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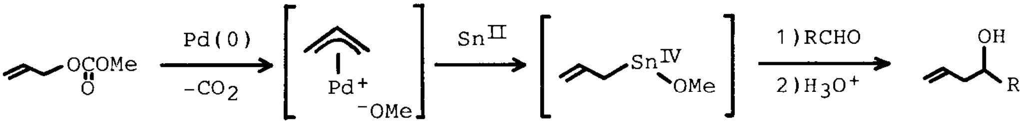
DIASTEREOSELECTIVITY IN CARBONYL ALLYLATION BY ALLYLIC CARBONATES USING $PdCl_2(PhCN)_2$-$SnCl_2$ SYSTEM

Yoshiro Masuyama,* Kiyotaka Otake, and Yasuhiko Kurusu
Department of Chemistry, Sophia University
7-1 kioicho, Chiyoda-ku, Tokyo 102, Japan

Summary: Allylic carbonates were more active than the corresponding allylic acetates in carbonyl allylation using $PdCl_2(PhCN)_2$-$SnCl_2$, and the carbonyl allylation by (E)-crotyl carbonate at 10 °C exhibited opposite diastereoselectivity (anti-selectivity) to that by (E)-crotyl acetate at 60 °C.

Charge reversal of electrophilic π-allylpalladium complex, namely conversion of the π-allylpalladium complex into synthon of allylic carbanion, has demonstrated further applicabilities of palladium chemistry in organic synthesis.[1] We have recently reported that allylic acetates function as synthons of the corresponding allylic carbanions using $Pd(PPh_3)_4$-Zn or $PdCl_2(PhCN)_2$-$SnCl_2$ to add to aldehydes regioselectively at the more substituted end of allyl units.[2] However, addition of (E)-crotyl acetate to benzaldehyde did not exhibit such a high diastereoselectivity (syn-selectivity) even in the case of $PdCl_2(PhCN)_2$-$SnCl_2$.[2a] The result should be dependent on relatively high reaction temperature (60 °C),[3] which the preparation of the π-allylpalladium complexes from allylic acetates should require.[4] We record a carbonyl allylation by allylic carbonates, which are more reactive than the corresponding acetates for the complexation with Pd(0),[5] using $PdCl_2(PhCN)_2$-$SnCl_2$ in 1,3-dimethyl-2-imidazolidinone (DMI) (Scheme 1).

Scheme 1



The results of carbonyl allylation by allyl carbonate are summarized in Table 1. The carbonyl allylation by allyl carbonate proceeded rapidly compared with allyl acetate.

