Synthetic Methods

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Metal Alkoxide Promoted Regio- and Stereoselective C=O and C=C Metathesis of Allenoates with Aldehydes**

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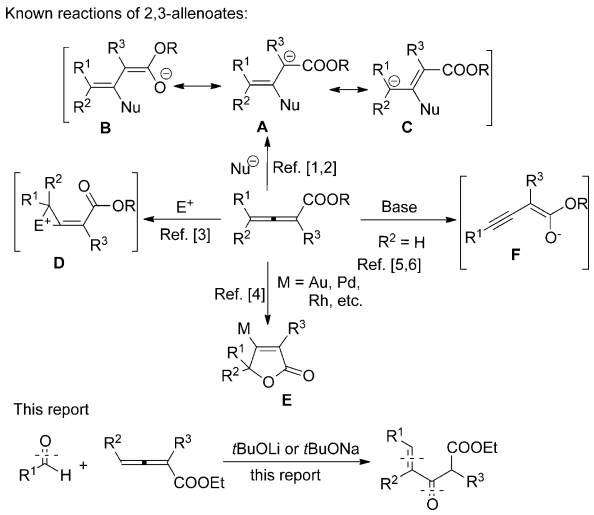
In memory of Run Run Shaw

Abstract: *The reaction of 2,3-allenoates and aldehydes in the presence of an alkoxide affords alkyl 4,5-diaryl-3-oxo-2-propylpent-4(E)-enoates and cis-3,4-diaryloxetanes through a formal C=O and C=C metathesis. A mechanism for this reaction has been proposed.*

It has been well established that 2,3-allenoates may readily accept the attack of nucleophiles[1,2] and electrophiles,[3] thus forming intermediates **A**–**C** and **D**, respectively (Scheme 1). In addition, they may also undergo cyclic oxametalation to form intermediate **E**,[4] and the treatment of 2-substituted 2,3-allenoates with a base such as TBAF may generate the corresponding alk-3-yn-2-enolate **F**, which could undergo 1,2-addition with aldehydes or conjugated enals or enones.[5,6]

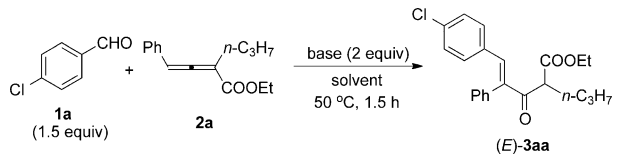


Scheme 1. Reactivities of 2,3-allenoates.

During our study on the reactions of 2,3-allenoates,[7] we noticed that the reaction of *p*-chlorobenzaldehyde (**1a**) and ethyl 2-propyl-4-phenylbuta-2,3-dienoate (**2a**) in the presence of *t*BuOLi at 50 °C unexpectedly afforded the stereodefined γ,δ-unsaturated β-ketoester (*E*)-**3aa** in 73 % (NMR) and 71 % (isolated) yield (Scheme 1 and see entry 1 in Table 1). For this synthetic operation, the C=O bond of the aldehyde is cleaved and the O atom is connected to the middle carbon atom of the allene moiety, while the remaining "R^1C=" is bonded to the C4 carbon atom of the allenoate. In addition, exclusive *E* selectivity of the C=C bond is observed.

Thus, with such an original observation, different solvents, such as DCE, MeCN, and Et_2O, were screened but they led to a decrease in the yield (entries 2–4, Table 1). Replacement of

Table 1: Optimization of the reaction conditions.[a]



Entry	Solvent	Base	Yield [%][b] (*E*)-**3aa**	Recovery [%] **1a**	Recovery [%] **2a**
1	THF	*t*BuOLi	73 (71)[c]	–	–
2	DCE	*t*BuOLi	0	0	36
3	MeCN	*t*BuOLi	55	–	–
4	Et_2O	*t*BuOLi	59	–	–
5	THF	*t*BuONa	45	–	–
6	THF	K_2CO_3	0	72	74
7	THF	$LiOH·H_2O$	0	11	15
8	THF	TBAF	0	24	8
9[d,e]	THF	*t*BuOLi	42	–	–
10[e]	THF	*t*BuOLi	72	–	–
11[f]	THF	*t*BuOLi	64	–	–
12[e,g]	THF	*t*BuOLi	28	0	19

[a] Used 0.3 mmol of allenoate, 0.45 mmol of aldehyde, and 0.6 mmol of base in this reaction. [b] The yields were determined by ^{1}H NMR analysis with CH_2Br_2 as the internal standard. [c] Yield of isolated product. [d] Added 1.5 equiv of 12-crown-4. [e] Added 1.5 equiv of base. [f] Added 1.2 equiv of aldehyde **1a**. [g] The reaction was conducted at 10 °C. DCE = 1,2-dichloroethane, THF = tetrahydrofuran.

