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Phosphine-Mediated Stereoselective Reductive Cyclopropanation of α-Substituted Allenoates with Aromatic Aldehydes

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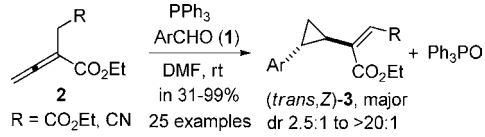
ABSTRACT



A novel phosphine-mediated reductive cyclopropanation between α-substituted allenoates 2 and aldehydes 1 is described. It represents a new member of the allene-based annulations, which provides facile and efficient access to highly functionalized cyclopropanes 3 from simple and readily available starting materials. It also unveils an unprecedented reactivity pattern of allenoates with aldehydes.

The development of efficient methods to construct the cyclopropane motif is of great importance in synthetic organic chemistry since this molecular architecture is present in a large number of naturally occurring and medicinally relevant substances.[1] Moreover, the rigid structure and strain-driven reactivity make cyclopropyl derivatives attractive as versatile intermediates in organic synthesis.[2] Over the past decades, vast efforts from chemists have been engaged by this area. As a result, many effective methodologies enabling the generation of diverse three-membered carbocycles with high chemo- and stereoselectivity have been developed,[3] which could be simply classified as the Simmons−Smith process,[4] metal−carbenoid reaction,[5] Michael-initiated ring closure (MIRC) reaction,[6] and recently emerging organocatalytic cyclopropanation.[7] Even so, complementary new approaches with high synthetic efficiency to build this all-carbon triangular structure from simple and readily available starting materials remain highly desirable.

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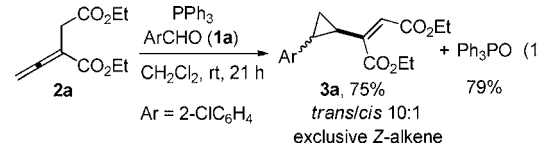
During the past decade, phosphine-triggered annulation reactions employing electron-deficient allenes have emerged as a facile protocol for the construction of a variety of carbocycles and heterocycles.[8] For example, the extensively studied Lu's [3 + 2] cycloadditions of allenoates with activated olefins or imines provide convenient and practical access to various five-membered carbocycles and nitrogen heterocycles;[9] using α-substituted allenoates as a reactant, both [4 + 2] annulation with activated olefins or imines and [3 + 3] annulation with aziridines have been realized by Kwon, providing facile entries into highly functionalized cyclohexenes and tetrahydropyridines.[8j,k,10] Up to date, these allene-based annulations with various electrophiles constitute a valuable platform to build five-, six-, and seven-membered ring systems. Some of them have also been successfully utilized in the syntheses of natural or biologically important substances.[11] In this context, herein we wish to report a phosphine-mediated reductive cyclopropanation of α-substituted allenoates with aldehydes as the first example of the allene-based synthesis of the smallest carbocycle.

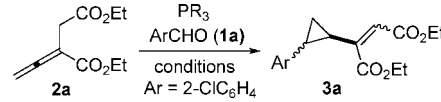
Regarding those with activated olefins or imines, the reactivities of electron-poor allenes with aldehydes under the mediation of a nucleophilic phosphine were much less explored. The pioneering works by Kwon revealed interesting and distinctive reactivity patterns between nonsubstituted allenoates and aldehydes, leading to efficient syntheses of oxygen-containing heterocycles like 1,3-dioxanes, pyrones, and dihydropyrones.[12] Very recently, two new phosphine-mediated reactivity modes of γ-substituted allenoates with aldehydes were reported by our group: typically, γ-methyl allenoates underwent a phosphane-catalyzed [3 + 2] annulation with aromatic aldehydes to form tetrahydrofurans,[8l] and γ-benzyl allenoates gave rise to a stoichiometric phosphine-mediated olefination with both aliphatic and aromatic aldehydes to yield 1,3-dienes with high stereoselectivity.[13] Intrigued by these exciting findings together with those specific reactivity patterns like [4 + 2] annulations of α-substituted allenoates with activated olefins or imines,[8j,10] we attempted to investigate the possible reactions between α-substituted allenoates and aldehydes under the influence of a nucleophilic phosphine.[14] Gratifyingly, this attempt led to the discovery of a new allene-based annulation.