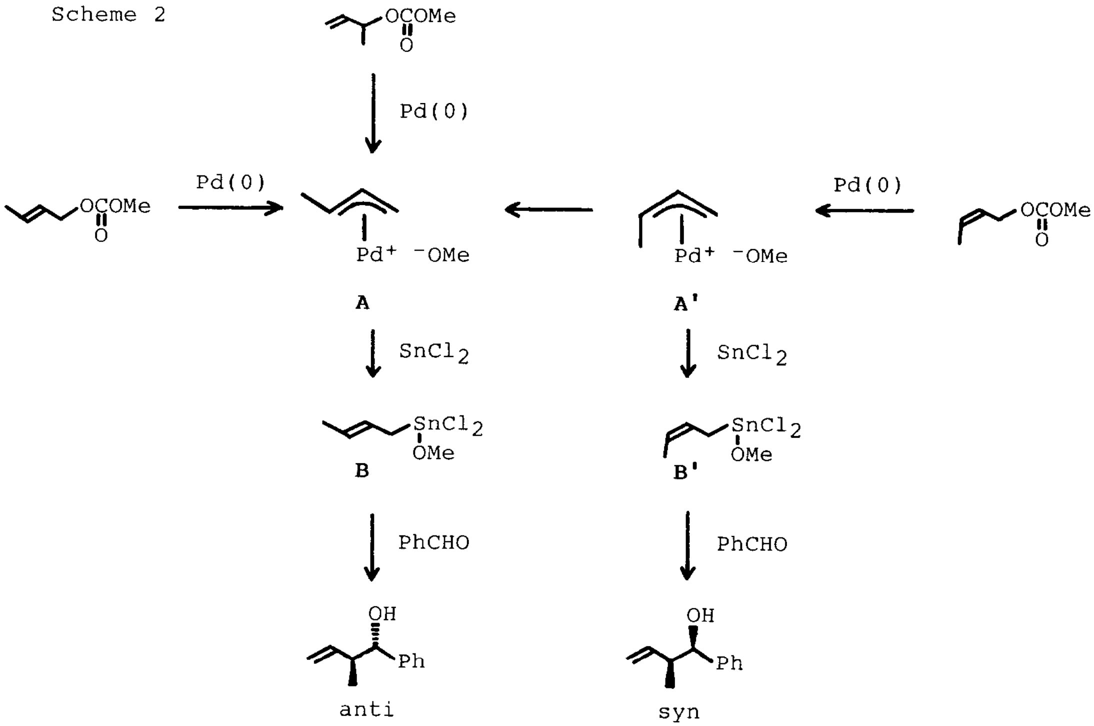
Diastereoselectivity in the carbonyl allylation was investigated using (E)-crotyl, (Z)-crotyl, and 1-methylallyl carbonate at below 25 °C as summarized in Table 2. (E)-Crotyl carbonate caused preferentially anti-addition to benzaldehyde. The ratio (syn:anti=27:73) at 10 °C was opposite to that (syn:anti=61:39) using (E)-crotyl acetate at 60 °C. In addition, (E)-

Table 1. Carbonyl allylation by allyl carbonate[a]

aldehyde	time(h)	yield(%)[b]
hexanal	10	49
octanal	10	57
10-undecenal	10	75
piperonal	7(60)[c]	95(63)[c]
cinnamaldehyde	7(57)[c]	92(60)[c]

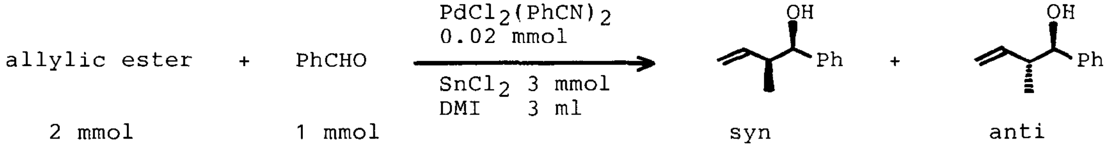
a) Addition reaction of allyl carbonate (2 mmol) to aldehydes (1 mmol) with $PdCl_2(PhCN)_2$ (0.02 mmol) and $SnCl_2$ (3 mmol) was carried out at 25 °C in DMI (3 ml). b) The yields of isolated pure products based on aldehydes. c) The carbonyl allylation was carried out using allyl acetate. See ref. 2a.

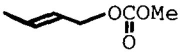
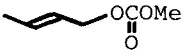
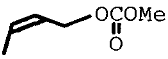
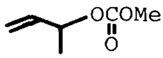
Scheme 2



crotyl acetate did not react with benzaldehyde at 10°C. Addition of 1-methylallyl carbonate exhibited the same diastereoselectivity value as that of (E)-crotyl carbonate. As a result, it is presumed that syn-π-allylpalladium complex **A**, which has been prepared from both the carbonates and Pd(0), has reacted with $SnCl_2$ to produce (E)-crotyltin intermediate **B**, which has caused nucleophilic addition at the γ-position to benzaldehyde (Scheme 2). The anti-