*t*BuOLi with a stronger base (*t*BuONa) or a weaker base was less effective (entries 5–8, Table 1). Notably, the presence of 12-crown-4, which is proposed to enhance the basicity of the lithium salt, led to unsatisfactory results (entry 9, Table 1). Lowering the amount of base to 1.5 equivalents showed no influence on the yield whereas a reduced amount of **1a**

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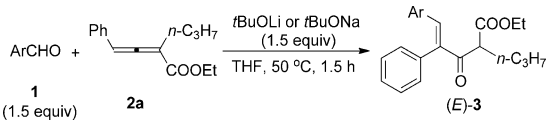
proved to be deleterious (entries 10 and 11, Table 1). When the reaction was conducted at 10 °C, only 28 % of (*E*)-**3aa** was formed with recovery of 19 % of **2a** (entry 12, Table 1). Thus, 1.5 equivalents of *t*BuOLi and 1.5 equivalents of **1a** in THF at 50 °C for 1.5 hours were established as the standard reaction conditions for further study.

With the optimized reaction conditions in hand, the scope of the aromatic aldehydes **1** was firstly investigated as shown in Table 2. Reactions proceeded smoothly under the standard

Table 2: The reaction of different aldehydes with **2a**.[a]



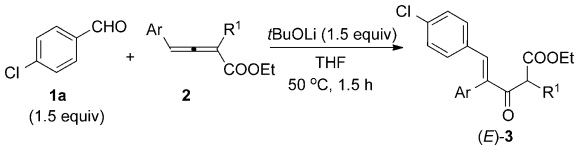
Entry	Ar	Yield [%]
1	*p*-ClC_6H_4 (**1a**)	68 [(*E*)-**3aa**]
2[b]	*p*-ClC_6H_4 (**1a**)	74 [(*E*)-**3aa**]
3	*p*-BrC_6H_4 (**1b**)	59 [(*E*)-**3ba**]
4	*p*-FC_6H_4 (**1c**)	62 [(*E*)-**3ca**]
5	*o*-BrC_6H_4 (**1d**)	65 [(*E*)-**3da**]
6	*m*-ClC_6H_4 (**1e**)	64 [(*E*)-**3ea**]
7	*p*-NCC_6H_4 (**1f**)	64 [(*E*)-**3fa**]
8	*p*-$MeOOCC_6H_4$ (**1g**)	64 [(*E*)-**3ga**]
9[c]	C_6H_5 (**1h**)	52 [(*E*)-**3ha**]
10[c]	*m*-$MeOC_6H_4$ (**1i**)	48 [(*E*)-**3ia**]
11[c]	furan-2-yl (**1j**)	61 [(*E*)-**3ja**]
12[c]	*N*-Me-pyrrol-2-yl (**1k**)	51 [(*E*)-**3ka**]
13[c]	pyridin-4-yl (**1l**)	45 [(*E*)-**3la**]

[a] The reaction was carried out with 1.0 mmol of allenoate, 1.5 equiv of aldehyde, and 1.5 equiv of *t*BuOLi at 50 °C in 6.0 mL of THF for 1.5 h. Yield is that of isolated product. [b] The reaction was conducted on a gram scale using 1.0012 g **2a**. The reaction proceeded for 2.0 h. [c] *t*BuONa was used instead of *t*BuOLi and the reactions proceed for 1.0 h.

reaction conditions, thus affording differently substituted ethyl 3-oxo-4,5-diaryl-2-propylpent-4(*E*)-enoates [(*E*)-**3**] in moderate to good yields. Substituents, such as a halogen at the *para*, *ortho*, or *meta* positions of the aromatic ring in the aldehyde furnished the corresponding products (*E*)-**3aa-ea** in decent yields (entries 1–6, Table 2). Both CN and COOMe groups, which are active under basic conditions, were also well tolerated (entries 7 and 8, Table 2). When benzaldehyde and aromatic aldehydes bearing electron-donating groups were introduced, *t*BuONa instead of *t*BuOLi was used (entries 9 and 10, Table 2). In addition, aldehydes having a heteroaromatic ring such as furan, pyrrole, and pyridine are also suitable substrates for the reaction. It is noteworthy that the reaction can be easily conducted using **1a** with 1.5 equivalents of **2a** on a gram scale, thus affording (*E*)-**3aa** in 74 % yield (entry 2, Table 2).

