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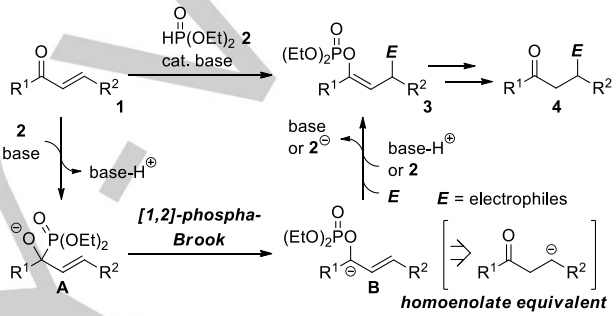
Generation and Application of Homoenolate Equivalents Utilizing [1,2]-Phospha-Brook Rearrangement under Brønsted Base Catalysis

Azusa Kondoh,[a] Takuma Aoki,[b] and Masahiro Terada*[a,b]

Abstract: A novel method for catalytic generation of a homoenolate equivalent and its application to carbon-carbon bond formation was developed by utilizing the [1,2]-phospha-Brook rearrangement under Brønsted base catalysis. The *α*-oxygenated allyl anions, which can serve as homoenolate equivalents, were catalytically generated *in situ* by treating readily available chalcones with diethyl phosphite or the pre-formed 1,2-adducts of diethyl phosphite with chalcones in the presence of a catalytic amount of a phosphazene base, P2-*t*Bu. The resulting allyl anions were subsequently trapped by various electrophiles, including Michael acceptors, imines, and aldehydes, providing the corresponding adducts in good yields with moderate to good diastereoselectivities.

Carbon-carbon bond forming reactions based on inversion of the inherent polarity of functional groups, so called *umpolung*, are a privileged class of reactions in organic synthesis.[1] Specifically, the reactions of homoenolates are powerful tools for developing new strategies toward the synthesis of complex molecules. Homoenolates enable the introduction of an electrophile to a carbon at the *β*-position of a carbonyl group where nucleophiles are generally introduced by conjugated addition with *α*,*β*-unsaturated carbonyl compounds.[2] Therefore, intensive studies have focused on the development of new methodologies for the generation of homoenolates, and the design of synthetic equivalents of homoenolates. Recent dramatic evolution of catalytic reactions utilizing homoenolates generated from *α*,*β*-unsaturated aldehydes using *N*-heterocyclic carbene catalysts emphasizes the importance of molecular transformations based on such *umpolung* reactivity, particularly in a catalytic fashion.[3,4] Meanwhile, allyl anions possessing a heteroatom-substituent at the *α*-position are useful synthetic homoenolate equivalents.[5] Various types of such allyl anions, including those having a chiral auxiliary, have been developed and utilized in organic synthesis. However, the generation of allyl anions generally requires tedious pre-synthesis of the corresponding allyl compounds and subsequent deprotonation at the allylic position by using a stoichiometric amount of a strong Brønsted base, such as *n*BuLi, due to the low acidity at the allylic position. Thus, the development of a novel methodology for the catalytic generation of *α*-heteroatom-substituted allyl anions, i.e., homoenolate equivalents, from readily available compounds under mild reaction conditions would pave the way to new useful synthetic reactions exploiting the *umpolung* reactivity. In this context, we envisioned the generation of *α*-oxygenated allyl anions, which can serve as homoenolate equivalents, utilizing the [1,2]-phospha-Brook rearrangement[6,7] under Brønsted base catalysis, and its application to carbon-carbon bond formation. Our proposed reaction system is shown in Scheme 1.



Scheme 1. Proposed Reaction System.

