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Mild and Efficient Allylation of Aldehydes by using Copper Fluorapatite as Catalyst

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Abstract: A facile synthesis of homoallylic alcohols is achieved by the allylation of aldehydes with allylic metal reagents or allyl halides using copper fluorapatite (CuFAP) as catalyst under mild reaction conditions. A variety of aldehydes were converted to the corresponding homoallylic alchohols, demonstrating the versatility of the reaction.

Keywords: aldehydes; allylation; copper fluorapatite; homoallylic alcohols

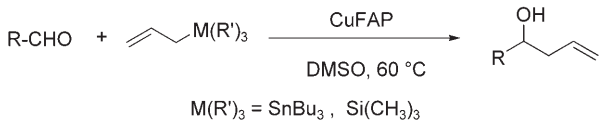
Allylation of aldehydes by various allylic metals is an important synthetic transformation[1] as the resultant homoallylic alcohols are versatile synthons in the preparation of materials, natural products, bioactive compounds and many complex molecules.[2] The general practice for the preparation of homoallylic alcohols involves nucleophilic addition of an allylic metal reagent to carbonyl compounds. Previously, numerous reports on such transformations carried out using various Lewis acids, Brønsted acids,[3] metal salts,[4] β-cyclodextrin,[5] organometallic reagents in organic media, aqueous media, ionic liquids[6] and PEG[7] have been published. The Barbier reaction[8] is an alternative method for the synthesis of homoallylic alcohols, this is the reaction of a carbonyl compound with an organic halide in the presence of magnesium metal. Aluminum,[9] magnesium,[10] manganese,[11] indium,[12] antimony,[13] bismuth,[14] lead,[15] gallium,[16] zinc,[17] and tin[18] mediated Barbier reactions in aqueous medium are well known in the literature. Although good yields can often be obtained in these reactions, the use of zero-valent metals causes metal oxide or hydroxide precipitation on the surface of the metal in some cases which leads to termination or increased duration of ther reaction. Furthermore, some zero-valent metals are too reactive and significant by-products like pinacol can be produced in the reaction. Roy et al. reported the first example of carbonyl allylation in heterogenous media involving SnO and catalytic Cu_2O.[19] However, in the above methods the use of an organic co-solvent such as THF was necessary. Guo et al. reported the $SnCl_2$-mediated carbonyl allylation in aqueous media using various Lewis acid additives.[20]

The development of more improved synthetic methods for the preparation of homoallylic alcohols remains an active research area.

Apatites are basic metal phosphates for which the chemical formula is $M_{10}(PO_4)_6(X)_2$ [M = divalent metal, X = monovalent anion] and various kinds of cations and anions can be readily introduced into their frameworks due to their large ion exchange ability and such exchanged apatites are already in use in several organic transformations.[21,22] Very recently, we reported the preparation of recyclable, heterogeneous, Cu-exchanged fluorapatite and copper exchanged *tert*-butoxyapatite catalysts, for the *N*-arylation of imidazoles and other heterocycles with iodo-, bromo-, chloro- and fluoroarenes (EW) with good to excellent yields.[23a,b] We also reported the PdFAP catalyst (fluorapatite-supported palladium catalyst) for Suzuki and Heck coupling reactions.[23c]

We herein report a convenient method involving the use of the CuFAP catalyst for the allylation of aldehydes with allyltributylstannane or allytrimethylsilane (Scheme 1) and Barbier-type allylation of carbonyl compounds with allyl halides for the synthesis of homoallylic alcohols (Scheme 2).

In an effort to evolve a better catalytic system, various reaction parameters were screened in the allylation reaction between benzaldehyde and allyltributylstannane and it was found that CuFAP catalyst in



Scheme 1. Allylation of aldehydes with allyltributylstannane and allytrimethylsilane catalyzed by CuFAP.