Initially, we examined the reaction of diethyl 2-vinylidenesuccinate (**2a**, 0.75 mmol) and 2-chlorobenzaldehyde (**1a**, 0.5 mmol) with PPh_3 (0.75 mmol) (eq 1). To our delight, the reaction proceeded smoothly in dichloromethane (5 mL) at room temperature, affording vinyl cyclopropane **3a** in 75% yield and excellent diastereoselectivity (*trans*/*cis* = 10:1, *Z* alkene isomer only). Identification of the product **3a**, in combination with isolation of the byproduct triphenylphosphine oxide in comparable yield, clearly implied that a stoichiometric phosphine-mediated reductive cyclopropanation between allenoate **2a** and aldehyde **1a** occurred. To our knowledge, this reaction unveiled an unprecedented reactivity pattern of allenoates with aldehydes, as well as a new synthesis for highly functionalized cyclopropanes.



Further survey on reaction conditions was carried out by using the reaction of **2a** and **1a** as a probe (Table 1). Among a series of nucleophilic phosphorus reagents screened, trimethyl phosphite and hexamethyl phosphorus triamide

Table 1. Survey on Conditions for the Reductive Cyclopropanation of the Allenoate **2a** with Aldehyde **1a**[a]



entry	PR_3	solvent	time (h)	yield (%)[b]	dr[c]
1	$P(OMe)_3$	CH_2Cl_2	120	0	N/A
2	$P(NMe_2)_3$	CH_2Cl_2	120	0	N/A
3	PPh_3	CH_2Cl_2	21	75	10:1
4	Ph_2PMe	CH_2Cl_2	24	62	3:1
5	$PhPMe_2$	CH_2Cl_2	21	50	3:1
6	PBu_3	CH_2Cl_2	14	68	3:1
7	PPh_3	THF	47	46	10:1
8	PPh_3	toluene	22	72	10:1
9	PPh_3	DMSO	8	85	10:1
10	PPh_3	1,4-dioxane	21	65	10:1
11	PPh_3	DMF	23	96	10:1
12	PPh_3	CH_3CN	13	68	10:1
13	PPh_3	ethanol	13	0	N/A
14[d]	PPh_3	DMF	41	73	10:1
15[e]	PPh_3	DMF	6	99	10:1

[a] Typical conditions: under N_2 atmosphere and at room temperature, to a stirred solution of aldehyde **1a** (0.5 mmol) and phosphorus reagent (0.75 mmol) in solvent (2 mL) was added a solution of allenoate **2a** (0.75 mmol) in solvent (3 mL). [b] Combined yield of isolated diastereomers (based on **1a**). [c] Calculated by the major (*trans*,*Z*)-**3a** versus the sum of other isolated diastereomers. [d] PPh_3 and **2a** were used in 1.2 equiv. [e] PPh_3 and **2a** were used in 2.0 equiv.

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could not mediate the reaction (entries 1, 2), and phosphines with relatively stronger nucleophilicity such as Ph_2PMe, $PhPMe_2$, and Bu_3P also readily produced the cyclopropane **3a** in comparable yield, but only in modest diastereoselectivity (entries 4−6). With 1.5 equiv of Ph_3P used, screening of common solvents revealed that DMF was the best, affording **3a** in 96% yield and high diastereoselectivity (entry 11). Other solvents also gave moderate to good yields (entries 7−10, 12) except that ethanol completely inhibited the cyclopropanation (entry 13).[15] Lowering the amounts of the allenoate and PPh_3 to 1.2 equiv resulted in substantial decrease in the yield (entry 14), while increasing the amounts to 2.0 equiv led to almost quantitative yield (entry 15). Thus, the cyclopropanation was best run in DMF at room temperature with 1.5 or 2.0 equiv of both allenoate and PPh_3.

