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Ruthenium- and Copper-Catalyzed Enantioselective Propargylic Alkylation of Propargylic Alcohols with β-Keto Phosphonates

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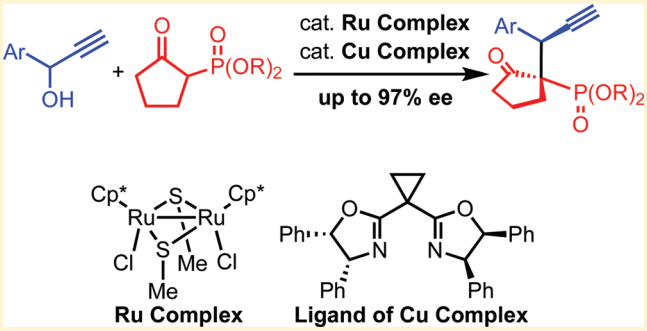
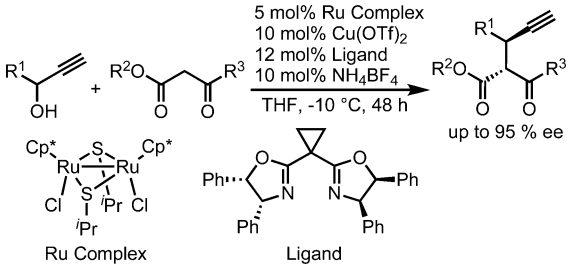
Supporting Information

ABSTRACT: The enantioselective propargylic alkylation of propargylic alcohols with β-keto phosphonates in the presence of a thiolate-bridged diruthenium complex and a copper complex as cocatalysts gives the corresponding propargylic alkylated products in excellent yields with high diastereo- and enantioselectivities (up to 97% ee).



In our continuing studies of the cooperative dual catalytic reactions[1] and enantioselective propargylic substitution reactions,[2] we have quite recently found the ruthenium- and copper-catalyzed propargylic alkylation of propargylic alcohols with β-keto esters to give the corresponding propargylic alkylated products in high yields with excellent enantioselectivity.[3] In this reaction system, both transition-metal catalysts (ruthenium and copper complexes) activate propargylic alcohols and β-keto esters, respectively, and cooperatively promote the propargylic alkylation enantioselectively (Scheme 1). The enolates generated in situ from copper complexes[4,5]

Scheme 1



and β-keto esters have been used as carbon-centered nucleophiles, but successful examples are limited to the enantioselective addition to carbonyls and their related compounds. This finding is the first application of the enolates to asymmetric propargylic substitution reactions. We believe that the method described in this article provides a new type of enantioselective dual catalytic reaction using a pair of distinct transition-metal catalysts.[6,7]

In the cooperative catalytic reactions, we have now envisaged that the use of other carbon-centered nucleophiles in place of the β-keto esters, such as β-keto phosphonates,[8] may promote the propargylic alkylation of propargylic alcohols using a similar reaction system. In fact, the propargylic alkylation of propargylic alcohols with β-keto phosphonates proceeded in the presence of a thiolate-bridged diruthenium complex and a copper complex as cocatalysts to give the corresponding propargylic alkylated products in excellent yields with high diastereo- and enantioselectivities. This is the first successful example of β-keto phosphonates as carbon-centered nucleophiles in the enantioselective propargylic alkylation. Typical results are described here.