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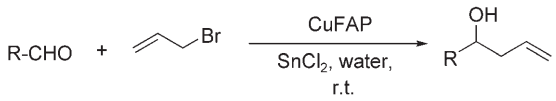
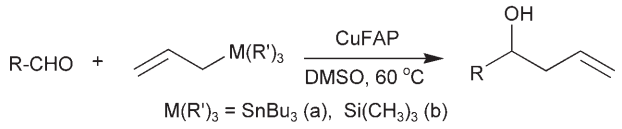


Scheme 2. Barbier-type allylation of aldehydes catalyzed by CuFAP.

DMSO at 60 °C afforded good yields of the desired product. Allyltrimethysilane also reacted equally well with benzaldehyde under similar conditions with good yields of corresponding homoallylic alcohols. The controlled reaction conducted under identical conditions devoid of CuFAP did not give any product despite prolonged reaction times. CuFAP was recovered quantitatively by simple centrifugation and reused for four cycles with consistent activity (Table 1, entry 1), moreover, the absence of copper in the filtrate was demonstrated by AAS which confirms no leaching of copper during the reaction and provides evidence for heterogeneity throughout the reaction.

Table 1. Allylation of carbonyl compounds with allyltributylstannane and allytrimethylsilane catalyzed by CuFAP.[a]



Entry	Substrates (R)	Time [h]		Yield [%] [b]	
		a	b	a	b
1	C_6H_5	3	3	96, 95,[c] 78[d]	92
2	4-Cl-C_6H_4	3	3	94	90
3	2-Cl-C_6H_4	3	4	95	89
4	4-Br-C_6H_4	5	8	90	85
5	4-CN-C_6H_4	4	4	93	90
6	4-NO_2-C_6H_4	4	4	90	89
7	4-CF_3-C_6H_4	6	8	88	85
8	4-CH_3-C_6H_4	8	10	82	80
9	4-pyridyl	2	2	93	90
10	2-pyridyl	1	1	95	90
11	2-Furfuryl	3	3	90	85
12	$C_6H_5(CH)_2$	3	4	90	87
13	C_6H_{11}	5	7	87	87
14	C_2H_5	7	10	82	82

[a] *Reaction conditions:* aldehyde (1 mmol), allylic metal reagent (1.2 mmol), CuFAP (0.1 g), DMSO (3 mL), 60 °C.
[b] Isolated yields
[c] Yield after fourth cycle.
[d] *Reaction conditions:* aldehyde (10 mmol), allylic metal reagent (12 mmol), CuFAP (1 g), DMSO (30 mL), 60 °C.

In order to understand the scope and limitations of the CuFAP-catalyzed allylation reaction, various structurally divergent aldehydes possessing a wide range of functional groups were reacted with allyltributylstannane and allytrimethylsilane to give the corresponding homoallylic alcohols and the results are summarized in Table 1.

As per expectation, aldehydes with an electron-donating group gave lower yields of the desired product whereas the presence of electron-withdrawing groups produced better yields (Table 1, entries 1–8).

Heteroaromatic aldehydes such as 4-pyridinecarboxaldehyde, 2-pyridine-carboxaldehyde and 2-furaldehyde (Table 1, entries 9–12), gave good yields of the corresponding homoallylic products with shorter reaction times. Highly conjugated aromatics like cinnamaldehyde and aliphatic aldehydes such as cyclohexanecarboxaldehyde and propionaldehyde afforded moderate yields of the corresponding homoallylic alcohols after long reaction durations (Table 1, entries 13 and 14).

Impressed by the results on the allylation reaction with allyltributylstannane and allytrimethylsilane, we further extended the scope of our catalytic system for the Barbier-type allylation of carbonyl compounds with allyl halides mediated by $SnCl_2$ in aqueous media.