In the proposed reaction system, an easily-prepared *α*,*β*-unsaturated ketone **1** is employed as the precursor of a homoenolate equivalent. Treatment of **1** with diethyl phosphite (**2**) in the presence of a Brønsted base catalyst would result in the deprotonation of **2** followed by chemoselective 1,2-addition to provide alkoxide **A**. Subsequently, the migration of the diethoxyphosphoryl moiety from carbon to oxygen, i.e., the [1,2]-phospha-Brook rearrangement, would proceed to form *α*-oxygenated allyl anion **B**. Finally, the addition of **B** to an electrophile ("***E***") at the *γ*-position followed by protonation by the conjugated acid of the Brønsted base catalyst or **2** would afford the adduct **3** along with regeneration of the Brønsted base catalyst or the anion of **2**, completing the catalytic cycle. Hydrolysis of the alkenyl phosphate moiety of **3** would provide *β*-substituted ketone **4**, which is the formal adduct of the homoenolate with the electrophile. In order to establish the proposed reaction system, some issues must be overcome. First for the generation of the key allyl anion **B**, the addition of diethyl phosphite to the *α*,*β*-unsaturated ketone **1** must proceed in the 1,2-fashion over the 1,4-fashion. Second, the resulting allyl anion **B** should react with the electrophile selectively at the *γ*-position, not at the *α*-position, to serve as the homoenolate equivalent. Finally, anion **B** should react with the electrophile preferentially over protonation, which is a potential side reaction arising from the high basicity of **B**. Once the corresponding allyl compound is formed by the protonation of **B**, it cannot re-enter the catalytic cycle via deprotonation due to its low acidity. We successfully managed to solve these issues and report herein a novel method for catalytic generation of a homoenolate

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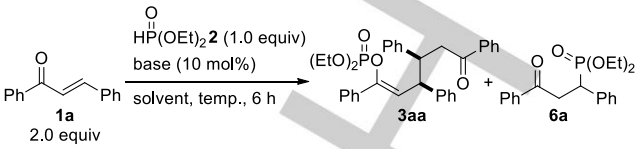
equivalent and its application to carbon-carbon bond formation under Brønsted base catalysis.

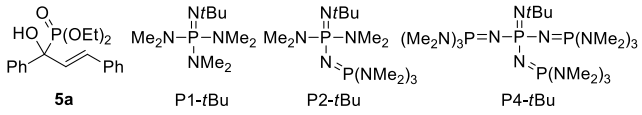
To ascertain the viability of the proposed reaction system, we began our investigation by evaluating the catalytic generation of the *α*-oxygenated allyl anion from chalcone (**1a**) with diethyl phosphite (**2**). As an initial experiment, 2 equivalents of **1a** were treated with 1 equivalent of **2** in the presence of 10 mol% P2-*t*Bu in THF at room temperature for 6 h in order to homo-dimerize **1a,** i.e., trap the allyl anion generated *in situ* with another chalcone. As a result, the dimerized product **3aa** was obtained as the major product in fairly good yield along with **6a** which is the 1,4-adduct of **2** with **1a** (Table 1, entry 1). **3aa** would be formed through the generation of the *α*-oxygenated allyl anion, as expected, followed by trapping with another chalcone at the *γ*-position in 1,4-fashion, which clearly demonstrated the proposed reaction system. Furthermore, undesired products derived from the allyl anion intermediate, such as *α*-adducts and protonated products, were not observed at all. This result prompted us to step into the optimization of the conditions for the homo-dimerization of chalcones (Table 1). Screening of Brønsted bases revealed that the choice of Brønsted base was critical for generation of the homoenolate equivalents. Phosphazenes having strong basicity, such as P2-*t*Bu (pK_{BH^+} = 21.5 in DMSO)[8] and P4-*t*Bu (pK_{BH^+} = 30.3), provided **3aa** in good yield (entries 1 and 2), while the use of P1-*t*Bu (pK_{BH^+} = 15.7) resulted in no reaction (entry 3). Furthermore, inorganic bases having strong basicity, such as *t*BuOK and KHMDS, were less effective than phosphazenes, and 1,4-adduct **6a** was obtained as the major product (entries 4 and 5). Screening of solvents was then carried out (entries 6-9), and THF was found to be the best solvent in terms of diastereoselectivity. Decreasing the reaction temperature was beneficial for improving the yield and diastereoselectivity (entry 10). At −78 °C, the competing 1,4-addition of **2** to **1a** was suppressed, and thus the yield of **3aa** was increased. Finally, the use of 1.1 equivalents of **2** further improved the yield, and **3aa** was quantitatively obtained with high diastereoselectivity (entry 11). As a control experiment, the reaction was performed with KHMDS at −78 °C. Even though the formation of 1,4-adduct **6a** was suppressed as in the case with P2-*t*Bu, allylic alcohol **5a** was obtained in 74% yield instead of **3aa** (entry 12). The difference between P2-*t*Bu and KHMDS (entries 10 and 12) was attributed to the effect of the countercation of the anionic intermediate. Phosphazenes are known to generate a “naked” anion possessing high nucleophilicity due to delocalization of the positive charge on the bulky conjugated acid.[9] Therefore, P2-*t*Bu would facilitate the [1,2]-phospha-Brook rearrangement by generating a highly active alkoxide intermediate, resulting in the formation of allyl anion intermediate **B**. In contrast, potassium alkoxide generated by KHMDS would not be active enough to accelerate the [1,2]-phospha-Brook rearrangement at −78 °C, and thus **5a** was obtained. Increasing the reactivity of potassium alkoxide by using 18-crown-6 as an additive resulted in the formation of **3aa** in moderate yield, which would support our hypothesis (entry 13). The optimum conditions for the homo-dimerization were applicable to a variety of chalcone derivatives having substituents on the aryl groups on the keto moiety and at the *β*-position (Table S1).[10,11] It should be mentioned that both of the aryl groups on the keto moiety and at the *β*-position were