RESULTS AND DISCUSSION

Treatment of 1-(1-naphthyl)-2-propyn-1-ol (**1a**) with 3 equiv of diethyl 2-oxocyclopentylphosphonate (**2a**) in the presence of catalytic amounts of the thiolate-bridged diruthenium complex[9,10] $[Cp^*RuCl(\mu_2\text{-}SMe)]_2$ (Cp^* = η^5-C_5Me_5; **3a**), the copper complex $Cu(OTf)_2$, and (4*R*,4′*R*,5*S*,5′*S*)-2,2′-(cyclopropane-1,1-diyl)bis(4,5-diphenyl-4,5-dihydrooxazole) (**4a**), and NH_4BF_4 in tetrahydrofuran (THF) at room temperature for 40 h gave diethyl 1-(1-(naphthalen-1-yl)prop-2-ynyl)-2-oxocyclopentylphosphonate (**5a**) in 63% isolated yield as a mixture of two diastereoisomers (*anti*-**5a**/*syn*-**5a** = 15/1) with 89% ee of *anti*-**5a** (Table 1, entry 1). This result is in sharp contrast to that when ethyl 2-oxocyclopentanecarboxylate was used as a carbon-centered nucleophile under the same reaction conditions (87% yield, *anti*/*syn* = 6/1, 7% ee (*anti*)).[3] The reaction was carried out in other solvents such as dichloromethane, 1,4-dioxane, diethyl ether, and toluene; unsatisfactory results were observed in all cases (Table 1, entries 2−5). Other bis(oxazoline) ligands such as **4b** worked effectively, but substantially lower diastereo- and enantioselectivities were

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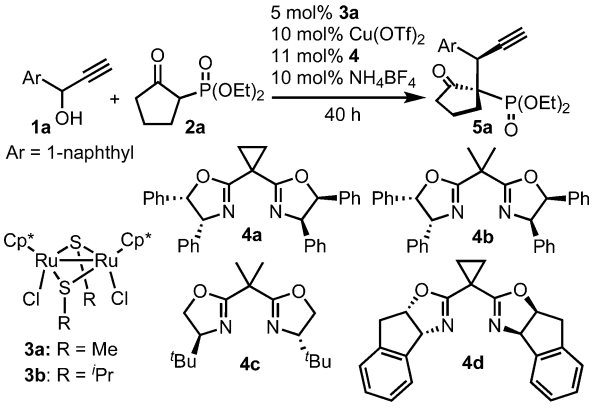
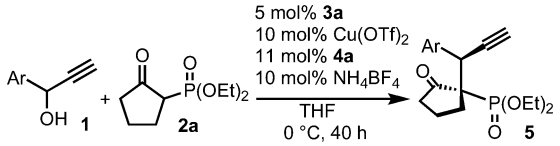
Table 1. Enantioselective Propargylic Alkylations of Propargylic Alcohol (1a) with β-Keto Phosphonate (2a)[a]



run	amt of **2a** (equiv)	**4**	solvent	temp (°C)	yield of **5** (%)[b]	*anti*-**5**/*syn*-**5**[c]	ee of *anti*-**5** (%)[d]
1	3.0	**4a**	THF	room temp	63	15/1	89
2	3.0	**4a**	CH_2Cl_2	room temp	7	>20/1	92
3	3.0	**4a**	1,4-dioxane	room temp	78	14/1	78
4	3.0	**4a**	Et_2O	room temp	26	13/1	86
5	3.0	**4a**	toluene	room temp	23	11/1	80
6	3.0	**4b**	THF	room temp	59	16/1	70
7	3.0	**4c**	THF	room temp	0		
8	3.0	**4d**	THF	room temp	18	>20/1	92
9	1.5	**4a**	THF	room temp	77	19/1	87
10	1.5	**4a**	THF	0	89	>20/1	91
11[e]	1.5	**4a**	THF	0	99	>20/1	82

[a]All reactions of **1a** (0.20 mmol) with **2a** were carried out in the presence of **3a** (0.010 mmol), $Cu(OTf)_2$ (0.020 mmol), **4** (0.022 mmol), and NH_4BF_4 (0.020 mmol) in 2 mL of solvent. [b]Isolated yield. [c]Determined by ^1H NMR. [d]Determined by HPLC. [e]**3b** was used instead of **3a**.