In an effort to develop a better catalytic system, various catalysts were screened in the allylation reaction between 4-chlorobenzaldehyde and allyl bromide in the presence of $SnCl_2$ in water and the results are summarized in Table 2. CuFAP, afforded very good yields whereas CuHAP (copper hydroxyapatite) and homogeneous $Cu(OAc)_2$ provided moderate yields. Other supported copper catalysts such as Cu/NaY, Cu/SiO_2, Cu/Al_2O_3, and Cu/TiO_2 were also screened and the results are summarized in Table 2. The order of efficiency is CuFAP > Cu/NaY > CuHAP > Cu/TiO_2 > $Cu(OAc)_2$ > Cu/Al_2O_3 > Cu/SiO_2. There is no reaction in the control experiment conducted in the absence of catalyst under identical conditions. CuFAP was recovered quantitatively by simple filtration and reused with consistent activity (Table 2, entry 2).

We chose a variety of structurally divergent aldehydes possessing a wide range of functional groups for our study to understand the scope and the generality of the CuFAP-catalyzed allylation of aldehydes and the results are summarized in Table 3. Among the various aldehydes tested, heteroaromatic aldehydes such as 4-pyridinecarboxaldehyde, 2-pyridinecarboxaldehyde and 3-pyridinecarboxaldehyde (Table 3, entries 12–14) gave very good yields of the coupling product with shorter duration of reaction. Allylation was slow with 2-naphthaldehyde when compared with the other aromatic aldehydes (Table 3, entry 11). Electron-donating groups on the aromatic ring gave lower yields of desired product compared

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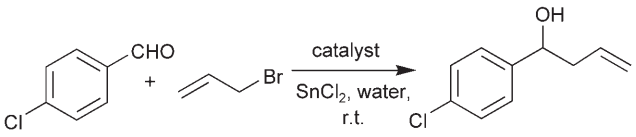
Table 2. Allylation of 4-chlorobenzaldehyde with allyl bromide using different catalysts.[a]



Entry	Catalyst	Time [h]	Yield [%][b]
1	CuHAP	1.5	62
2	CuFAP	1.5	96, 92[c]
3	$Cu(OAc)_2$	1.5	57, 59[d]
4	Cu/Al_2O_3	1.5	46
5	Cu/SiO_2	1.5	30
6	Cu/TiO_2	1.5	57
7	Cu/NaY	1.5	65

[a] *Reaction conditions:* 4-chlorobenzaldehyde (1 mmol), allyl bromide (1.2 mmol), copper (0.073 mmol), water (1 mL), reaction time (1.5 h), room temperature.
[b] Isolated yields.
[c] Yield after third cycle.
[d] 10 mol% catalyst.

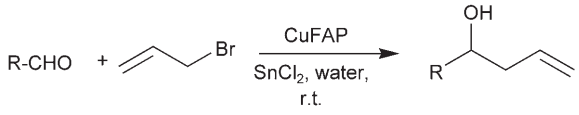
with electron-withdrawing groups which produced better yields with shorter reaction time (Table 3, entries 1–7, 10 and 19). Nitrobenzaldehyde gave the desired product in excellent yields without reduction of nitro group (Table 3, entry 3). Aliphatic aldehydes such as propionaldehyde, heptaldehyde and cyclohexanecarboxaldehyde gave satisfactory yields with longer reaction times (Table 3, entries 20–22). Nevertheless, the CuFAP-catalyzed allylation does not work efficiently for ketones. Among the various allyl halides used, allyl bromide proved to be a good allylating agent in the above reaction (Table 3, entry 1).

In order to study the effect of the CuFAP catalyst on the regio- and diasteroselectivities of the allylation reaction, we have carried out a reaction between cinnamyl bromide and benzaldehyde in the presence of $SnCl_2$/CuFAP under similar reaction conditions. It is well known in the literature that allylation reactions involving cinnamyl halides can provide both α- and γ-adducts. The γ-adduct can be either the *anti*- or *syn*-product (Scheme 3). The reaction with CuFAP catalyst gave an 80% yield in which the γ-adduct is obtained as the favorable isomer (98% determined by 300 MHz ^{1}H NMR) with good diasteroselectivity to the *anti*-product (85% determined by 300 MHz ^{1}H NMR).

