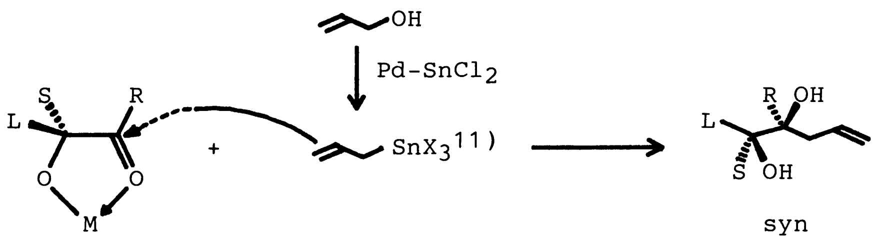
CHEMISTRY LETTERS, pp. 1647-1650, 1989.

# Palladium-Catalyzed Carbonyl Allylation of Diketo Compounds by Allylic Alcohols with $SnCl_2$

Yoshiro MASUYAMA,* Tomoyoshi TSUNODA, and Yasuhiko KURUSU
Department of Chemistry, Sophia University,
7-1 Kioicho, Chiyoda-ku, Tokyo 102

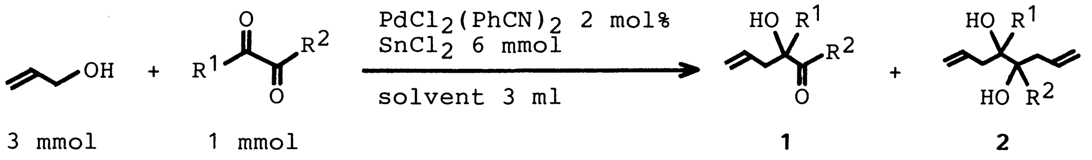
Palladium-catalyzed diallylation of 1,2-diketones and 1,2-ketoaldehyde by allyl alcohol with $SnCl_2$ in DMI was accelerated and proceeded diastereoselectively thanks to a chelation of a carbonyl group to Sn(IV) (tin alkoxide) in the corresponding monoallylated intermediates.

Allylic alcohols and esters have been found to function as synthons of allylic carbanions for carbonyl allylation, when a $PdCl_2(PhCN)_2$-$SnCl_2$/DMI system is used.1-3) Diastereocontrol in the allylation of benzaldehyde by (E)-2-butenol with $PdCl_2(PhCN)_2$-$SnCl_2$ has been achieved by the choice of polar solvents; use of DMSO at 25 °C leads to syn selection via an acyclic antiperiplanar transition state, while anti selection via a six-membered cyclic transition state is found at -10 °C in THF.4) On the other hand, the coordination of Lewis acids to aldehydes plays an important role in the diastereocontrol of carbonyl allylation by allylic tin compounds; (1) the addition of $BF_3 \cdot Et_2O$ leads to syn selection via an acyclic antiperiplanar transition state in the reaction of crotyltrialkyltin with aldehydes, regardless of the geometry of the crotyl unit5-7) and (2) the chelation of α-alkoxy-α-alkylacetaldehyde to $MgBr_2$ or $TiCl_4$ in the reaction with allyltrialkyltin leads to syn selection, in contrast to anti selection in Cram's model.8,9) Indeed, the palladium-catalyzed allylation of benzaldehyde by (E)-2-butenol with $SnCl_2$ in any polar solvent, where $SnCl_2$ was dissolved, did not exhibit any effect due to $BF_3 \cdot Et_2O$; the diastereomer ratio was the same as that without $BF_3 \cdot Et_2O$. No chelation of $MgBr_2$ or $TiCl_4$ was recognized in the allylation of 2-benzyloxypropanal by allyl alcohol with $PdCl_2(PhCN)_2$-$SnCl_2$/THF system.10) Hence, if aldehydes or ketones bearing a metal-oxygen bond stronger than the coordination of ether oxygen to Lewis acid could be formed in situ, a chelation of a carbonyl group to the metal would occur to achieve diastereocontrol in polar solvents such as THF, DME, DMF, and DMI (Scheme 1).



Scheme 1.

