New and Stereoselective Synthesis of 1,4-Disubstituted Buten-4-ols (Homoallylic Alcohol α-Adducts) from the Corresponding γ-Isomers (3,4-Disubstituted Buten-4-ols) via an Acid-Catalyzed Allyl-Transfer Reaction with Aldehydes

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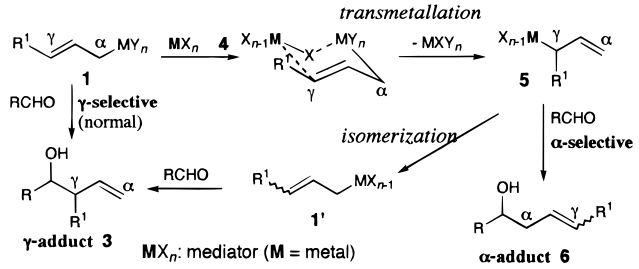
Abstract: The γ-adducts of homoallylic alcohols **3**, derived from aldehydes via the usual reaction with common allylic metals **1**, were converted to the corresponding α-adducts **6** by an acid-catalyzed allyl-transfer reaction. In the allyl-transfer reaction, anti- and syn-γ-adducts **3** gave *E*- and *Z*-α-adducts **6**, respectively, and the optical purity of the γ-adducts **3** was transferred to the α-adducts **6** with >98%ee. This suggests that the allyl-transfer reaction proceeds stereoselectively via six-membered cyclic transition states [**T**]. The reaction was catalyzed by various metal triflates as well as Lewis acids and Brønsted acids.

Introduction

The allylation of aldehydes by allylic nucleophiles leading to homoallylic alcohols is one of the most important and popular C−C bond formation reactions. In widespread allylations of aldehydes with *allylic metals* to afford homoallylic alcohols,[1] much attention has focused on the stereoselectivity of the pathway leading to the α- or γ-adducts that are produced regioselectively, i.e., ratio of *E*- or *Z*-olefins in the α-adducts and ratio of anti or syn isomers in the γ-adducts. The diastereoselective allylation of aldehydes has already been achieved by Lewis acid promoted allylation with allylic tin reagents via acyclic transition states to give syn isomers **3**[2] and by reaction with *E*- and *Z*-allylic metals **1** (without Lewis acid) via six-membered cyclic transition states **2** to give anti and syn isomers **3**, respectively.[3] However, only a few methods for the stereoselective synthesis of α-adducts have been reported,[4] because almost all allylic metals react with aldehydes to give the γ-adducts exclusively.

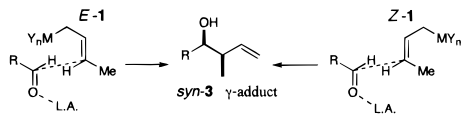
The α-selective allylations of aldehydes by allylic metals explored to date have used common allylic metal reagents **1** (M = Sn, Mg, Li) along with mediators **4**, such as Sn(IV) chlorides[4a−e] or $AlCl_3$,[4g,h] as well as allylic barium reagents prepared from active barium metal and allylic chlorides.[5] In most of these cases, it is assumed that transmetalation of the allylic unit of the α-allylmetal nucleophile **1** to the mediator **4** gives the γ-allylmetal nucleophile **5**, which in turn reacts with aldehyde to give the α-adduct **6** (Scheme 1). Support for this scheme has been reported by Naruta, who showed via an NMR study that the transmetalation of an allylic unit from 2-butenyltributyltin (R^1 = Me, M = Sn, Y = Bu, n = 3) **1a** to $SnCl_4$ (**4a**) gave (1-methyl-2-propenyl)trichlorotin **5a**.[6] It is, however, generally rather difficult to perform the allylation of aldehydes to give only α-adducts **6**, due to isomerization of the γ-allylmetal nucleophile **5** to the α-allylmetal species **1′**. Furthermore, these procedures are not very satisfactory in terms of practical use, because the desired products **6**, formed using 2-butenyltributyltin **1a**, were contaminated with a large amount of tributyltin residues

Scheme 1

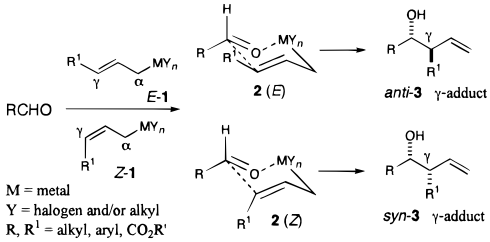


(1) For a recent review on allylation reactions using allylic metals, see: Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207 and references therein.