Table 1. Optimization of Reaction Conditions[a]



entry	base	solvent	temp.	yield [%][b] 3aa	dr of 3aa[c]	6a
1	P2-*t*Bu	THF	rt	76	79:13:8:<1	24
2	P4-*t*Bu	THF	rt	82	67:22:9:2	18
3	P1-*t*Bu	THF	rt	<1	-	<1
4	*t*BuOK	THF	rt	24	52:33:8:7	76
5	KHMDS	THF	rt	22	52:33:8:7	78
6	P2-*t*Bu	DMF	rt	72	64:30:6:<1	17
7	P2-*t*Bu	CH_3CN	rt	85	71:23:6:<1	14
8	P2-*t*Bu	CH_2Cl_2	rt	87	75:18:7:<1	13
9	P2-*t*Bu	toluene	rt	69	77:14:9:<1	31
10	P2-*t*Bu	THF	−78 °C	90	92:5:3:<1	1
11[d]	P2-*t*Bu	THF	−78 °C	99 (90)	93:5:2:<1	<1
12	KHMDS	THF	−78 °C	2[e]	-	<1
13[f]	KHMDS	THF	−78 °C	46[g]	80:7:13:<1	<1

[a] Conditions: **1a** (0.20 mmol), **2** (0.10 mmol), base (0.010 mmol), solvent (1.0 mL). [b] Yields were determined by ^{1}H and ^{31}P NMR analyses of the crude mixtures. Trimethyl phosphate was used as the internal standard. The isolated yield of the major diastereomer is shown in parentheses. [c] Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude mixture. [d] 1.1 equivalents of **2** (0.11 mmol) were used. [e] **5a** was obtained in 74% yield. [f] 10 mol% 18-crown-6 (0.010 mmol) was used. [g] **5a** was obtained in 54% yield.



essential for generating the *α*-oxygenated allyl anion. Substrates having an alkyl substituent on the keto moiety or at the *β*-position did not undergo the [1,2]-phospha-Brook rearrangement and 1,2-adduct **5** and/or 1,4-adduct **6** were obtained. The relative configuration of the major diastereomer of **3** was determined by single crystal X-ray diffraction analysis to have the *syn*-configuration of substituents at the C-3 and C-4 positions, and *Z* configuration of the alkene moiety.[12]

With this methodology in hand, we turned our attention to the investigation of the cross-addition reaction of homoenolate equivalents with other electrophiles. However, the generation of homoenolate equivalents from chalcones and diethyl phosphite in the presence of other electrophiles did not seem feasible

