dienes **4v** and **4w** or the triene **4x** in 63–91% yields and high stereoselectivity (Table 2, entries 25–27). However, α -butyl allenolate **1e** and α -methyl allenolate **1f** both failed to afford the corresponding olefination products.¹⁷ This fact implies that an unsaturated conjugative group R¹ in **1** is required to effect the phosphine-mediated olefination.

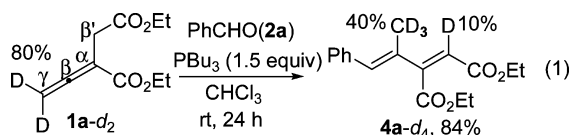
In all cases of the olefination listed in Table 2, the diastereoselectivity of the olefination products **4** remained on a modest to high level (8:1 to 20:1) with the illustrated isomer **4** as the major product. The structures and relative stereochemistry of the olefination products **4** and **5** were well

(16) The exceptional reactivity of *o*-substituted benzaldehydes, which presumably results from the increased steric hindrance, in the reactions with allenates was also observed in ref 12a.

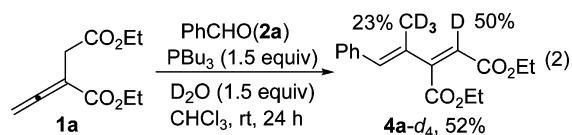
(17) A distinct Wittig olefination of α -methyl allenolate **1f** with salicylaldehydes or aromatic aldehydes to form *trisubstituted* dienes was observed: (a) He, Z.; Tang, X.; He, Z. *Phosphorus Sulfur Silicon Relat. Elem.* **2008**, *183*, 1518. (b) Khong, S. N.; Tran, Y. S.; Kwon, O. *Tetrahedron* **2010**, *66*, 4760.

identified by ^1H and ^{13}C NMR spectra and in some cases also by NOESY and X-ray crystallographic analyses (for characterization data, see Supporting Information).

The mechanism of the phosphine-mediated olefination was investigated through ^{31}P NMR tracking and deuterium-labeling experiments (for details, see Supporting Information). The reaction between the allenolate **1a** (0.075 mmol), *p*-chlorobenzaldehyde (0.05 mmol), and PBU_3 (0.075 mmol) in CDCl_3 (0.5 mL) was run in an NMR tube and monitored by ^{31}P NMR spectroscopy. An appreciable signal at δ 21.7 ppm appeared in the course of the reaction, along with two signals (δ 48.6 and -30.8 ppm) which corresponded to Bu_3PO and PBU_3 , respectively. This signal could disappear in 5 min upon addition of more *p*-chlorobenzaldehyde (up to 0.025 mmol) into the sample. This result, in combination with the ^{31}P NMR chemical shift (δ 21.7 ppm), strongly implied that the emerging signal most likely came from a tetracoordinate phosphorus ylide intermediate.¹⁸ In the deuterium-labeling experiments, a deuterated allenolate **1a-d**₂ (80% D) was subjected to the PBU_3 -mediated olefination with benzaldehyde, resulting in a deuterated diene **4a-d**₄ in 84% yield with 40% and 10% deuterium at the γ - and β' -carbons, respectively (eq 1). In contrast with this result,



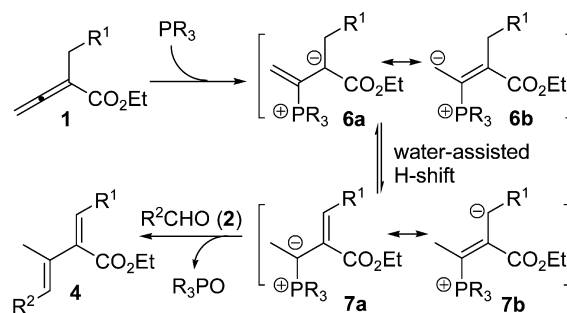
addition of D_2O (1.5 equiv) into the reaction of the nondeuterated allenolate **1a** with benzaldehyde also brought about partially deuterated product **4a-d**₄ in 52% yield with similar deuterium incorporations at the same carbons under otherwise identical conditions (eq 2). These results clearly indicated that a water-involved hydrogen shift occurred between the γ - and β' -hydrogens of the allenolate **1a**.