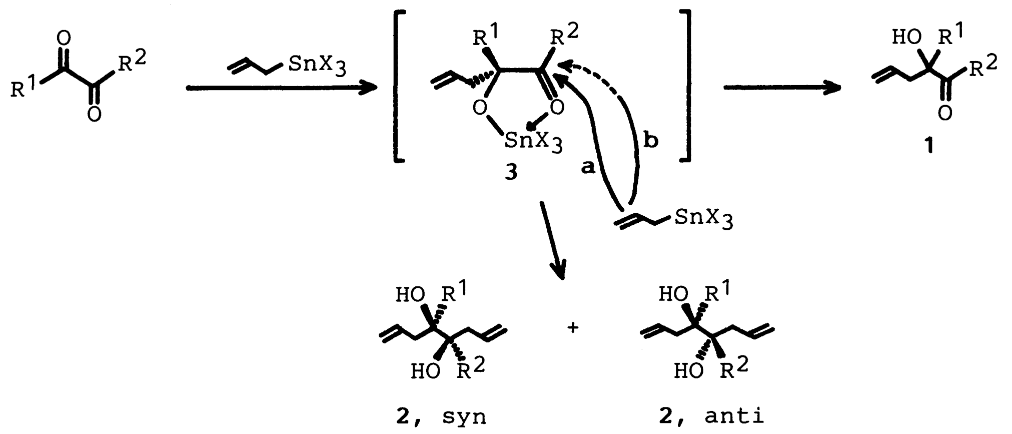
Table 1. Diallylation of 1,2-diketones by allyl alcohol with Pd-$SnCl_2$



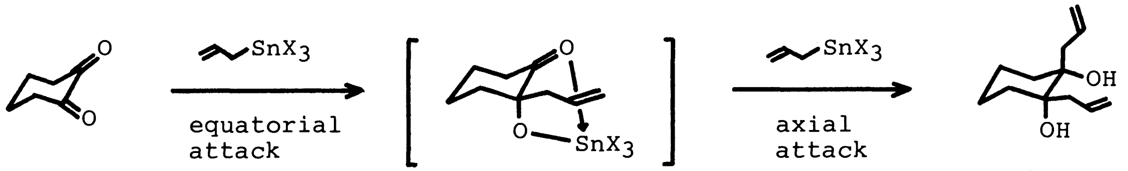
| Entry | Diketone $R^1$ | Diketone $R^2$ | Solvent | Temp /°C | Time /h | Yield/% 1 | Yield/% 2 | Diastereomer ratio of 2[a] syn : anti |
|---|---|---|---|---|---|---|---|---|
| 1 | $CH_3$ | $CH_3$ | DMI | 25 | 48 | 0 | 59 | 70 : 30 |
| 2 | $CH_3$ | $CH_3$ | THF[b] | 25 | 48 | 0 | 53 | 61 : 39 |
| 3 | $CH_3$ | $CH_3$ | DMSO[b] | 25 | 88 | 0 | 33 | 89 : 11 |
| 4 | $CH_3$ | $CH_3CH_2$ | DMI | 25 | 48 | 0 | 47 | 62 : 38 |
| 5 | $CH_3$ | $CH_3CH_2$ | THF[b] | 25 | 48 | 0 | 51 | 55 : 45 |
| 6 | $(CH_2)_4$ | | DMI | 25 | 48 | 0 | 46 | 100 : 0[c] |
| 7 | Ph | Ph | DMI | 50 | 55 | 22 | 61 | 0 : 100 |
| 8 | Ph | Ph | THF[b] | 50 | 19 | 19 | 36 | 0 : 100 |
| 9 | Ph | Ph | DMSO[b] | 50 | 57 | 27 | 55 | 0 : 100 |
| 10 | H | Ph | DMI | 25 | 45 | 5 | 12 | 0 : 100 |
| 11 | H | Ph | DMI | 0 | 68 | 7 | 19 | 0 : 100 |

a)The ratio was determined by GC (capillary column: PEG 20M, 0.25 mm × 30 m) and 270 MHz $^1H$ NMR (GX-270). See Ref. 12. b)$H_2O$ (5 mmol) was added. c)See Ref. 13.

