Tetrahedron Letters,Vol.30,No.26,pp 3437-3440,1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Maxwell Pergamon Macmillan plc

PALLADIUM-CATALYZED CARBONYL ALLYLATION BY ALLYLIC ALCOHOLS WITH $SnCl_2$. A SOLVATION-CONTROLLED DIASTEREOSELECTION

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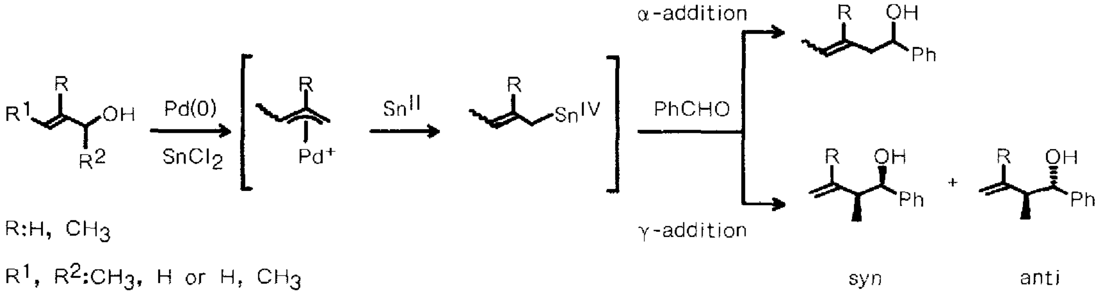
Summary: Diastereocontrol in the allylation of benzaldehyde by (E)-but-2-en-1-ol using catalyst $PdCl_2(PhCN)_2$ and $SnCl_2$ was achieved by the choice of polar solvents; use of DMSO at 25 °C led to syn selection, while anti selection was found at -10 °C in THF. The addition of 3-10 equivalents of H_2O in any solvent enhanced the selectivities, and the control of the amount of H_2O in DMSO permitted both syn selection (a small amount of H_2O) and anti selection (a large amount of H_2O).

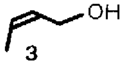
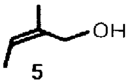
Allylic alcohols can be applied to carbonyl allylation, using catalyst $PdCl_2(PhCN)_2$ and $SnCl_2$ in 1,3-dimethyl-imidazolidinone (DMI) (Scheme 1).[1] The carbonyl allylation proceeds via the formation of π-allylpalladium complexes followed by the reductive elimination to produce allylic tin(IV) intermediates.[2] The reaction is both highly chemoselective and highly regioselective (γ-addition). The diastereoselectivity in the allylation of benzaldehyde with (E)-but-2-en-1-ol is not so high (syn:anti=29:71).[3] The solvation of DMI to the Sn(IV) probably depresses anti selectivity.[4] Hence, the diastereoselectivity should be changed by the solvation modes of various polar solvents at many different temperatures.[5]

Scheme 1



Indeed the allylation of benzaldehyde with (E)-but-2-en-1-ol took place in any polar solvent, where $SnCl_2$ was dissolved, to give homoallylic alcohols in good yields (Table 1). The diastereoselectivity revealed a slight solvent dependency. The reactions in both ethylene glycol (EG) and DMSO possessed syn selectivity, contrary to the anti selectivity found in DMI (entries 6, 7). Both regio- (γ-addition) and diastereoselectivity (anti) were enhanced at lower reaction temperatures in THF (entries 3, 8-10). Although carbonyl allylations using allylic organometallic reagents are generally inhibited by the presence of H_2O, the palladium-catalyzed carbonyl allylation by (E)-but-2-en-1-ol with $SnCl_2$ was accelerated by the addition of H_2O (3-10 equiv based on the aldehyde) in any solvent used.[6] Furthermore, in the presence

Table 1. Palladium-Catalyzed Allylation of Benzaldehyde by Allylic Alcohols in Various Solvents[a]

entry	allylic alcohol	solvent (ml)	H_2O mmol	temp °C	time h	yield[b] %	syn:anti: α[c]
1		DMI(3)		25	36	63	29 : 71[d]
2	**1**	DMF(3)		25	63	89	30 : 70
3		THF(3)		25	24	72	22 : 25 : 53
4		BuOH(3)		25	65	72	36 : 58 : 6
5		EtOH(3)		25	72	79	38 : 41 : 21
6		EG(3)		25	37	78	58 : 42
7		DMSO(3)		25	136	34	65 : 35
8		THF(3)		0	95	80	16 : 78 : 6
9		THF(3)		-10	130	81	10 : 90
10		THF(3)		-15	135	62	7 : 93
11		THF-DMI(1:1,3)		0	96	40	11 : 89
12		THF(4)	10	25	6	74	16 : 84
13		THF(4)	10	-20	144	35	6 : 94
14		DMSO(3)	3	25	88	84	86 : 14
15		DMSO(3)	20	25	69	77	68 : 32
16		DMSO(3)	28	25	70	65	49 : 51
17		DMSO(3)	43	25	50	71	39 : 61
18		DMSO(3)	170	25	70	70	16 : 84
19		DMSO(3)	3	25	92	95	84 : 16
20	**2**	DMSO(3)	170	25	55	60	24 : 76
21		THF(4)	10	25	6	91	27 : 73
22		DMSO(3)	3	25	95	51	84 : 16
23	**3**	DMSO(3)	170	25	95	48	64 : 36
24		THF(4)	10	25	6	80	56 : 44
25		DMSO(3)	3	25	109	83	27 : 73[e]
26	**4**	DMSO(3)	54	25	68	67	3 : 97
27		THF(4)	20	25	47	63	11 : 89
28		DMSO(3)	3	25	113	87	38 : 62[e]
29	**5**	DMSO(3)	54	25	71	88	81 : 19
30		THF(4)	20	25	35	79	87 : 13