(2) It is known that both (*E*)- and (*Z*)-2-butenylmetal reagents give syn-γ-adducts predominantly by Lewis acid (L.A.) promoted reactions. For the reaction mechanism, the following acyclic transition model was proposed. (a) Yamamoto, Y.; Yatagai, H.; Naruta, Y.; Maruyama, K. *J. Am. Chem. Soc*. **1980**, *102*, 7107. (b) Yamamoto, Y.; Maruyama, K. *Heterocycles* **1982**, *18*, 357.



(3) It is also well-known that (*E*)- and (*Z*)-2-butenylmetals predominantly give anti and syn isomers, respectively, by allylations via a six-membered cyclic transition state **2**. For example: (a) Buse, C. T.; Heathcock, C. H. *Tetrahedron Lett*. **1978**, 1685. (b) Hiyama, T.; Kimura, K.; Nozaki, H. *Tetrahedron Lett*. **1981**, *22*, 1037. (c) Sato, F.; Iida, K.; Moriya, H.; Sato, M. *J. Chem. Soc., Chem. Commun*. **1981**, 1140. (d) Hoffman, R. W.; Zeiss, H.-J. *Angew. Chem., Int. Ed. Engl*. **1979**, *18*, 306. (e) Collum, D. B.; McDonald, J. H., III; Still, W. C. *J. Am. Chem. Soc*. **1980**, *102*, 2118.



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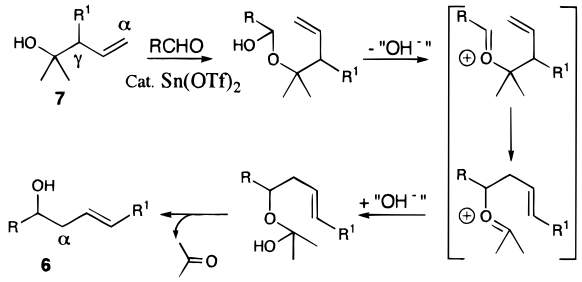
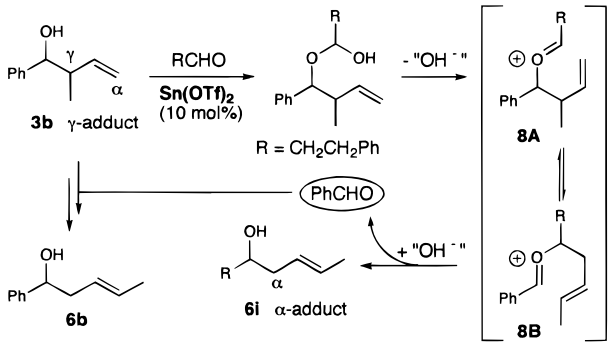
Scheme 2



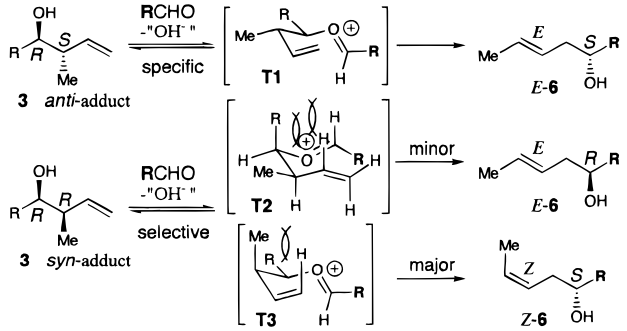
Scheme 3



that were not easy to separate. Therefore, there still remains a great interest in the development of more practical and versatile methods for the stereoselective synthesis of homoallylic alcohols of type **6**.