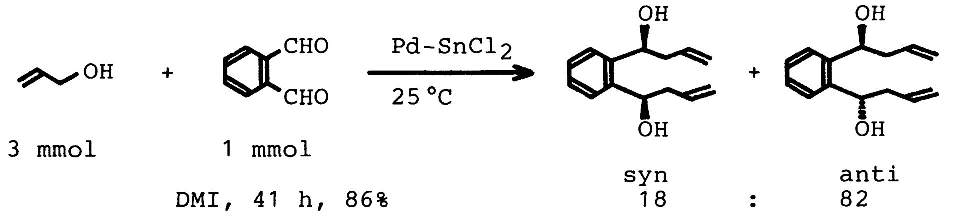
Indeed, diallylation of 1,2-diketones (1 mmol) by allyl alcohol (3 mmol) with $PdCl_2(PhCN)_2$ (0.02 mmol) and $SnCl_2$ (6 mmol) in DMI (3 ml) proceeded diastereoselectively at 25 °C to give the corresponding 1,2-diols. The results are summarized in Table 1. Dialkyl-substituted diketones did not react with even one equimolar amount of allyl alcohol without undergoing diallylation (Entries 1-6). As shown in Scheme 2, the second allylation should be promoted by a coordination of the second carbonyl group to Sn(IV) in monoallylated tin alkoxide intermediate **3**. On the contrary, in cases of phenyl-substituted diketones ($R^2$:Ph), steric hindrance of the phenyl group probably led to isolation of monoallylated products (Entries 7-11). Diallylation of 2,3-butanedione and 2,3-pentanedione exhibited syn selectivity (Entries 1-5), and that of benzil and phenylglyoxal led to complete anti-selection (Entries 7-11). These results also established the existence of a chelation of the second carbonyl group to Sn(IV) in the monoallylated tin alkoxide intermediate **3** (Scheme 2).[14,15] That is to say, the allylation of **3**, where $R^1$ is a more bulky phenyl group than allyl group, presumably proceeds on path **b** to lead to anti-selection. In the case of $R^1$=$CH_3$, which is less bulky than allyl group, path **a** is superior to path **b** in leading to syn-selection. In contrast with the diallylation of benzil, carbonyl allylation of monoallylated α-hydroxyketone, derived from benzil and allyl alcohol, with $PdCl_2(PhCN)_2$-$SnCl_2$ in DMI exhibited slight syn-selectivity (syn:anti=59:41).[16]



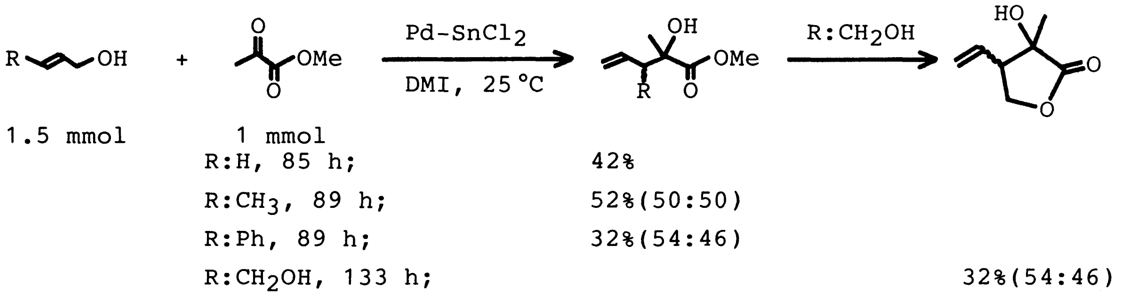
Scheme 2.



Scheme 3.



Scheme 4.



Scheme 5.

The existence of the chelate intermediate **3** is further supported by this result. In the case of 1,2-cyclohexanedione, the first allylation probably occurred on an equatorial approach to a carbonyl group,3) followed by the second allylation on an axial approach to another carbonyl group via a chelate intermediate to produce syn-diol(Scheme 3). Diallylation of phthalaldehyde, which was a kind of 1,4-diketo compound, also caused a diastereofacial selection via a 7-membered chelate intermediate (Scheme 4).14) Methyl pyruvate was allylated at only keto position (Scheme 5). 2-Butene-1,4-diol reacted with methyl pyruvate to give α-hydroxy-γ-butyrolactone under the same conditions.

We demontrated the possibility of chelation-controlled diastereoselection in polar solvents. Further studies on chelation-controlled diastereoselective carbonyl allylation of ω-hydroxy carbonyl compounds in polar solvents are in progress.