Table 2. Diastereoselectivity in addition of crotyl or 1-methylallyl esters



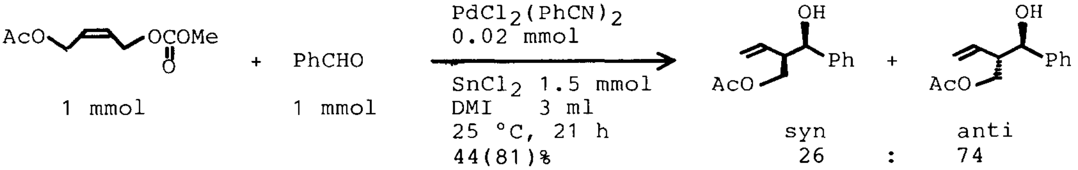
allylic ester	temp.(°C)	time(h)	yield(%)[a]	syn : anti[b]
	60	20	69	61 : 39[c]
	25	90	61	43 : 57
	25	48	80	33 : 67
	10	72	90	27 : 73
	25	60	42	48 : 52
	10	84	95	31 : 69

a) The yields of isolated pure products based on aldehydes. b) The ratio was determined by ^{1}H NMR (GX-270). See ref. 1d. c) See ref. 2a.

selectivity should be explained by a chair form of six-membered cyclic transition state.[3] The minor syn-addition seems to be based on an acyclic transition state,[3] since coordination of DMI instead of benzaldehyde to Sn metal prevents the formation of the six-membered cyclic transition state. It is known that the addition of (Z)-crotyltin compound **B'** has exhibited syn-selectivity in both the transition states. However, the ratio of syn vs. anti was 48:52. Therefore, the anti-addition presumably occurred via the isomerization of anti-π-allylpalladium complex **A'** to stable syn-complex **A**.

High chemoselectivity toward a carbonate group was observed in the reaction of 4-acetoxy-2-butenyl methyl carbonate with benzaldehyde under the same conditions, similarly to the reaction of that carbonate with nucleophile (Scheme 3).[5] The diastereoselectivity was the same as that of (E)-crotyl carbonate.[6]

Scheme 3



Allylic carbonates should enhance applicability of the palladium-catalyzed carbonyl allylation in organic synthesis, because the reactivity of the carbonates is higher than that of the corresponding acetates. Further studies on stereoselection which will apply the carbonyl allylation are in progress.

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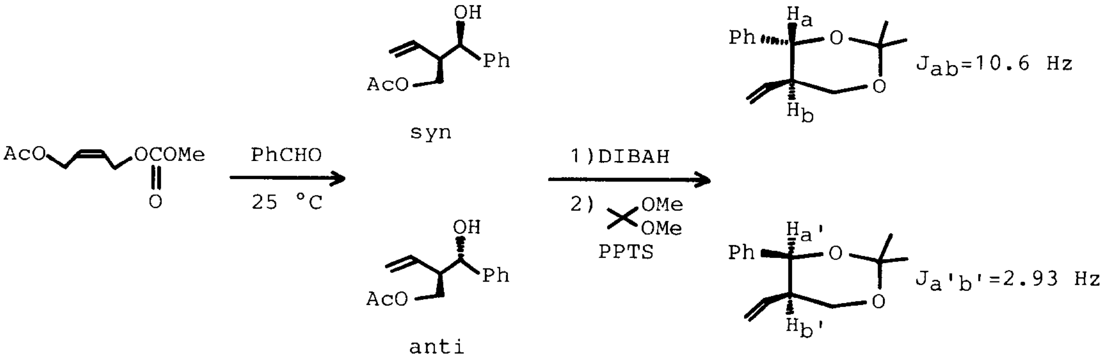
6) In Scheme 3, yield in parentheses is based on the consumed carbonate. The anti-selectivity should be dependent on the isomerization of anti-π-allylpalladium complex to syn-complex easily occurring by steric hindrance of the bulky substituent, an acetoxy group. The ratio of diastereomers was determined by ^1H NMR (GX-270) and the 1,3-dioxane method as shown below, see: K. Koga, S. Yamada, Chem. Pharm. Bull., 20, 526 (1972).



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