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Editor's Choice

Catalytic Organic Reactions on the Surface of Silver(I) Oxide in Water

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We have developed Ag_2O-catalyzed allylation reactions of aldehydes with allylsilanes in water, providing homoallylic alcohols in high yields with high *anti*-selectivities. It was found that the reactions proceeded not in the water solution but on the surface of Ag_2O. We could reduce the amount of the catalyst to less than 0.01 mol %. Moreover, an asymmetric allylation reaction was performed in water with high yield and moderate enantioselectivity by using a chiral phosphine ligand.

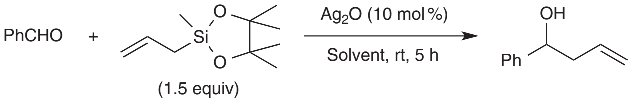
Recently, from the viewpoint of the environment and sustainable development, alternative media to commonly used organic solvents for organic reactions have been extensively studied. In particular, attention has been paid to water as a solvent because it is safe, benign, environmentally friendly, and inexpensive as compared with organic solvents.[1] Furthermore, unique reactivities and selectivities, which are observed only in water, have been reported.[2–4]

Catalytic reactions are also important from the standpoint of green sustainable chemistry.[5] In catalytic reactions in water, solubility of organic substrates and catalysts is an important issue. Water-soluble catalysts are not necessarily efficient because organic substrates are not soluble in water. To address this issue, surfactant-like amphiphilic catalysts have been developed;[6] however, separation of such catalysts after the reaction poses another problem. We report here a different catalysis in water: catalytic reactions proceeding efficiently on the surface of an inorganic solid (Ag_2O). Allylation reactions of water-insoluble substrates proceeded smoothly in 100% water.

We have recently developed enantioselective 1,4-additions of diboron to α,β-unsaturated carbonyl compounds and nitrile catalyzed by $Cu(OH)_2$ with a chiral bipyridine ligand in water.[2f] Interestingly, all the components (catalyst, chiral ligand, and substrates) are insoluble in water, but the reactions proceeded smoothly, effective asymmetric environments were created on the surface of the metal catalyst, and very efficient catalyst turnover was achieved with high enantioselectivity. Inspired by this work, we investigated silver(I) oxide (Ag_2O)-catalyzed allylation reactions of aldehydes in water.

The allylation reaction of aldehydes to provide homoallylic alcohols is one of the most important carbon–carbon bond-forming reactions.[7] Recently, we developed $Zn(OH)_2$–dimethylphenanthroline complex-catalyzed *syn*-selective allylation reactions of aldehydes with allylboronates in aqueous media.[3] This reaction system was applied to asymmetric reactions using a chiral bipyridine ligand instead of dimethylphenanthroline.[3b] We also reported[8] Ag_2O-catalyzed *anti*-selective allylation reactions of aldehydes with allyltin in aqueous media.[4] In searching for more environmentally friendly reagents, we found that allysilanes[9] also worked as allylation reagents.

Table 1. Effect of solvents



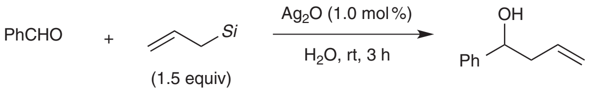
Entry	Solvent	Yield/%	Entry	Solvent	Yield/%
1	$DME/H_2O = 6/1$	70	9	EtOH	80
2	$THF/H_2O = 6/1$	52	10	H_2O	80
3	$MeCN/H_2O = 6/1$	42	11[a]	H_2O	NR
4	$acetone/H_2O = 6/1$	69	12[b]	H_2O	86
5	$hexane/H_2O = 6/1$	61	13	neat (No solvent)	31
6	$MeOH/H_2O = 6/1$	65	14	THF	22
7	$EtOH/H_2O = 6/1$	81	15[c]	$EtOH/H_2O = 1/1$	23
8	$^iPrOH/H_2O = 6/1$	80	16[c]	H_2O	62

[a]Without catalyst. [b]1.0 mol % Ag_2O was used. [c]$PhCH_2CH_2CHO$ was used instead of PhCHO.