A plausible mechanism for the olefination is depicted in Scheme 3. Initially, nucleophilic attack of the phosphine on the allenolate **1** forms the resonance-stabilized zwitterionic intermediate **6**. Via a water-assisted hydrogen shift,¹⁹ **6** reversibly converts into the allylic phosphorus ylide **7**, which also exists in two resonance forms **7a** and **7b**. When R^1 in **7** is an unsaturated conjugative group such as CO_2Et , CN, Ph, or styryl, it is believed that the more stable form **7a** should be the major contributor to the phosphorus ylide **7** which is subsequently intercepted by an aldehyde **2** via a Wittig reaction yielding the olefination product **4**.

(18) Hudson, H. R.; Dillon, K. B.; Walker, B. J. ^{31}P NMR Data of Four Coordinate Phosphonium Salts and Betaines. In *Handbook of Phosphorus-31 Nuclear Magnetic Resonance Data*; Tebb, J. C., Ed.; CRC Press: Boca Raton, FL, 1991; pp 181–226.

Scheme 3. Proposed Mechanism for Formation of **4**



The high chemoselectivity in the olefination between allenolates **1** and aldehydes **2** may be ascribed to the increased reactivity of the in situ formed phosphorus ylide **7** for the Wittig reaction by employing electron-rich phosphines like PBU_3 .^{4b} Also, the high stereoselectivity of the olefination in this study could be well rationalized in terms of the Wittig reaction of the stabilized allylic phosphorus ylide **7** under neutral and salt-free conditions.²⁰

In conclusion, a novel phosphine-mediated olefination of α -substituted allenolates with aldehydes has been successfully realized by choosing more nucleophilic phosphines. This olefination provides an efficient method for stereoselective synthesis of 1,2,3,4-tetrasubstituted 1,3-dienes from readily available starting materials. On the basis of the results in this work, the in situ generated phosphorus ylide **7** is believed to be the key intermediate which is responsible for the subsequent Wittig reaction with the aldehyde. Recently, in situ formed phosphorus ylides have proven to be powerful in construction of carbon carbon double bonds.²¹ Future efforts on this olefination will be directed toward broadening its application in the synthesis of conjugated dienes and polyenes.

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Supporting Information Available: Experimental details, characterization data for new compounds, ^1H and ^{13}C NMR spectra for **3**, **4**, and **5**, as well as the X-ray crystallographical data (CIF files) for **4b** and **4k**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(19) For representative studies on the water-assisted hydrogen shift in nucleophilic phosphine catalyses of allenolates, see: (a) refs 9c and 9d. (b) Guo, H.; Xu, Q.; Kwon, O. *J. Am. Chem. Soc.* **2009**, *131*, 6318. (c) Xia, Y.; Liang, Y.; Chen, Y.; Wang, M.; Jiao, L.; Huang, F.; Liu, S.; Li, Y.; Yu, Z.-X. *J. Am. Chem. Soc.* **2007**, *129*, 3470. (d) Liang, Y.; Liu, S.; Xia, Y.; Li, Y.; Yu, Z.-X. *Chem.-Eur. J.* **2008**, *14*, 4361. (e) Liang, Y.; Liu, S.; Yu, Z.-X. *Synlett* **2009**, 905.

(20) (a) Robiette, R.; Richardson, J.; Aggarwal, V. K.; Harvey, J. N. *J. Am. Chem. Soc.* **2006**, *128*, 2394. (b) Zhou, R.; Wang, C.; Song, H.; He, Z. *Org. Lett.* **2010**, *12*, 976.

(21) For representative examples, see: (a) Refs 10 and 20b. (b) Low, K. H.; Magomedov, N. A. *Org. Lett.* **2005**, *7*, 2003. (c) McDougal, N. T.; Schaus, S. E. *Angew. Chem., Int. Ed.* **2006**, *45*, 3117.