Table 2. Enantioselective Propargylic Alkylations of Propargylic Alcohols (1) with β-Keto Phosphonate (2a)[a]



run	Ar	yield of **5** (%)[b]	*anti*-**5**/*syn*-**5**[c]	ee of *anti*-**5** (%)[d]
1	1-naphthyl (**1a**)	89 (**5a**)	>20/1	91
2	2-naphthyl (**1b**)	94 (**5b**)	3/1	96
3	Ph (**1c**)	97 (**5c**)	2/1	81
4	*p*-MeC_6H_4 (**1d**)	94 (**5d**)	4/1	87
5	*p*-ClC_6H_4(**1e**)	95 (**5e**)	7/1	82
6	*p*-$MeOC_6H_4$ (**1f**)	93 (**5f**)	2/1	89
7	*o*-$MeOC_6H_4$ (**1g**)	93 (**5g**)	>20/1	64
8	4-methyl-1-naphthyl (**1h**)	82 (**5h**)	>20/1	97

[a]All reactions of **1** (0.20 mmol) with **2a** (0.30 mmol) were carried out in the presence of **3a** (0.010 mmol), $Cu(OTf)_2$ (0.020 mmol), **4a** (0.022 mmol), and NH_4BF_4 (0.020 mmol) in 2 mL of solvent. [b]Isolated yield. [c]Determined by ^1H NMR. [d]Determined by HPLC.

observed when **4c**,**d** were used as bis(oxazoline) ligands (Table 1, entries 6−8). Only the use of 1.5 equiv of **2a** with respect to **1a** was enough to promote the propargylic alkylation (Table 1, entry 9). The reaction proceeded smoothly even at 0 °C, higher diastereo- and enantioselectivities being observed (Table 1, entry 10). Other diruthenium complexes such as the complex bearing the sterically more demanding S^{i}Pr moiety [Cp*RuCl-(μ_2-S^{i}Pr)]$_2$ (**3b**) exhibited a lower enantioselectivity (Table 1, entry 11). Separately, we confirmed that the use of only **3a** or copper complex did not promote the propargylic alkylation. This result indicates that both **3a** and copper complex worked cooperatively as catalysts to promote the catalytic reaction enantioselectively.

Next, propargylic alkylation of a variety of propargylic alcohols was carried out by using **3a** and the copper complex with **4a** as cocatalysts. Typical results are shown in Table 2. Similarly, a high enantioselectivity was observed when 1-(2-naphthyl)-2-propyn-1-ol (**1b**) was used as a substrate (Table 2, entry 2). Introduction of a methyl or a chloro group at the para position of the benzene ring of propargylic alcohols did not greatly affect the reactivity and enantioselectivity of the propargylic alkylated products (Table 2, entries 4 and 5), but a high enantioselectivity was observed when a methoxy group was introduced at the para position of the benzene ring of the propargylic alcohol (Table 2, entry 6). Interestingly, the introduction of a methoxy group at the ortho position of the

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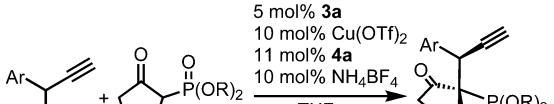
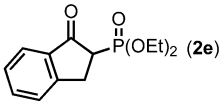
benzene ring of propargylic alcohols substantially decreased the enantioselectivity (Table 2, entry 7). When a methyl group was introduced at the 4-position of the naphthalene ring of propargylic alcohol, the enantioselectivity was dramatically improved up to 97% ee (Table 2, entry 8). No reaction occurred at all under the same reaction conditions when 1-cyclohexyl-2-propyn-1-ol was used as a substrate, indicating that the presence of an aryl moiety at the propargylic position of **1** is necessary to achieve the reaction.