Recently, we reported a new method for the α-specific allylation of aldehydes, in which an allylic unit was transferred from the homoallylic alcohol **7**, derived from a *ketone* (acetone), to an aldehyde to give the α-adduct **6** in the presence of $Sn(OTf)_2$.[7] We proposed a reaction mechanism that proceeds via an oxycarbenium ion intermediate that undergoes a 2-oxonia [3,3]-sigmatropic rearrangement, as shown in Scheme 2. We also suggested that the reaction could be driven toward products deriving from the most stable cations or those containing sterically less hindered homoallylic alcohols and/or thermodynamically more stable olefins.

Scheme 4. Stereochemistry of the Allyl Transfer[a]



[a] The absolute configurations (*S* and *R*) are shown as R = CH_2CH_2Ph.

This is very different from the previously reported intramolecular C−C bond formation reactions between an oxycarbenium ion and π-nucleophile (C=C),[8] in which six- and five-membered cyclic ethers are obtained via an intramolecular Prins reaction. In some of these cases, the 2-oxonia [3,3]-sigmatropic rearrangement is driven by a subsequent C−C bond-forming event.[8l,m]

Based on the considerations outlined above, we performed additional investigations of the α-selective allylation of aldehydes via allyl-transfer reactions of homoallylic alcohols, derived from *aldehydes*.

Results and Discussion

Allyl Transfer from Benzaldehyde to 3-Phenylpropanal. First, we expected that 2-methyl-1-phenyl-3-buten-1-ol **3b**, prepared from benzaldehyde and 2-butenylmetal reagents,[9] would serve as an allyl donor in the allyl-transfer reactions and react with 3-phenylpropanal to give the corresponding α-adduct **6i**. This is because (i) the benzyl cation **8B** is more stable than **8A**, (ii) **6i** is less hindered than **3b**, and (iii) the internal olefin **6i** is more stable than the terminal olefin **3b**. In view of this, **3a**−**g** were treated with 3-phenylpropanal in the presence of 10 mol % of $Sn(OTf)_2$ in CH_2Cl_2.

As shown in Table 1, the α-adducts **6h**−**l** were obtained in moderate yields, together with the byproducts **6b**−**e** (entries 2−5), which were formed in the allyl-transfer reaction of **3b**−**e** to benzaldehyde liberated from the desired allyl-transfer of **3b**−**e**

(4) For example, (a) 2-butenyltributyltin **1a** (2-butenylmetal)/Bu_2SnCl_2 **4c** (mediator)/25 °C (reaction temperature): Gambaro, A.; Gains, P.; Marton, D.; Peruzzo, V.; Tagliavini, G. *J. Organomet. Chem.* **1982**, *231*, 307. (b) **1a**/$BuSnCl_3$ **4b**/25 °C: Gambaro, A.; Boaretto, A.; Marton, D.; Tagliavini, G. *J. Organomet. Chem.* **1984**, *260*, 255. (c) **1a**/**4a**, **4b**, or **4c**, and then $HClO_4$ (4 M)/20 °C: Marton, D.; Tagliavini, G.; Vanzan, N. *J. Organomet. Chem.* **1989**, *376*, 269. (d) **1a**/$SnCl_4$ **4a**/−78 °C: Keck, G. E.; Abbott, D. E.; Boden, E. P.; Enholm, E. J. *Tetrahedron Lett.* **1984**, *25*, 3927. (e) (*Z*)-**1a**/**4b**/room temperature or 0 °C: Miyake, H.; Yamamura, K. *Chem. Lett.* **1992**, 1369. (f) *E*-allylic alcohols, Me_3SiCl, NaI, H_2O, Sn/room temperature: Kanagawa, K.; Nishiyama, Y.; Ishii, Y. *J. Org. Chem.* **1992**, *57*, 6988. (g) **1a**/$AlCl_3$, *i*-PrOH/−78 °C: Yamamoto, Y.; Maeda, N.; Maruyama, K. *J. Chem. Soc., Chem. Commun.* **1983**, 742. (h) 2-butenylmagnesium chloride/$AlCl_3$/0 °C or room temperature: Yamamoto, Y.; Maruyama, K. *J. Org. Chem.* **1983**, *48*, 1564. (i) 2-butenyllithium/$CeCl_3$/−78 °C: Guo, B.-S.; Doubleday: W.; Cohen, T. *J. Am. Chem. Soc.* **1987**, *109*, 4710. (j) **1a**/$CoCl_2$/room temperature: Iqbal, J.; Joseph, S. P. *Tetrahedron Lett.* **1989**, *30*, 2421. The degrees of both α-selectivity and *E*/*Z* selectivity in each of these allylations were very variable, and would depend on the structure of aldehydes, allylic metal reagents, meditators, and the reaction conditions.