Next, we examined the reaction of different ethyl 2-alkyl-4-arylbuta-2,3-dienoates (**2**) with **1a** (Table 3). R^1 could be an alkyl group such as methyl or ethyl (entries 1 and 2, Table 3), while Ar could be substituted with both electron-donating and electron-withdrawing groups (entries 3–7, Table 3). The structures of the products were unambiguously established by the X-ray diffraction study of (*E*)-**3ab**, which displayed the

Table 3: The reaction of different 2,3-allenoates with **1a**.[a]

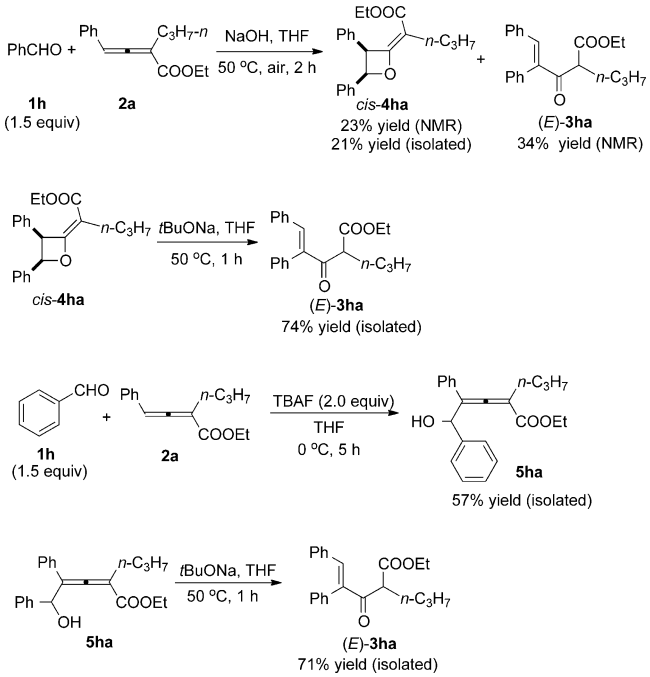


Entry	R^1	Ar	Yield [%]
1	Me	C_6H_5 (**2b**)	52[b] [(*E*)-**3ab**]
2	Et	C_6H_5 (**2c**)	49 [(*E*)-**3ac**]
3	*n*Pr	*p*-MeC_6H_4 (**2d**)	69 [(*E*)-**3ad**]
4	*n*Pr	*p*-$MeOC_6H_4$ (**2e**)	63 [(*E*)-**3ae**]
5	*n*Pr	*p*-BrC_6H_4 (**2f**)	75 [(*E*)-**3af**]
6	*n*Pr	*m*-ClC_6H_4 (**2g**)	58 [(*E*)-**3ag**]
7	*n*Pr	*p*-FC_6H_4 (**2h**)	77 [(*E*)-**3ah**]

[a] The reaction was carried out with 1.0 mmol of allenoate, 1.5 equiv of aldehyde, and 1.5 equiv of *t*BuOLi at 50 °C in 6.0 mL of THF for 1.5 h. Yield is that of isolated product. [b] The purity of (*E*)-**3ab** is 82 %, as determined by ^1H NMR analysis with CH_2Br_2 as the internal standard.

exclusive *E* selectivity of the double bond (see Figure S1 in the Supporting Information).[8]