a) The allylation of benzaldehyde (1 mmol) by allylic alcohols (1.5 mmol) with $PdCl_2(PhCN)_2$ (0.02 mmol) and $SnCl_2$ (3 mmol) was carried out. b) Isolated purified products. c) The ratio was determined by GC (capillary column: PEG 20M, 0.25 mm × 30 m, 155 °C). d) See ref. 1. e) $PhCHO$/allylic alcohol/$SnCl_2$=1:3:3.

of H_2O, the reaction was more selective, with respect to both γ-addition (regiocontrol) and syn:anti addition (diastereocontrol). Thus, use of THF-H_2O medium led to highly selective anti addition without α-addition even at 25 °C (entry 12). The diastereoselectivity of the carbonyl allylation in THF-H_2O at -20 °C further enhanced (syn:anti=6:94, entry 13). Surprisingly, the control of the amount of H_2O in DMSO medium permitted both syn selection (a small amount of H_2O) and anti selection (a large amount of H_2O) (entries 14-18).[7]

Scheme 2

Six-Membered Cyclic Transition States in THF-H_2O

A

(R:H, CH_3)

B

(R:H, CH_3)

Scheme 3

Acyclic Transition States in DMSO-H_2O(small)

C, Antiperiplanar

(R:H)

D, Synclinal

(R:CH_3)

In DMSO-H_2O(large) or THF-H_2O medium, (E)-but-2-en-1-ol **1**, but-3-en-2-ol **2**, and (E)-2-methylbut-2-en-1-ol **4** caused anti addition (entries 12, 18, 20, 21, 26, 27) and (Z)-but-2-en-1-ol **3** and (Z)-2-methylbut-2-en-1-ol **5** caused syn addition (entries 23, 24, 29, 30). These results can be explained by chair forms of six-membered cyclic transition states **A** and **B** (Scheme 2).[3] *Less syn selectivity in the addition of (Z)-but-2-en-1-ol presumably depended on* the preparation of an (E)-but-2-en-1-yltin intermediate via the rapid isomerization of an anti-π-allylpalladium complex to a syn complex.[1,5] Both additions of (E)-**1** and (Z)-**3** in DMSO-H_2O(small) medium exhibited syn selectivity without depending upon double-bond geometry (entries 14, 22). Thus, this syn selection suggests an acyclic antiperiplanar transition state **C** (Scheme 3).[3] *Both (E)-**4** and (Z)-**5** caused anti addition in DMSO-H_2O(small) medium* (entries 25, 28). Since (1) an anti-π-allylpalladium complex derived from (Z)-**5** has hardly isomerized to a syn complex in THF-H_2O or DMSO-H_2O(large) and (2) the reactions of (E)-**1** and (Z)-**3** have proceeded via an acyclic transition state **C** in DMSO-H_2O(small), we propose one possible acyclic transition state, namely acyclic synclinal transition state **D** in the reactions of **4** and **5** in DMSO-H_2O(small), which has been hitherto unknown in the intermolecular carbonyl allylation (Scheme 3).[8] Steric hindrance due to the 2-methyl group in **4** and **5**, which is more bulky than 2-proton in **1** and **3**, presumably led to the synclinal transition state **D**.

In contrast with solvents such as DMI and DMF, DMSO should strongly coordinate to Sn(IV) in the allylic tin intermediates, thus disturbing the formation of the six-membered cyclic transition states **A** or **B**. The small amount of H_2O (3 equiv) seems to cause the hydrolysis of Sn^{IV}-Cl bonds to activate the allylic tin intermediates,[6] and the large amount of H_2O in DMSO seems not only to hydrolyze the Sn^{IV}-Cl bonds but also to rupture the coordination of DMSO to the Sn(IV).

Using the $PdCl_2(PhCN)_2$-$SnCl_2$ reagent, desirable diastereocontrol in any allylic moiety should be easily achieved by the choice of solvent, since the starting materials, pure (E)- and (Z)-allylic alcohols, are available. Further studies confirming the structures of the solvated and/or hydrated allylic tin intermediates are in progress.

References and notes

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(Received in Japan 29 March 1989)