(5) Among the various allylation reactions reported, the reaction of allylic barium compounds is particularly useful, because it always gave α-adducts selectively without using any mediators. However, the preparation of allylic barium compounds required the reduction of barium iodide by 2 equiv of lithium biphenylide: (a) Yanagisawa, A.; Habaue, S.; Yamamoto, H. *J. Am. Chem. Soc.* **1991**, *113*, 8955. (b) Yanagisawa, A.; Habaue, S.; Yasue, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1994**, *116*, 6130.

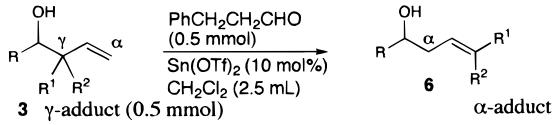
(6) Naruta, Y.; Nishigaichi, Y.; Maruyama, K. *Tetrahedron* **1989**, *45*, 1067.

(7) Nokami, J.; Yoshizane, K.; Matsuura, H.; Sumida, S. *J. Am. Chem. Soc.* **1998**, *120*, 6609.

(8) Synthesis of tetra- or dihydropyran derivatives: (a) Gambaro, A.; Boaretto, A.; Marton, D.; Tagliavini, G. *J. Organomet. Chem.* **1983**, *254*, 293. (b) Boaretto, A.; Marton, D.; Tagliavini, G. *Inorg. Chim. Acta* **1983**, *77*, L153. (c) Gambaro, A.; Furlani, D.; Marton, D.; Tagliavini, G. *J. Organomet. Chem.* **1986**, *299*, 157. (d) Wei, Z. Y.; Li, J. S.; Wang, D.; Chan, T. H. *Tetrahedron Lett.* **1987**, *28*, 3441. (e) Wei, Z. Y.; Wang, D.; Li, J. S.; Chan, T. H. *J. Org. Chem.* **1989**, *54*, 5768. (f) Coppi, L.; Ricci, A.; Taddei, M. *Tetrahedron Lett.* **1987**, *28*, 973. (g) Coppi, L.; Ricci, A.; Taddei, M. *J. Org. Chem.* **1988**, *53*, 911. (h) Mekhalfia, A.; Markó, E. I.; Adams, H. *Tetrahedron Lett.* **1991**, *32*, 4783. (i) Markó, I. E.; Mekhalfia, A. *Tetrahedron Lett.* **1992**, *33*, 1799. (j) Markó, I. E.; Chellé, F. *Tetrahedron Lett.* **1997**, *38*, 2895. (k) Hoffman, R. W.; Giesen, V.; Fuest, M. *Liebigs Ann. Chem.* **1993**, 629. (l) Lolkema, L. D. M.; Hiemstra, H.; Semeyn, C.; Speckamp W. N. *Tetrahedron* **1994**, *50*, 7115. (m) Lolkema, L. D. M.; Semeyn, C.; Hiemstra, H.; Speckamp W. N. *Tetrahedron* **1994**, *50*, 7129. (n) Nishizawa, M.; Shigaraki, T.; Takao, H.; Imagawa, H.; Sugihara, T. *Tetrahedron Lett.* **1999**, *40*, 1153. Synthesis of 3-acyltetrahydrofuran derivatives: (o) Hopkins, M. H.; Overman, L. E. *J. Am. Chem. Soc.* **1987**, *109*, 4748. (p) Hopkins, M. H.; Overman, L. E.; Rishton, G. M. *J. Am. Chem. Soc.* **1991**, *113*, 5354.