Encouraged by the results of the allylation of aromatic, aliphatic, conjugated and heteroaromatic aldehydes with allyltributylstannane and allytrimethylsilane, we further tried to extend the scope of the allylation to 2,3-*O*-isopropylidene-1-*O*-methyl-*R*-D-*xylo*-pentodialdo-1,4-furanose (Scheme 4). We obtained good yields of the corresponding homoallylic alcohol with a diastereomeric ratio 1.8:1 (diastereomeric ratio of the product was calculated by proton NMR). Studies on the allylations of various sugar aldehydes using CuFAP catalyst are under progress.

In conclusion, we have developed a simple and efficient method for the preparation of homoallylic alcohols from aldehydes and allyltributylstannane or ally-

Table 3. Allylation of aldehydes catalyzed by CuFAP.[a]



Entry	Substrates	Time [h]	Yield [%][e]
1	4-Cl-C_6H_4	1.5,[b] 2.5,[c] 2[c]	96,[b] 94,[c] 92[d]
2	3-NO_2-C_6H_4	1.5	97
3	4-NO_2-C_6H_4	1.5	97
4	3-Br-C_6H_4	1.5	96
5	2-Br-C_6H_4	1.5	95
6	4-Br-C_6H_4	4	90
7	4-CF_3-C_6H_4	2.5	93
8	2,4,6-CH_3-C_6H_2	2	97
9	C_6H_5	1.5	96
10	4-CH_3-C_6H_4	2	89
11	$C_{10}H_7$	2.5	89
12	4-pyridyl	1	97
13	2-pyridyl	1	96
14	3-pyridyl	1	96
15	4-CN-C_6H_4	2.5	90
16	2-Cl-C_6H_4	2	94
17	$C_6H_5(CH)_2$	4	90
18	2-Furfuryl	2	91
19	4-MeO-C_6H_4	4	80
20	C_2H_5	6	80
21	*n*-C_6H_{13}	6	82
22	C_6H_{11}	8	71

[a] *Reaction conditions:* aldehyde (1 mmol), allyl halide (1.2 mmol), catalyst (0.1 g), water (1 mL), room temperature.
[b] Isolated yield with allyl bromide as allylating agent.
[c] Isolated yield with allyl chloride as allylating agent.
[d] Isolated yield with allyl iodide as allylating agent.
[e] Isolated yields.

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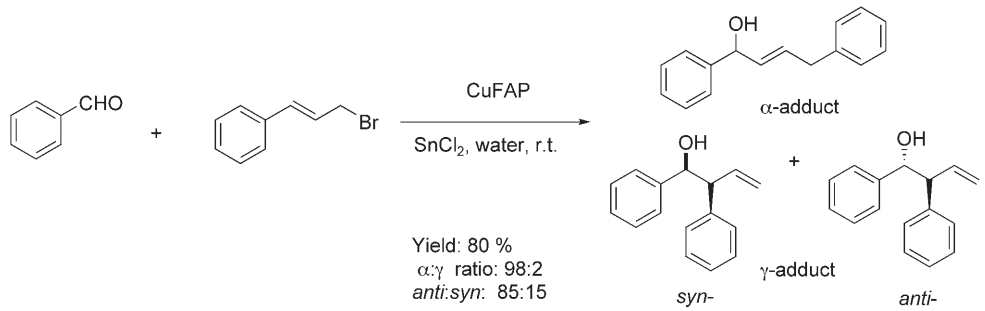
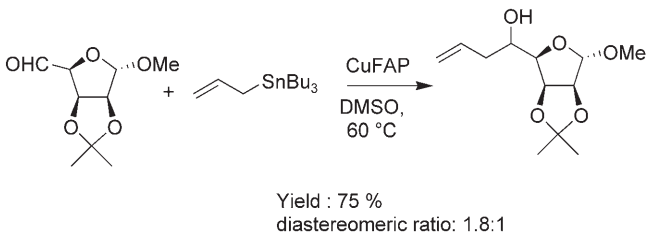


Scheme 3. Barbier-type allylation of benzaldehyde with cinnamyl bromide catalyzed by CuFAP.