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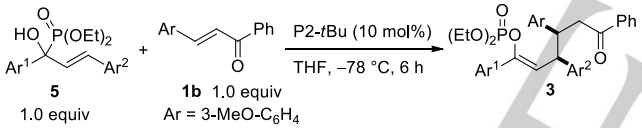
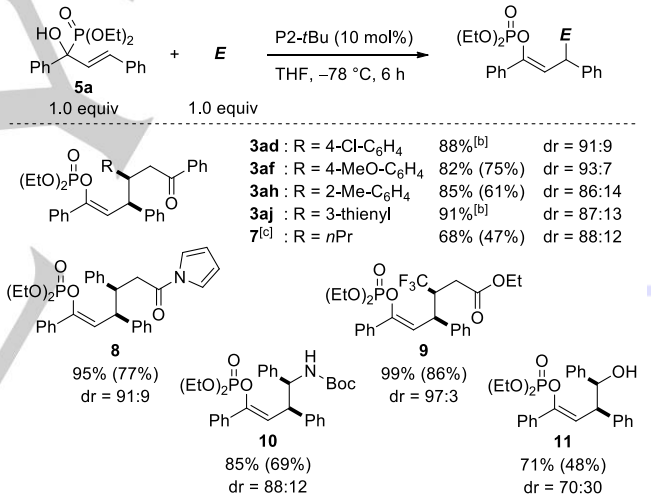
because the direct addition of diethyl phosphite to the electrophiles would compete against the 1,2-addition to chalcones. Indeed, treatment of **1a** with **2** in the presence of other electrophiles, such as different chalcone derivatives, resulted in the formation of complex mixtures of products. Therefore, in order to avoid the issue of chemoselectivity, allylic alcohols **5**, which were easily prepared from **1** by treatment with **2** in the presence of a catalytic amount of KHMDS (cf. Table 1, entry 12) or $TMSCH_2MgCl$,[10] were employed as the precursor of the homoenolate equivalent, and the cross-addition reaction was explored. Initially, the reaction of **5a** with chalcone derivative **1b** was attempted under the conditions for the homo-dimerization reaction (Table 2, entry 1). As expected, the desired adduct **3ab** was obtained in good yield with good diastereoselectivity. Following this result, the scope of the cross-addition was examined (Table 2 and Scheme 2). First, the screening of allylic alcohols **5** was carried out by using **1b** as an electrophile (Table 2). The allylic alcohols **5c** and **5d** having an electron-withdrawing chloro group at the para position of the aryl group on the keto moiety or at the *β*-position underwent the reaction smoothly to afford the desired products in good yields with good diastereoselectivities (entries 2 and 3). On the other hand, in the case of **5e** and **5f** having an electron-donating methoxy group, the reaction was sluggish (entries 4 and 5). In addition, particularly in the reaction of **5e**, the elimination of diethyl phosphite competed with the [1,2]-phospha-Brook rearrangement, resulting in the formation of **3eb** in moderate yield along with a significant amount of **3bb** which was the dimerized product of **1b**. The reaction of *o*-tolyl-substituted **5g** and **5h** provided the corresponding products **3gb** and **3hb** in good yields while the diastereoselectivities were moderate (entries 6 and 7). Heteroaryl-substituted **5i** and **5j** were also applicable to this reaction to provide the products **3ib** and **3jb**, respectively, in good yields with good diastereoselectivities (entries 8 and 9). Next, the scope of electrophiles was investigated with **5a** as the precursor of the homoenolate equivalent (Scheme 2).[13] These results clearly reveal that this methodology is applicable to a variety of Michael acceptors including chalcone derivatives having different substituents at the *β*-position, an alkyl-substituted enone, an *α*,*β*-unsaturated acyl pyrrole, and a trifluoromethyl-substituted *α*,*β*-unsaturated ester, to afford the corresponding products in good yields with good diastereoselectivities. Furthermore, in addition to Michael acceptors, imines and aldehydes were suitable electrophiles. *N*-Boc imine provided the corresponding amine **10** in high yield with good diastereoselectivity. Trapping with benzaldehyde resulted in the formation of alcohol **11** with moderate diastereoselectivity. In this case, a small amount of *α*-adduct was observed as a by-product.