Under the optimized conditions, the generality of this cyclopropanation was further explored (Table 2). A variety of aldehydes were examined with the allenoate **2a**. Aromatic aldehydes with halogen or electron-withdrawing groups readily gave the desired cyclopropanes **3** in fair to excellent yields and modest to high diastereoselectivity (entries 1−13). Heteroaromatic aldehydes like pyridyl- and furylaldehydes also worked well (entries 14−17). Relatively electron-rich benzaldehydes were less reactive and afforded only moderate yields but high diastereoselectivity (entries 18−20). Conversely, alkyl aldehydes like propylaldehyde and butyraldehyde were totally ineffective in this cyclopropanation.

Table 2. Synthesis of Highly Functionalized Cyclopropanes **3** from Allenoates **2** and Aldehydes **1**[a]

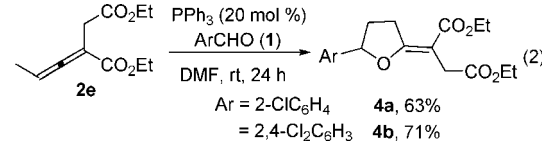
entry	Ar	R	time (h)	yield (%)[b]	dr[c]
1	2-ClC_6H_4	CO_2Et	23	**3a**, 96	10:1
2	4-ClC_6H_4	CO_2Et	46	**3b**, 71	10:1
3	2-FC_6H_4	CO_2Et	16	**3c**, 84	9:1
4[d]	4-FC_6H_4	CO_2Et	41	**3d**, 57	>20:1
5[e]	2,4-$Cl_2C_6H_3$	CO_2Et	12	**3e**, 97	5:1
6[d]	4-IC_6H_4	CO_2Et	45	**3f**, 78	>20:1
7	2-$NO_2C_6H_4$	CO_2Et	14	**3g**, 99	3:1
8[e]	3-$NO_2C_6H_4$	CO_2Et	6	**3h**, 98	5:1
9	4-$NO_2C_6H_4$	CO_2Et	5	**3i**, 82	4:1
10	2-$CF_3C_6H_4$	CO_2Et	19	**3j**, 93	>20:1
11	4-$CF_3C_6H_4$	CO_2Et	11	**3k**, 98	>20:1
12	2-CNC_6H_4	CO_2Et	17	**3l**, 91	3:1
13	3-CH_3O-2-$NO_2C_6H_3$	CO_2Et	13	**3m**, 88	5:1
14	2-pyridyl	CO_2Et	22	**3n**, 78	8:1
15	3-pyridyl	CO_2Et	12	**3o**, 99	6:1
16	4-pyridyl	CO_2Et	3	**3p**, 86	>20:1
17	2-furyl	CO_2Et	71	**3q**, 71	>20:1
18[d]	C_6H_5	CO_2Et	60	**3r**, 50	>20:1
19[d]	4-$CH_3C_6H_4$	CO_2Et	60	**3s**, 35	>20:1
20[d]	2-$CH_3OC_6H_4$	CO_2Et	69	**3t**, 31	>20:1
21[f]	4-$CF_3C_6H_4$	CN	24	**3u**, 53	>20:1
22[f]	4-$NO_2C_6H_4$	CN	7	**3v**, 51	>20:1
23[f]	3-CH_3O-2-$NO_2C_6H_3$	CN	12	**3w**, 68	2.5:1
24[f]	2,4-$Cl_2C_6H_3$	CN	22	**3x**, 63	>20:1
25[f]	2-pyridyl	CN	13	**3y**, 57	>20:1

[a] For a typical procedure, see Supporting Information. [b] Combined yield of isolated diastereomers of **3** (based on aldehyde **1**). [c] Calculated by the major (*trans*,*Z*)-**3** versus the sum of other diastereomers on the basis of the isolated yields or ^1H NMR assay. [d] Allenoate **2** and PPh_3 were both used in 2.0 equiv. [e] Reaction temperature: −10 °C. [f] Run at −20 °C.

Several structurally similar α-substituted allenoates were also investigated. Ethyl 2-(cyanomethyl) buta-2,3-dienoate (R = CN, **2b**) possessed reactivity similar to that of **2a** and readily underwent the cyclopropanation with representative aromatic aldehydes at a lowered temperature (−20 °C), giving the corresponding cyclopropanes **3** in moderate yields (Table 2, entries 21−25). However, following the optimal conditions, neither α-methyl allenoate (R = H, **2c**) nor α-benzyl allenoate (R = Ph, **2d**) afforded any expected cyclopropanation products with **1a**. Assumingly, a strongly electron-withdrawing group R in **2** is required to effect this cyclopropanation.