First, we optimized the reaction conditions for the allylation reaction of benzaldehyde with allylmethylpinacolsilane in the presence of Ag_2O (Table 1). By the screening of cosolvents, it was found that the reaction proceeded smoothly not only in polar solvents (Entries 1–4) and a nonpolar solvent (Entry 5), but also in protic solvents (Entries 6–8). When ethanol (Entry 9) or water (Entry 10) was used as a solvent, the reaction proceeded smoothly with high yield. In this reaction, Ag_2O was necessary as a catalyst (Entry 11); however, 1.0 mol % of the catalyst was sufficient to promote the reaction (Entry 12). It is noted that water is essential for the reaction because the yield decreased when the reaction was conducted under neat conditions or using THF as a solvent (Entries 13 and 14). When we conducted the reaction of 3-phenylpropanal, a better yield was obtained by using only water rather than water–organic solvent mixtures as solvents. Water is best not only for the environment but also as a medium for this reaction (Entries 15 and 16).

Previously, we found that the structure of the boronate parts of allylboronates strongly affected the reactivity in the $Zn(OH)_2$-catalyzed allylation reactions of aldehydes with allylboronates in aqueous media.[3c] Therefore, we synthesized several types of allysilanes and examined the reactivities in water (Table 2). Interestingly, the allylation reaction proceeded smoothly when allylmethylpinacolsilane was used; however, the reaction did not proceed at all when allyltrimethylsilane or allyltrimethoxysilane was used as an allylation reagent (Entries 1–3). Yoshida et al. reported that 10 mol % of silver acetate-catalyzed allylation reactions of aldehydes with allyldimethyl(2-pyridyl)silane in an organic solvent.[10a] In that study, they also used a stoichiometric amount of Ag_2O with moderate yield (74%). They also reported the allylation of aldehydes, ketones, and imines by using 10 mol % of CuI and 2.0 equiv of CsF.[10b] When allyldimethyl(2-pyridyl)silane was employed in our system, the reaction proceeded sluggishly (Entry 4). We also conducted the reactions

Table 2. Reactivity of allylsilanes



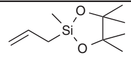
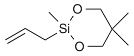
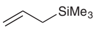
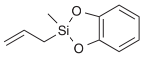
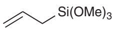
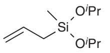
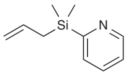
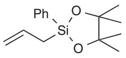
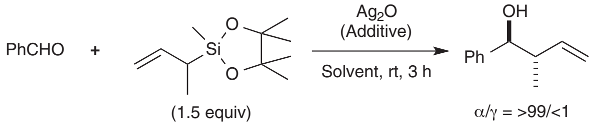
Entry	Allylsilane	Yield/%	Entry	Allylsilane	Yield/%
1		86	5		11
2		NR	6		2
3		NR	7		NR
4		10	8		95

Table 3. Allylation reactions with α-methylallylsilane



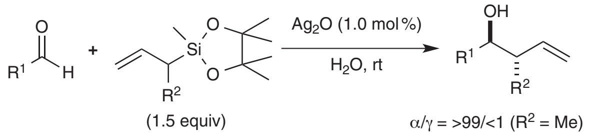
Entry	Solvent	Ag_2O /mol %	Additive /mol %	Yield /%	*syn*/*anti*
1	$MeCN/H_2O = 6/1$	10	—	84	12/88
2	H_2O	10	—	78	22/78
3	H_2O	10	DMAP/48	72	10/90
4	H_2O	1.0	DMAP/5	94	12/88

using allysilanes derived from 2,2-dimethylpropanediol, catechol, or ^{i}PrOH instead of pinacol, and in all cases, the reactions did not proceed well (Entries 5–7). Almost the same reactivity was observed when we used allylphenylpinacolsilane as an allylation reagent (Entry 8).

We next examined the reactions with α-methyl-substituted allylmethylpinacolsilane (Table 3). Similar to the reactions with allyltin,[4] the corresponding α-adduct was obtained exclusively in high yields with good *anti*-selectivities. Accordingly, a reaction mechanism including transmetalation from silicon to silver was proposed.[11] The *anti*-selectivity was decreased in water (Entries 1 and 2). To improve the selectivity, we screened additives and found that the addition of 4-dimethylaminopyridine (DMAP) was effective for obtaining high diastereoselectivities (Entry 3). Even in the presence of 1.0 mol % catalyst, the yield and the selectivity remained at high levels (Entry 4). We then surveyed the substrate scope under the optimal conditions (Table 4). In all cases, the reactions proceeded smoothly to afford the desired homoallylic alcohols in moderate to high yields.