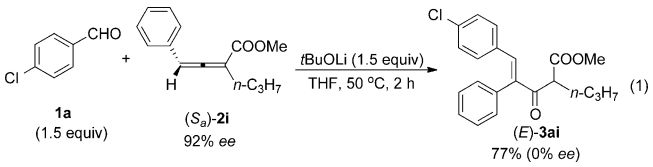
To unveil the mechanism, some control experiments were conducted. When sodium hydroxide, a relatively weaker base, was used for the reaction of **1h** and **2a**, (*E*)-**3ha** was afforded in a 34 % yield as determined by ^1H NMR analysis, and in addition 23 % yield of the substituted oxetane *cis*-**4ha** was observed (Scheme 2). The stereochemistry of *cis*-**4ha** was secured through the information from the vicinal ^1H-^1H coupling constant ($J = 4.0$ Hz) and 2D NMR data (COSY, HSQC, HMQC, and phase-sensitive NOESY; see the Supporting Information). This compound could be further transformed into the corresponding final product (*E*)-**3ha** under the standard reaction conditions in 74 % yield. Although the



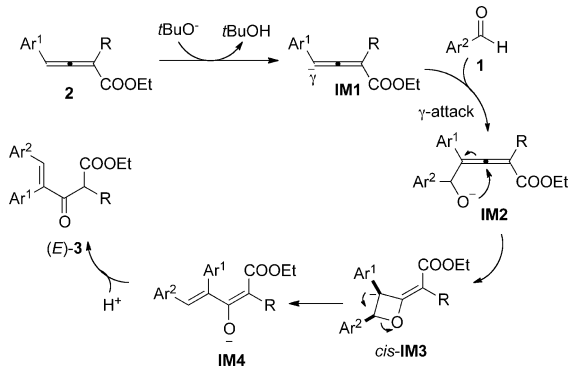
Scheme 2. Some control reactions for mechanistic studies. TBAF = tetra-*n*-butylammonium fluoride.

formation of ethyl 5-hydroxy-4,5-diphenyl-2-propylpenta-2,3-dienoate (**5ha**) was not observed, **5ha** prepared from a reported procedure[5a] reacted with *t*BuONa in THF at 50 °C and afforded (*E*)-**3ha** in 71 % yield.

Furthermore, the reaction of the optically active 2,3-allenoate (S_a)-**2i**, having a defined S_a axial chirality in the allene moiety,[9] with **1a** under the optimized reaction conditions afforded racemic (*E*)-**3ai** [Eq. (1)].



Based on these results, we envisioned that anion *cis*-**IM3** may be the key intermediate for this transformation as depicted in Scheme 3. In the presence of *t*BuO$^-$, the deprotonation of the γ-hydrogen atom of **2** would occur, thus affording the intermediate **IM1** or its equivalent.[5a,6] Then γ-addition of the aromatic aldehyde **1** to **IM1** affords the 5-hydroxy-2,3-allenoate anion **IM2**, which could be followed by intramolecular nucleophilic oxygen attack at the β-position to form the four-membered ring *cis*-**4**. Finally, *cis*-**4** undergoes ring cleavage at the C–O bond, thus generating **IM3** which is then isomerized to the acyclic products, highly functionalized α,β-enones *E*-**3**. The stereoselectivity is believed to be determined by the *cis* orientation of Ar^1 and Ar^2 in *cis*-**IM3**.

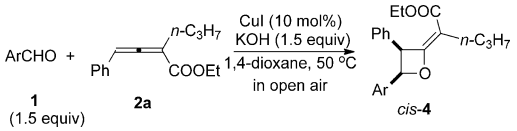


Scheme 3. Proposed mechanism.

Because of the existence of the reactive oxetane[10] and the exocyclic double bond,[11] the in situ generated oxetanes *cis*-**4** may be widely employed as useful building blocks in the construction of complicated organic molecules. However, the literature on the synthesis of *cis*-**4** is limited.[12–14] Herein, after studying the effect of solvent, base, and catalyst, the optimized reaction conditions for affording *cis*-**4a** were identified (see Tables S1–S3). The scope of the aromatic aldehydes **1** was investigated as shown in Table 4.