Propargylic alkylation with other β-keto phosphonates also proceeded smoothly to give the corresponding propargylic alkylated products with a high enantioselectivity. Typical results are shown in Table 3. When methyl, propyl, and butyl groups

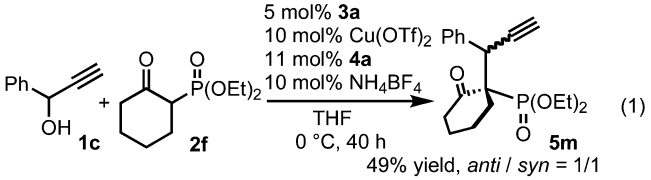
Table 3. Enantioselective Propargylic Alkylations of Propargylic Alcohol (1a) with β-Keto Phosphonates (2)[a]



run	2	yield of 5 (%)[b]	*anti*-5/*syn*-5	ee of *anti*-5 (%)[d]
1	R = Et (**2a**)	89 (**5a**)	>20/1	91
2	R = Me (**2b**)	97 (**5i**)	19/1	90
3	R = ^{n}Pr (**2c**)	92 (**5j**)	>20/1	92
4	R = ^{n}Bu (**2d**)	78 (**5k**)	16/1	91
5	 (**2e**)	92 (**5l**)	>20/1	82

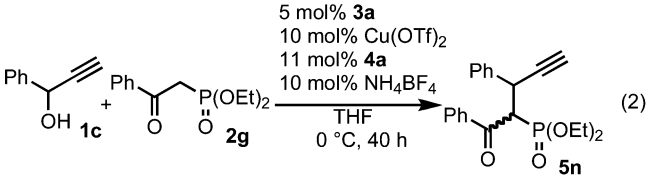
[a]All reactions of **1a** (0.20 mmol) with **2** (0.30 mmol) were carried out in the presence of **3a** (0.010 mmol), $Cu(OTf)_2$ (0.020 mmol), **4a** (0.022 mmol), and NH_4BF_4 (0.020 mmol) in 2 mL of solvent. [b]Isolated yield. [c]Determined by ^{1}H NMR. [d]Determined by HPLC.

were used as ester moieties in place of the ethyl group in **2a**, a similar high enantioselectivity was observed in all cases (Table 3, entries 2–4). The reaction of **1a** with β-keto phosphonate bearing an indane skeleton (**2e**) under the same reaction conditions gave the corresponding alkylated product in 92% yield with 82% ee (Table 3, entry 5). Unfortunately, the reaction of **1c** with 2-oxocyclohexylphosphonate (**2f**) gave only a mixture of two diastereoisomers in 49% yield with moderate enantioselectivity (eq 1). The use of acyclic phosphonates such as diethyl 2-oxo-2-phenylethylphosphonate (**2g**) afforded the corresponding alkylated product with 72% ee, but a mixture of



(1)

49% yield, *anti* / *syn* = 1/1
anti = 64% ee, *syn* = 92% ee



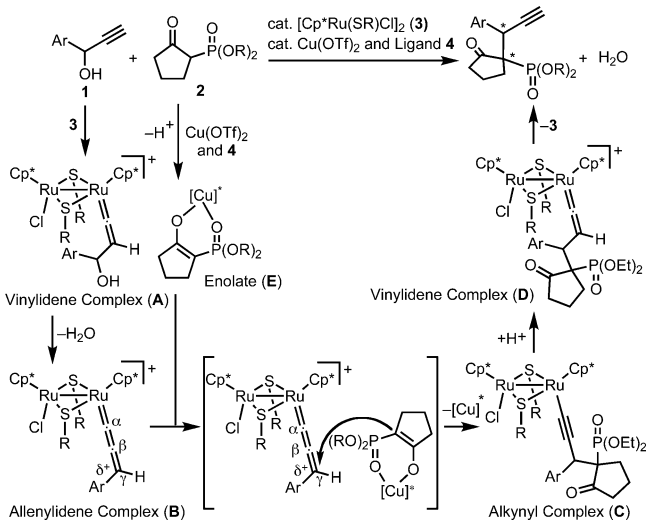
(2)

