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Diastereoselective Allylation of ω-Hydroxy Carbonyl Compounds by Allylic Alcohols with Pd-$SnCl_2$

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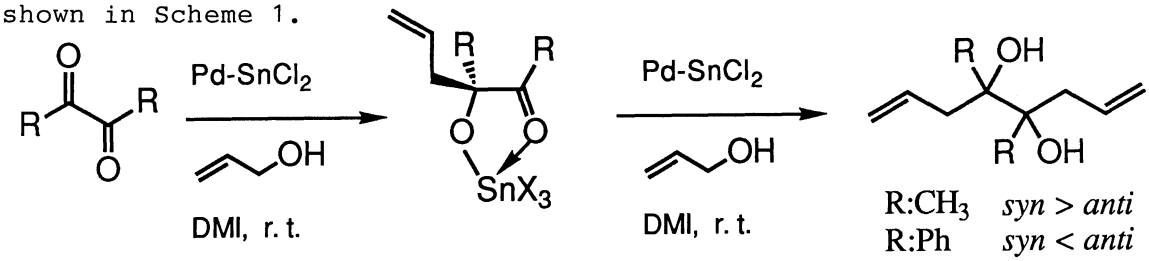
Allylation of ω-hydroxy carbonyl compounds by allylic alcohols with Pd-$SnCl_2$ proceeded smoothly in neutral polar medium with high regio- and diastereocontrol via chelated bicyclic transition state.

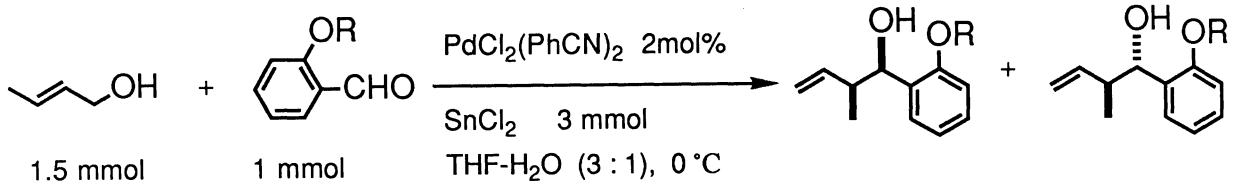
A chelation-controlled addition of nucleophiles such as organometallic compounds to carbonyl compounds is one of the effective methods for stereoselective synthesis.[1] A nonpolar solvent has to be used for the achievement of highly chelation-controlled diastereoselection.[2] Thus some organometallic reagents, which are insoluble in the solvent, cannot be employed. Effective chelation in a polar solvent allows us to use a variety of nucleophiles for the diastereoselective synthesis. In our previous report,[3] the chelation of carbonyl group to intramolecular tin alkoxide formed in polar solvent proved to be effective for diastereoselective diallylation of 1,2-diketones by allyl alcohol with Pd-$SnCl_2$, as shown in Scheme 1.



Scheme 1.

We here describe the effect of a chelation of a hydroxy group and a carbonyl group to Sn(IV) of allylic tin intermediate in diastereocontrolled allylation of ω-hydroxy carbonyl compounds with Pd-$SnCl_2$ in polar solvent.[4,5] We first employed salicylaldehyde as a hydroxy carbonyl compound; the reaction with (E)-crotyl alcohol in THF-H_2O (3:1) medium led

to syn selection (Scheme 2).[6] The allylation of aldehyde by (E)-crotyl alcohol with Pd-$SnCl_2$ in THF-H_2O usually proceeds via a chair form of six-membered cyclic transition state **A** in Fig. 1 to exhibit anti selectivity,[5] as has been found in the reaction of 2-methoxybenzaldehyde (Scheme 2).[6]



R = Me	63%	6	:	94
R = H	74%	94	:	6

Scheme 2.

The syn selectivity in the case of salicylaldehyde allowed us to posit the existence of 1,3-bridged six-membered bicyclic transition state **B** in Fig. 1 formed by a chelation of a carbonyl group and a hydroxy group to Sn(IV),[7] even in a neutral polar solvent.

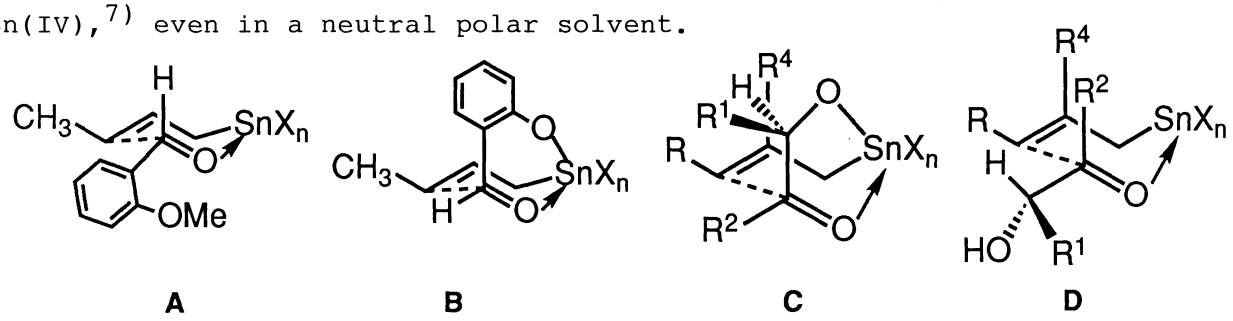
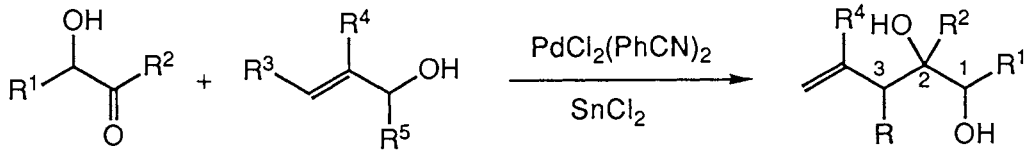


Fig. 1. Transition states.