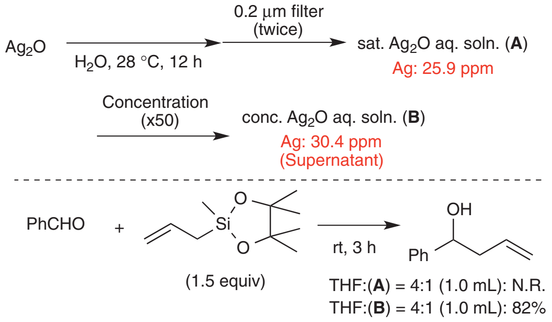
When we observed the reaction medium, Ag_2O seemed to be insoluble in the system. It is known that Ag_2O is slightly soluble in water, and in fact, we observed 25.9 ppm of silver in a solution after filtration (0.2 µm filter, twice), using inductively coupled plasma analysis. However, the reaction did not proceed when this solution was used as the catalyst. In contrast, solid Ag_2O was formed by concentrating the solution, and the reaction proceeded in the presence of this solid (Scheme 1). Judging from these experiments, the reaction proceeded only on the surface of Ag_2O, not in a partially dissolved solution. It was assumed from these results that not all of the Ag_2O was used as the catalyst.

Table 4. Substrate scope



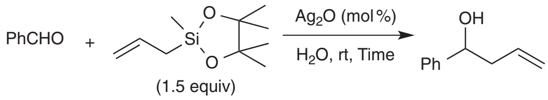
Entry	Aldehyde (R^1)	R^2	Time/h	Yield/%	*syn*/*anti*
1	Ph	H	3	86	—
2	1-Naphthyl	H	3	96	—
3	$4\text{-}MeOC_6H_4$	H	4	48	—
4	$4\text{-}MeC_6H_4$	H	2	85	—
5	$4\text{-}BrC_6H_4$	H	3	90	—
6	PhCH=CH	H	2	75	—
7	$PhCH_2CH_2$	H	3	62	—
8	$^{n}C_9H_{19}$	H	24	49	—
9[a]	Ph	Me	3	94	12/88
10[a]	1-Naphthyl	Me	3	87	16/84
11[a]	$4\text{-}MeOC_6H_4$	Me	3	76	10/90
12[a]	$4\text{-}MeC_6H_4$	Me	3	92	11/89
13[a]	$4\text{-}BrC_6H_4$	Me	3	91	16/84
14[a]	PhCH=CH	Me	3	92	14/86
15[a]	$PhCH_2CH_2$	Me	4	92	11/89
16[a]	$^{n}C_9H_{19}$	Me	3	83	11/89

[a] 5.0 mol % of DMAP was added.



Scheme 1. Confirmation experiments whether the reaction proceeded "in the water solution" or "on the surface of Ag_2O."

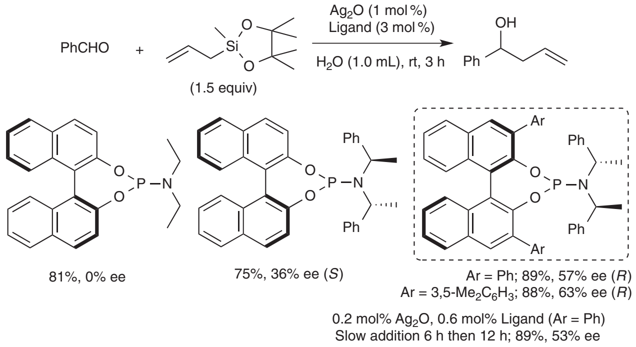
Table 5. Improvement of TON



Entry	Ag_2O/mol % (S/C)	Time/h	Yield/%	TON	TOF/h^{-1}
1	0.1 (1000)	6	75.8	758	127
2	0.02 (5000)	10	86.9	4340	434
3	0.01 (10000)	20	84.3	8430	422
4	0.005 (20000)	32	38.4	7680	240

We then performed the reaction using low catalyst loading of Ag_2O (Table 5), and even in the presence of 0.01 mol % Ag_2O, the reaction proceeded with high productivity (Entry 3).[12]

Finally, we performed an asymmetric variant of this reaction (Scheme 2). The addition of a chiral phosphine ligand[13] was found to be effective, and a high yield with moderate enantioselectivity was observed.



Scheme 2. Asymmetric allylation in water.

In conclusion, we have developed Ag_2O-catalyzed allylation reactions of aldehydes with allylsilanes in water. The reactions proceeded smoothly to afford homoallylic alcohols in high yields with high *anti*-selectivities. It is suggested that only the surface of Ag_2O was used as a catalyst, and we could reduce the amount of the catalyst to less than 0.01 mol %. Moreover, an asymmetric allylation reaction was performed to afford the desired product in high yield with moderate enantioselectivity by using a chiral phosphine ligand. Further investigations to elucidate the reaction mechanism as well as to develop general asymmetric reactions are now in progress.

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Supporting Information is available electronically on J-STAGE.

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