(9) For selective preparation of anti-γ-adducts, we employed the methods using 2-butenylchromium compounds reported by Hiyama and Nozaki, and Heathcock; (a) Okude, Y.; Hirano, S.; Hiyama, T.; Nozaki, H. *J. Am. Chem. Soc.* **1977**, *99*, 3179. (b) Buse, C. T.; Heathcock, C. H. *Tetrahedron Lett.* **1978**, 1685. (c) Hiyama, T.; Kimura, K.; Nozaki, H. *Tetrahedron Lett.* **1981**, *22*, 1037. (d) Hiyama, T.; Okude, Y.; Kimura, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 561.

Table 1. Allyl-Transfer Reaction from γ-Adducts Derived from Benzaldehyde to 3-Phenylpropanal



	γ-adducts **3**							γ-adducts **6**, yield[a]/% (*E*/*Z*)[b]	
run		R	R^1	R^2	anti/syn[b]	*T*/°C	time/h	R = CH_2CH_2Ph	R = Ph
1	**3a**	Ph	H	H		25	5	**6h**, 53[c]	
2	**3b**	Ph	Me	H	20/1	25	5	**6i**, 62 (33/1)	**6b**, 29 (17/1)
3	**3c**	Ph	Ph	H	33/1	25	1	**6j**, 47 (*E*)	**6c**, 50 (*E*)
4	**3d**	Ph	CO_2Et	H	1/1	40	9	**6k**, 47 (*E*)[d]	**6d**, 6 (*E*)[e]
5	**3e**	Ph	Me	Me		40	0.1	**6l**, 7	**6e**, 29
6	**3f**	Mes[f]	H	H		25	6	**6h**, 65[g]	
7	**3g**	Mes[f]	Me	H	3/1	−25	9	**6i**, 58 (*E*)[h]	
8[i]	**3g**	Mes[f]	Me	H	3/1	−25	4	**6i**, 84 (*E*)	

[a] Isolated yield. [b] Determined by ^1H NMR. [c] **3a** (37%) was recovered. [d] The *Z* isomer was obtained as the lactone **6k′** (18%). [e] The *Z* isomer was obtained as the lactone **6d′** (10%). [f] Mes = 2,4,6-$Me_3C_6H_2$. [g] **3f** (15%) was recovered. [h] **3g** (37%, anti/syn = 3/1) was recovered. [i] Performed with $Sn(OTf)_2$ (0.15 mmol).

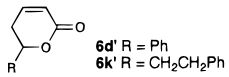
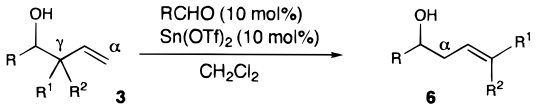


Table 2. Catalytic Conversion of γ-Adducts to α-Adducts[a]