Scheme 4. Allylation of mannose aldehyde (2,3-*O*-isopropylidene-1-*O*-methyl-*R*-D-*xylo*-pentodialdo-1,4-furanose) with allyltributylstannane catalyzed by CuFAP.

trimethylsilane using the CuFAP catalyst. Various structurally divergent aldehydes were reacted with allyltributylstannane and allytrimethylsilane to yield the corresponding homoallylic alcohols with moderate to excellent yields (80–97%). The Barbier-type allylation of carbonyl compounds with allyl halides was also carried out with this catalyst. This catalyst offers several advantages including mild reaction conditions, shorter reaction times, good yields of the products with low catalytic loading. We believe that this methodology will find widespread use in organic synthesis for the preparation of homoallylic alcohols.

Experimental Section

Typical Procedure for Preparation of Copper Fluorapatite

Calcium fluorapatite $[Ca_{10}(PO_4)_6(F)_2]$ was synthesized according to the literature procedure.[24] CaFAP (1 g) was stirred with aqueous copper acetate (400 mg, 2 mmol in 25 mL water) at 80 °C for a period of 10 h. The slurry obtained was filtered, washed with deionized water, and dried overnight at 110 °C, yielding copper-exchanged fluorapatite as a blue powder. Copper-exchanged fluorapatite (CuFAP) was characterized by XPS, AAS and IR. XPS analysis of the CuFAP catalyst indicated the same binding energy values for Ca, P and O as in CaFAP. A narrow scan of Cu $2p_{3/2}$ for CuFAP showed the binding energy peak at 934.9 eV [the binding energy of Cu in Cu(II) is around 935 eV],[19] which indicates copper in the +2 oxidation state in CuFAP. The copper contents in the fresh and the used catalyst (CuFAP) were analyzed by AAS and the leaching of copper is about 1.2% after the Barbier-type allylation reaction.

Typical Procedure for Allylation of Benzaldehyde with Allyltributylstannane

CuFAP (100 mg) was added to a mixture of benzaldehyde (1 mmol) and allyltributylstannane (1.2 mmol) in DMSO (3 mL). The mixture was stirred for an appropriate time at room temperature. After completion of the reaction, as indicated by TLC, the reaction mixture was quenched with aqueous sodium hydrogen carbonate and extracted with ethyl acetate (3×10 mL). The combined organic extract was dried over anhydrous sodium sulfate and concentrated under reduced pressure to give the crude product. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate, 90/10) to afford pure 1-(phenyl)-3-buten-1-ol. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.32$ (br, s 1H), 2.44 (t, $J = 6.7$ Hz, 2H), 4.62 (t, $J = 6.7$ Hz, 1H), 5.04–5.14 (m, 2H), 5.65–5.82 (m, 1H), 7.18–7.32 (m, 5H).

Typical Procedure for CuFAP/$SnCl_2$-Mediated Carbonyl Allylation

CuFAP (100 mg) was added to a mixture of 4-chlorobenzaldehyde (1 mmol), allyl bromide (1.2 mmol) and tin chloride (1.2 mmol) in water (1.5 mL). The mixture was stirred for 1 h at room temperature. After completion of the reaction, as indicated by TLC, the product was extracted with ethyl acetate (3×10 mL). The combined extract was concentrated under vacuum and the resulting product was purified by column chromatography on silica gel with ethyl acetate and *n*-hexane as eluent to afford pure 1-(4-chlorophenyl)-3-buten-1-ol. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.90$–2.32 (br, 1H), 2.45(dd, J=5.63, 6.64 Hz, 2H), 4.68(t, J=7.29 Hz, 1H), 5.15 (t, $J = 11.7$ Hz, 2H), 5.66–5.83 (m, 1H), 7.21–7.32 (m, 4H). The products were characterized by comparison of their NMR and mass spectra with those of authentic samples.[25–27]

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