In all cases of the cyclopropanation, the overall diastereoselectivity remained on a modest to high level. The diastereomeric ratio of the major (*trans*,*Z*)-**3** versus the sum of other isomers fell in the range of 2.5:1 to >20:1 (Table 2). The structures and relative stereochemistry of the cyclopropanes **3** were well identified by ^1H and ^{13}C NMR spectra and in some cases also by NOESY spectra and X-ray crystallographic analyses[16] (for details, see Supporting Information).

Interestingly, the introduction of a methyl group into the allenoate **2a** at the γ-carbon dramatically changed its reactivity pattern: under similar conditions for the cyclopropanation, the resulting α,γ-disubstituted allenoate **2e** predominantly underwent a phosphine-catalyzed [3 + 2] annulation with aldehydes, producing tetrahydrofurans **4** in good yields (eq 2). This result is well consistent with our findings in the prior study on γ-substituted allenoates and aldehydes.[8l]



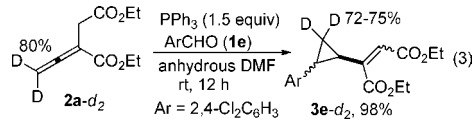
To better elucidate the cyclopropanation mechanism, deuterium-labeling and ^{31}P NMR monitoring experiments were run. A deuterated allenoate **2a**-d_2 (80% D) was subjected to the reaction with 2,4-dichlorobenzaldehyde (**1e**) under anhydrous conditions (eq 3). Four deuterated isomeric cyclopropanes **3e**-d_2 were obtained in 98% combined yield with 72−75% deuterium at the γ-carbon. This result clearly indicated that the γ-hydrogen of the allenoate did not

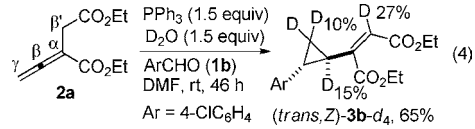
(14) A phosphine-mediated olefination of salicylic aldehydes with α-methyl allenoate was reported: He, Z.; Tang, X.; He, Z. *Phosphorus Sulfur Silicon Relat. Elem.* **2008**, *183*, 1518–1525.

(15) Our speculation about the failure of the cyclopropanation in ethanol is that ethanol inhibited the transformation from **8** to **9** according to the proposed mechanism (Scheme 1).

(16) The ORTEP presentations and CIF files of (*trans*,*E*)-**3i** and (*trans*,*Z*)-**3v** (CCDC 752167; 752168) are available in the Supporting Information.

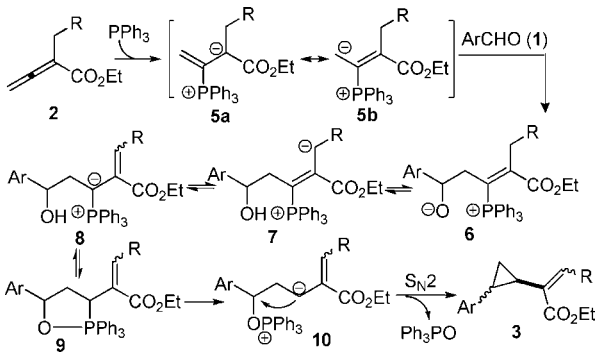
significantly participate in any intramolecular hydrogen exchanges. In contrast, with 1.5 equiv of D_2O added, the nondeuterated **2a** reacted with 4-chlorobenzaldehyde (**1b**), solely giving deuterated (*trans,Z*)-**3b** in 65% yield with 10−27% D incorporations at the β-, β'-, and γ-carbons (eq 4). This result implied that in the presence of D_2O H/D exchanges took place at the aforementioned carbons during the reaction. Furthermore, monitoring the reaction between **2a** and **1a** under the mediation of PPh_3 by ^{31}P NMR revealed the formation of two phosphorus-containing intermediate corresponding signals at δ 20.73 and 16.47 ppm with a relative intensity ratio of ca. 3:1. These ^{31}P NMR chemical shifts strongly implied that the intermediates were tetravalent phosphorus species,[17] which disappeared over 24 h at the completeness of the reaction (for details, see Supporting Information).