Table 2. Scope of Allylic Alcohols **5**[a]



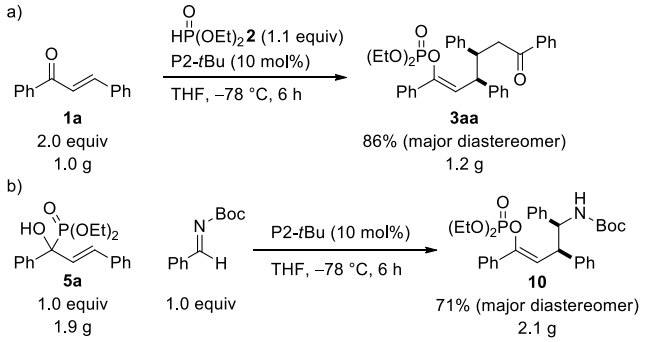
entry	5	Ar^1	Ar^2	3	yield [%][b]	dr[c]
1	**5a**	Ph	Ph	**3ab**	88 (74)	90:10
2	**5c**	4-Cl-C_6H_4	Ph	**3cb**	90 (68)	91:9
3	**5d**	Ph	4-Cl-C_6H_4	**3db**	90 (82)	94:6
4[d]	**5e**	4-MeO-C_6H_4	Ph	**3eb**	52[e]	79:21
5[d]	**5f**	Ph	4-MeO-C_6H_4	**3fb**	87 (56)	85:15
6	**5g**	2-Me-C_6H_4	Ph	**3gb**	83 (55)	70:30
7	**5h**	Ph	2-Me-C_6H_4	**3hb**	89 (47)	74:26
8	**5i**	3-pyridyl	Ph	**3ib**	81[e]	92:8
9	**5j**	Ph	3-thienyl	**3jb**	94 (80)	91:9

[a] Conditions: **5** (0.10 mmol), **1b** (0.10 mmol), P2-*t*Bu (0.010 mmol), THF (1.0 mL), −78 °C, 6 h. [b] NMR yields. Isolated yields of major diastereomers are shown in parentheses. [c] The ratio of major diastereomer to the sum of the other three diastereomers. [d] Reaction was conducted with 20 mol% P2-*t*Bu. [e] Major diastereomer was not separable from a small amount of impurity.



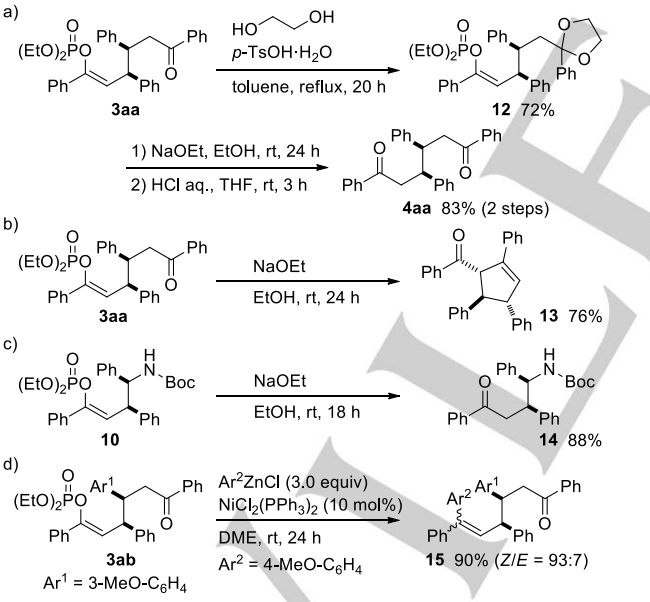
Scheme 2. Scope of Electrophiles.[a] [a] Conditions: **5a** (0.10 mmol), electrophile (0.10 mmol), P2-*t*Bu (0.010 mmol), THF (1.0 mL), −78 °C, 6 h. Yields are NMR yields. Isolated yields of major diastereomers are shown in parentheses. Diastereomeric ratio (dr) is the ratio of major diastereomer to the sum of the other three diastereomers. [b] Major diastereomer was not separable from a small amount of impurity. [c] 1.2 equivalents of the electrophile were used.