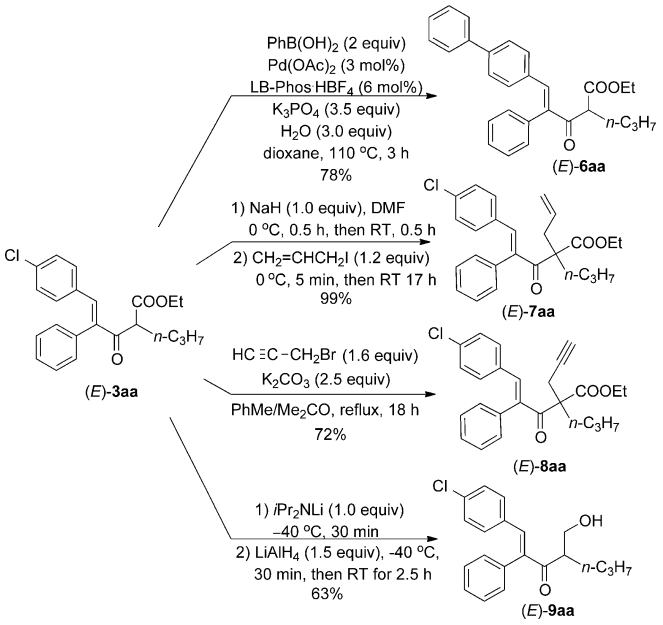
In addition, γ,δ-unsaturated β-ketoesters have emerged as useful synthons in organic synthesis (Scheme 4). The C–Cl bond in (*E*)-**3aa** can easily be converted into the biphenyl product (*E*)-**6aa** in 78 % yield by using the electron-rich and

Table 4: The reaction of different aldehydes (**1**) with **2a** to afford *cis*-**4**.[a]



Entry	Ar	*t* [h]	Yield [%]
1	*p*-ClC_6H_4 (**1a**)	3	42 (*cis*-**4aa**)
2	*p*-BrC_6H_4 (**1b**)	3	43 (*cis*-**4ba**)
3	*p*-NCC_6H_4 (**1f**)	4	36 (*cis*-**4fa**)
4	C_6H_5 (**1h**)	2	45 (*cis*-**4ha**)
5	Pyridin-4-yl (**1l**)	8	30 (*cis*-**4la**)

[a] The reaction was carried out with 1.0 mmol of allenoate, 1.5 equiv of aldehyde, 1.5 equiv of KOH, and 10 mol % of CuI at 50 °C in 6.0 mL of 1,4-dioxane in open air. Yield is that of isolated product.



Scheme 4. Transformations of (*E*)-**3aa**. DMF = *N*,*N*-dimethylformamide, LB-Phos = 2,4,6-trimethoxyphenyldi(cyclohexyl)phosphine.

sterically bulky ligand LB-Phos (Scheme 4).[15] As usual, the reaction of (*E*)-**3aa** with 3-iodoprop-1-ene using NaH as a base in DMF or 3-bromoprop-1-yne in the presence of K_2CO_3 afforded the synthetically attractive diene (*E*)-**7aa**[16] and enyne (*E*)-**8aa**,[17] respectively, without the formation of any *O*-alkylation products. Interestingly, the ester functionality in (*E*)-**3aa** may be selectively reduced even in the presence of the ketone, thus affording (*E*)-**9aa**.[18]

In conclusion, we have developed a metal alkoxide promoted condensation between aromatic aldehydes and alka-2,3-dienoates, a reaction which provides a highly efficient synthetic approach to 4,5-diaryl-3-oxoalken-4(*E*)-enoates and the 2-alkylideneoxetanes *cis*-**4**. Considering the efficiency and the observed stereoselectivity, the mechanism, the highly functionalized nature of the products **3** and **4**, and the easy availability of the starting materials (see the Supporting Inforamtion for details), this transformation will be of high importance to organic chemists. Additional studies are being carried out in our laboratory.

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Keywords: aldehydes · alkali metals · allenes · reaction mechanisms · synthetic methods

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[8] Crystal data for (*E*)-**3ab**: $C_{20}H_{19}ClO_3$, MW = 342.80, monoclinic, space group P 21/c, final *R* indices [$I > 2\sigma(I)$], $R1 = 0.0398$, $wR2 = 0.0970$; *R* indices (all data), $R1 = 0.0627$, $wR2 = 0.1119$; $a = 11.910$ (2) Å, $b = 11.188$ (2) Å, $c = 15.031$ (4) Å, $\alpha = 90.00°$, $\beta = 118.702$ (15)°, $\gamma = 90.00°$, $V = 1756.8$ (6) Å3, $T = 293$ (2) K, $Z = 4$, reflections collected/unique 6665/2315 ($R_{int} = 0.0250$), number of observations [$> 2\sigma(I)$] 3211, parameters: 219. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, CCDC 945425 which contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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