On the basis of these results and previous studies by Kwon and others,[8n,12] a plausible mechanism for this reductive cyclopropanation is presented in Scheme 1, in which the

Scheme 1. Plausible Mechanism for the Cyclopropanation



phosphine fulfills two roles: a nucleophile and a deoxygenating agent. Initially, PPh_3 undertakes a nucleophilic attack at the allenoate **2**, producing a resonance-stabilized zwitterionic intermediate **5**. Addition of **5** to an aldehyde generates an alkoxyphosphonium zwitterion **6**, which undergoes proton transfer followed by double bond migration, leading to the formation of a more stable phosphorus ylide **8**.[18] It is believed that a conjugative and electron-withdrawing group R, e.g., CO_2Et or CN, in **2** facilitates the transformations from **6** to **8**. By this means, the nature of the R group critically affects this cyclopropanation, as observed in this study. Theoretically, the ylide **8** contains a pair of isomers (*E*)-**8** and (*Z*)-**8** owing to the variation of the alkene configuration. The observation of two ^{31}P signals at δ 20.73 and 16.47 ppm in ^{31}P NMR tracking experiment provides strong evidence on the existence of **8**.[19] Subsequently, the ylide **8** reversibly converts into an oxaphospholane **9** which undergoes C−P bond cleavage followed by intramolecular S_N2 displacement to bring about the cyclopropane **3** and phosphine oxide.[20] Accordingly, the *trans* stereoselectivity of the cyclopropane **3** can be well rationalized with regard to the S_N2 ring closure step.

In conclusion, a novel phosphine-mediated reductive cyclopropanation of α-substituted allenoates with aldehydes was demonstrated. This cyclopropanation represents a new allene-based annulation which provides facile access to highly functionalized cyclopropanes **3** from simple and readily available starting materials. It also unveils an unprecedented reactivity mode between allenoates and aldehydes under the mediation of nucleophilic phosphines. In the reaction, the phosphine acts as both a nucleophilic trigger to generate the reactive zwitterions **5** and a deoxygenating agent. Recently, dual-functional phosphine of strong nucleophilicity and deoxygenating ability has gained renewed interest in new organic transformations.[21] Following this new cyclopropanation mode, future efforts in our laboratory will focus on developing a general methodology to construct diversely functionalized cyclopropanes from readily available activated olefins or alkynes, aldehydes, and phosphines.

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Supporting Information Available: Experimental details and spectral data for all new compounds **3** and **4**, as well as the X-ray crystallographical data for representative compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) 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*; Tebby, J. C., Ed.; CRC Press: Boca Raton, FL, 1991; pp 181−226.

(18) Phosphorus has the ability to stabilize the ylide-like structure which is commonly proposed as a key intermediate in nucleophilic phosphine catalysis. For typical examples, see: (a) Ref 8b. (b) Evans, C. A.; Miller, S. J. *J. Am. Chem. Soc.* **2003**, *125*, 12394.

(19) Those ^{31}P NMR data provided diagnostic information to distinguish **8** from **9**. The 1−2λ^5-oxaphospholane ring system like **9** is expected to exhibit a ^{31}P NMR resonance signal in the δ −40 to −60 ppm range. See: Adam, W.; Harrer, H. M.; Treiber, A. *J. Am. Chem. Soc.* **1994**, *116*, 7581–7587.

(20) Similar mechanisms are commonly proposed in other phosphorus ylide-involved cyclopropanation reactions. For leading reports, see: (a) Denney, D. B.; Vill, J. J.; Boskin, M. J. *J. Am. Chem. Soc.* **1962**, *84*, 3944. (b) Schweizer, E. E.; Creasy, W. S. *J. Org. Chem.* **1971**, *36*, 2379. (c) Avery, T. D.; Fallon, G.; Greatrex, B. W.; Pyke, S. M.; Taylor, D. K.; Tiekink, E. R. T. *J. Org. Chem.* **2001**, *66*, 7955.

(21) For representative examples, see: (a) Ref 13. (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.