Next, we applied this kind of chelation of hydroxy carbonyl compound to the palladium-catalyzed diastereoselective allylation of α-hydroxy ketones. Some representative results are summarized in Table 1. 2,3-Syn selection was observed in 1-methylallylation of α-hydroxy ketones in THF (Entries 4-6 and 9). It suggests that these reactions also proceed via 1,3-bridged six-membered bicyclic transition states **C** (Fig. 1),[7] similarly to transition states **B** in the case of salicylaldehyde. Use of THF-H_2O as a solvent instead of THF led to anti selection (Entries 7 and 10). H_2O may disturb the chelation of hydroxy group, which needs in the formation of the bicyclic transition state **C**. Even in THF-H_2O, the 1-methylallylation of salicylaldehyde led to syn selection without the disturbance of H_2O. Hence, this kind of chelation should be dependent on acidity of hydroxy groups. 1,2-Syn selection was obtained in both THF and THF-H_2O (Entries 1-3 and 6-10). The 1,2-syn selection in THF can be explained by the chelated

Table 1. Allylation of α-hydroxy ketones by allylic alcohols[a)]



Entry	Ketone		Alcohol			Product	Solvent[b)]	Temp	Time	Yield	Ratio[c)]	
											C1-C2	C2-C3
	R^1	R^2	R^3	R^4	R^5	R		°C	h	%	syn:anti	syn:anti
1	Me	Me	H	H	H	H	A	0	70	75	82:18	-
2	Me	Me	H	H	H	H	B	0	25	80	76:24	-
3	Me	Me	H	Me	H	H	A	25	22	72	89:11	-
4	H	Me	Me	H	H	Me	A	0	91	60	-	81:19
5	H	Me	H	H	Me	Me	A	0	24	40	-	87:13
6	Me	Me	Me	H	H	Me	A	25	96	64	81:19	65:35[d)]
7	Me	Me	Me	H	H	Me	B	25	69	98	78:22	44:56[e)]
8	Ph	Ph	H	H	H	H	A	25	68	100	99:1	-
9	Ph	Ph	Me	H	H	Me	A	25	72	33	100:0	60:40
10	Ph	Ph	Me	H	H	Me	B	25	72	89	100:0	11:89

a) The allylation of ketones (1.0 mmol) by allylic alcohols (1.5 mmol) was carried out with $PdCl_2(PhCN)_2$ (0.02 mmol) and $SnCl_2$ (3.0 mmol) in solvent (3 ml) under air. b) A;THF, B;THF-H_2O (3:1). c) The ratio was determined by capillary GC (PEG20M 0.25 mm X 30 m) and ^1H NMR (JEOL GX-270).
d) 1,2-2,3 ; syn-syn : syn-anti : anti-anti : anti-syn = 62 : 19 : 16 : 3.
e) 1,2-2,3 ; syn-syn : syn-anti : anti-anti : anti-syn = 40 : 38 : 18 : 4.

bicyclic model **C** formed by the approach of allylic tin intermediate at the opposite to bulky substituent R^1 in the α-hydroxy ketone chelates of Sn(IV). Under non-chelation conditions (THF-H_2O), 1,2-syn 2,3-anti selection can be explained by a six-membered cyclic transition state **D** containing Felkin model (Fig. 1).[8)] The 1,2-syn selection was enhanced by the bulkiness of substituents in both allylic alcohols (Entries 1 and 3) and ketones (entries 1 and 8).

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allylation of α-hydroxy ketones. We thank the Ministry of Education, Science and Culture, Japan(Grant-in-Aid for Scientific Research No.02640407) for financial support.

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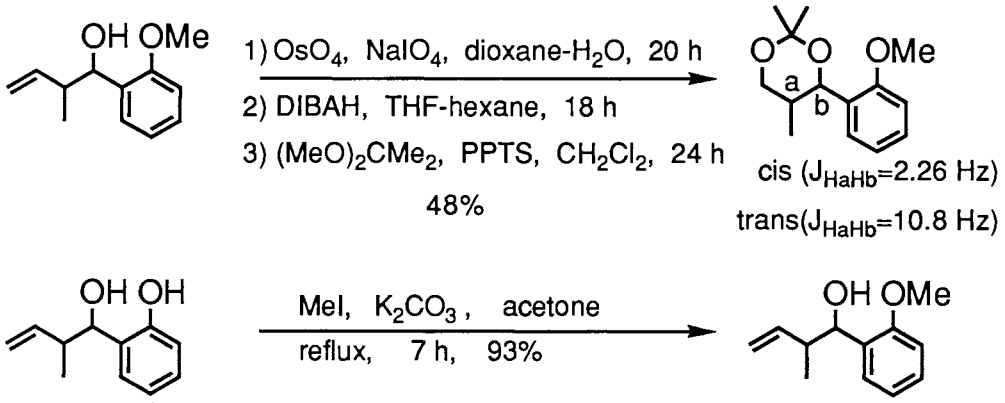
6) As shown in Scheme 3, the product, formed from 2-methoxybezaldehyde and (E)-crotyl alcohol, was converted to 1,3-dioxane derivative, and the configuration was determined by following reported results: K. Koga and S. Yamada, Chem. Pharm. Bull., 20, 526 (1972). The stereochemistry of the product, formed from salicylaldehyde and crotyl alcohol, was confirmed through the methylation of phenolic hydroxy gruop.



Scheme 3.

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