It is worth noting that this operationally simple methodology was reliable enough to perform both homo-dimerization and cross-addition reactions on the gram-scale, and the corresponding products **3aa** and **10** were obtained in good yields (Scheme 3). Finally, transformation of the products was demonstrated (Scheme 4). Acetal protection of the keto moiety of **3aa** followed by cleavage of the diethoxyphosphoryl group by treatment with NaOEt in ethanol and deprotection of the acetal moiety under acidic conditions provided the corresponding 1,6-dicarbonyl compound **4aa** in good overall yield (Scheme 4a). In contrast,



Scheme 3. Gram-Scale Reactions.

direct cleavage of the diethoxyphosphoryl group of **3aa** resulted in the formation of polysubstituted cyclopentene **13** as a single diastereomer through the intramolecular aldol condensation (Scheme 4b). The imine-adduct **10** was easily converted to the corresponding *γ*-aminoketone **14** in high yield (Scheme 4c). A transformation based on the cross-coupling reaction was also possible (Scheme 4d). Thus, a Ni-catalyzed Negishi-type cross-coupling reaction afforded the arylated product **15** in good yield. This result suggests that the newly-developed methodology can be regarded not only as the catalytic generation and addition of homoenolate equivalents, but also as those of stereo-defined polysubstituted allyl anions under Brønsted base catalysis.



Scheme 4. Transformation of Products.

In conclusion, a novel method for the catalytic generation of homoenolate equivalents and its application to carbon-carbon bond formation was developed by utilizing the [1,2]-phospha-Brook rearrangement under Brønsted base catalysis. The *α*-oxygenated allyl anion, which can serve as a homoenolate equivalent, was catalytically generated *in situ* from readily available chalcones and their derivatives via the [1,2]-phospha-Brook rearrangement using P2-*t*Bu as a superior Brønsted base catalyst. The resulting anion was subsequently trapped by various electrophiles, including Michael acceptors, imines and aldehydes, providing the corresponding adducts in good yields. Further investigations using this newly-developed methodology are now in progress, focusing on the development of enantioselective reactions.

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Keywords: Brønsted base catalysis • homoenolate • umpolung • [1,2]-phospha-Brook rearrangement • organocatalyst

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[10] See the Supporting Information for details.

[11] Other dialkyl phosphites, such as dimethyl phosphite, showed the reactivity similar to that of diethyl phosphite while diaryl phosphite resulted in no reaction.

[12] CCDC No. 1503914. See the Supporting Information for details.

[13] The relative configuration of the major diastereomer of each product was determined by derivatization and/or single crystal X-ray diffraction analysis. See the Supporting Information for details.

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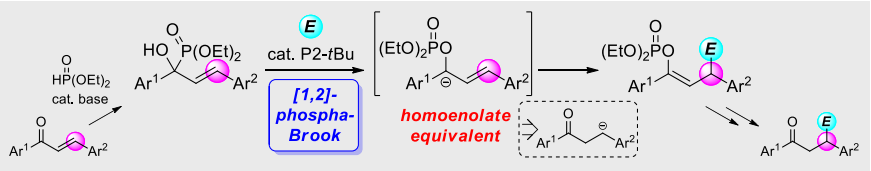

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Generation and Application of Homoenolate Equivalents Utilizing [1,2]-Phospha-Brook Rearrangement under Brønsted Base Catalysis

A novel method for catalytic generation of α-oxygenated allyl anions, which can serve as homoenolate equivalents, was developed by utilizing the [1,2]-phospha-Brook rearrangement under Brønsted base catalysis. The allyl anions generated *in situ* were subsequently trapped by various electrophiles, including Michael acceptors, imines, and aldehydes, providing the corresponding adducts in good yields with moderate to good diastereoselectivities.