This work was partially supported by a grant on Yamanouchi Pharmaceutical Co. Ltd. Award in Synthetic Organic Chemistry, Japan.

References

1) Y. Masuyama, R. Hayashi, K. Otake, and Y. Kurusu, J. Chem. Soc., Chem. Commun., 1988, 44.

2) Y. Masuyama, K. Otake, and Y, Kurusu, Tetrahedron Lett., 29, 3563 (1988).

3) Y. Masuyama, J. P. Takahara, and Y, Kurusu, J. Am. Chem. Soc., 110, 4473 (1988).

4) Y. Masuyama, J. P. Takahara, and Y. Kurusu, Tetrahedron Lett., in press.

5) Y. Yamamoto and K. Maruyama, Heterocycles, 18, 357 (1982).

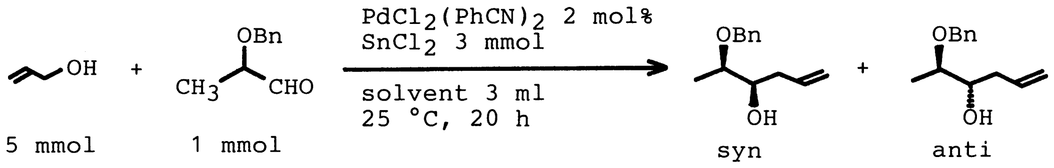
6) R. W. Hoffmann, Angew. Chem., Int. Ed. Engl., 21, 555 (1982).

7) Y. Yamamoto, Acc. Chem. Res., 20, 243 (1987).

8) G. E. Keck and E. P. Boden, Tetrahedron Lett., 25, 265 (1984).

9) Y. Yamamoto, T. Komatsu, and K. Maruyama, J. Organomet. Chem., 285, 31 (1985).

10) Y. Masuyama, unpublished results.



(Bn:$PhCH_2$)

| | syn | | anti |
|---|---|---|---|
| $MgBr_2$/THF 57% | 55 | : | 45 |
| none/DMI 58% | 44 | : | 56 |

11) This allyltin compound, derived from allyl alcohol with $PdCl_2(PhCN)_2$-$SnCl_2$, proved to be allyltrichlorotin by $^1H$ and $^{13}C$ NMR (Jeolco GX-270): Y. Masuyama, J. P. Takahara, and Y. Kurusu, unpublished results.

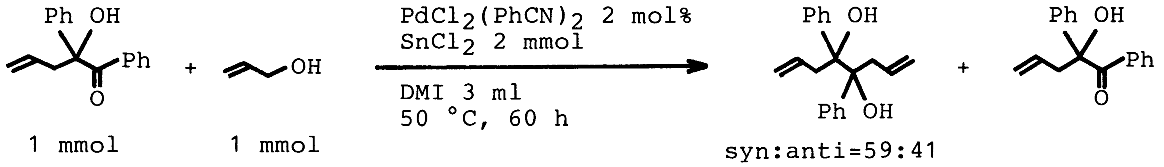
12) The determination of 1,2-diol structures was carried out by acetalization with 2,2-dimethoxypropane followed by $^1H$ NMR observation of the acetals. Two methyl groups in acetone acetal of syn-1,2-diallylcyclohexane-1,2-diol[13] were observed as two singlets (δ 1.48 and 1.54 ppm). Two methyl groups [$(CH_3)_2C$] in acetone acetal of a major stereoisomer of 2,3-diallylbutane-2,3-diol showed one signal (δ 1.44 ppm). Thus we determined the major isomer was syn-diol. The chemical shifts of those in a minor isomer were δ 1.43 and 1.46 ppm (two singlets).

13) E. N. Marvell and J. C.-P. Cheng, J. Org. Chem., 45, 4511 (1980).

14) M. T. Reetz, R. Steinbach, J. Westermann, R. Urz, B. Wenderoth, and R. Peter, Angew. Chem., Int. Ed. Engl., 21, 135 (1982); Angew. Chem. Suppl., 1982, 257.

15) G. A. Molander and D. C. Shubert, J. Am. Chem. Soc., 108, 4683 (1986).

16) Carbonyl allylation of monoallylated α-hydroxyketone was carried out in the following manner:



syn:anti=59:41
(37%) 45% recovered

(Received June 13, 1989)