68% yield, *anti* / *syn* = 1/1
anti = 72% ee, *syn* = 72% ee

two diastereoisomers (eq 2). These results indicate that the use of the β-keto phosphonates bearing a tertiary carbon at the α position is necessary to achieve a high diastereoselectivity. However, the reaction with diethyl 1-methyl-2-oxo-2-phenylethylphosphonate under the same reaction conditions did not proceed at all. As a result, a high enantioselectivity was observed when 2-oxocyclopentylphosphonate derivatives were used as carbon-centered nucleophiles in the present alkylation. The diastereoselectivity of the corresponding propargylic alkylated products in the present alkylation was higher than that of the previous alkylated products where β-keto esters were used as carbon-centered nucleophiles.[3]

A proposed reaction pathway is shown in Scheme 2. The initial step is the formation of an allenylidene complex (**B**) by

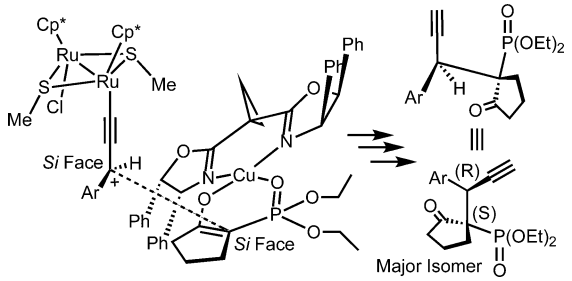
Scheme 2



the reaction of propargylic alcohol **1** with **3** via a vinylidene complex (**A**). Subsequent attack of an enolate (**E**), generated in situ from β-keto phosphonates **2** and $Cu(OTf)_2$ bearing **4**, on the γ carbon of **B** results in the formation of another vinylidene complex (**D**) via an alkynyl complex (**C**). After transformation of the vinylidene complex **D** into the corresponding π-alkyne complex, the alkylated product **5** is formed by ligand exchange with another molecule of propargylic alcohol **1**.

After one recrystallization of *anti*-**5a**, the enantiomerically pure *anti*-**5a** was isolated, and its absolute configuration was determined as 1*S*,1′*R* by X-ray analysis.[11] To account for the enantio- and diastereoselective formation of (1*S*,1′*R*)-**5**, we propose transition states between the ruthenium allenylidene complex and the copper enolate complex in Scheme 3.[12] In this

Scheme 3



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reaction system, the square-planar-like copper enolate proposed by Jørgensen and co-workers[13] attacks the *Si* face of the allenylidene complex from the *Si* face of the enolate, leading to the carbon−carbon bond formation. We consider that this is another successful example of the enantioselective propargylic alkylation of propargylic alcohols by using a cooperative catalytic system, where the corresponding propargylic alkylated products have a highly enantioselective tetrasubstituted carbon at the homopropargylic position.

In summary, we have found the ruthenium- and copper-catalyzed enantioselective propargylic alkylation of propargylic alcohols with β-keto phosphonates to give the corresponding propargylic alkylated products in excellent yields with high diastereo- and enantioselectivities (up to 97% ee). This catalytic reaction is considered to provide a new type of enantioselective propargylic substitution reaction,[14] where the enolates generated in situ from the copper complex and β-keto phosphonates enantioselectively attack the ruthenium-allenylidene complexes. In the present reaction system, both transition-metal catalysts (ruthenium complex and copper complex) activate propargylic alcohols and β-keto phosphonates, respectively, and both catalysts cooperatively and simultaneously work to promote the propargylic alkylation enantioselectively. The produced propargylic alkylated products have a highly enantioselective tetrasubstituted carbon at the homopropargylic position. We believe that the finding described herein will open up not only a new type of enantioselective propargylic substitution reaction but also a new aspect of cooperative catalytic reactions using distinct transition metals to achieve more valuable transformations that could not be realized by single catalysts. Further work is currently in progress to apply this strategy to other reaction systems.

■ ASSOCIATED CONTENT

Supporting Information

Text, figures, and tables giving experimental procedures and spectroscopic data for all compounds and a CIF file giving crystallographic data for *anti*-**5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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