	γ-adducts **3**							α-adducts **6**
entry		R	R^1	R^2	anti/syn[b]	*T*/°C	time/h	yield[c]/% (*E*/*Z*)[b]
1	**b**	Ph	Me	H	(20/1)	0	2	**b**, 78 (49/1)[d]
2	**c**	Ph	Ph	H	(35/1)	0	0.5	**c**, 76 (*E*)[e]
3	**d**	Ph	CO_2Et	H	(1/1.7)	40	40	**d**, 11 (*E*)[f,g]
4	**e**	Ph	Me	Me		25	0.1	**e**, 29
5	**i**	$PhCH_2CH_2$	Me	H	(33/1)	0−25	3	**i**, 89 (25/1)
6	**i**	$PhCH_2CH_2$	Me	H	(1/7.5)	25	2	**i**, 90 (1/5.3)[h]
7	**j**	$PhCH_2CH_2$	Ph	H	(14/1)	25	1	**j**, 82 (*E*)[i]
8	**j**	$PhCH_2CH_2$	CO_2Et	H	(1/1.3)	40	24	**k**, 41 (*E*)[j]
9	**l**	$PhCH_2CH_2$	Me	Me		40	22	**l**, 16[k]
10	**m**	$CH_3(CH_2)_8$	Me	H	(12/1)	0	2	**m**, 72 (11/1)
11[l]	**m**	$CH_3(CH_2)_8$	Me	H	(12/1)	−25−0	9	**m**, 91 (11/1)

[a] All reactions were performed with **3** (0.5 mmol), aldehyde (0.05 mmol), and $Sn(OTf)_2$ (0.05 mmol) in CH_2Cl_2 (2.5 mL), unless otherwise noted. [b] Determined by ^1H NMR. [c] Isolated yield. [d] 4% (anti/syn = 1/1) of **3b** was recovered. [e] 8% (anti/syn = 2/1) of **3c** was recovered. [f] The *Z* isomer was obtained as the lactone **6d′** (33%). [g] 19% (anti/syn = 14/1) of **3d** was recovered. [h] 3% (syn) of **3i** was recovered. [i] 6% (anti/syn = 1/23) of **3j** was recovered. [j] The *Z* isomer was obtained as the lactone **6k′** (51%). [k] 58% (syn) of **3*l*** was recovered. [l] Performed with $Sn(OTf)_2$ (0.15 mmol).

to 3-phenylpropanal (Scheme 3). To reduce the yield of the byproducts, 1-mesityl-2-methyl-3-buten-1-ol **3g** was employed as the allyl donor, and the desired product **6i** (84%) was obtained without formation of the corresponding byproduct. It is likely that steric hindrance due to the methyl groups at the 2,6-positions suppresses the α-allylation of mesitaldehyde via allyl-transfer with **3g**.

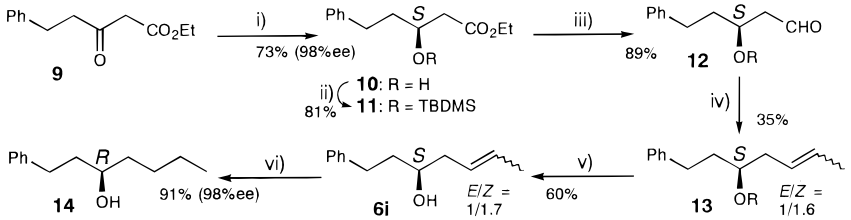
Conversion of γ-Adduct to α-Adduct and a Possible Reaction Mechanism. The results shown in Table 1 enabled us to design a conversion of γ-adducts **3**, easily derived from normal allylation of aldehydes with allylic metal reagents, into the corresponding α-adducts **6** by treatment with a very small amount of the parent aldehyde used in the preparation of **3**, as summarized in Table 2.

The results in Table 2 clearly show that the conversion of γ-adducts **3** to α-adducts **6** is very successful, although there is a small limitation that hindered homoallylic alcohols, such as **3e,l** (entries 4 and 9), are less reactive. The *E* selectivity of the α-adducts **6** formed from the anti isomers of **3b**,**c**,**i**,**j**,**m** (entries 1, 2, 5, 7, 10, and 11) can be explained by the transition-state models **T**, as shown in Scheme 4. The *E*-isomers of the α-adducts are obtained predominantly from anti homoallylic alcohol precursors via the sterically favored transition state **T1**. In contrast, when the syn isomer of **3i** is used (entry 6), the reaction proceeds via **T3** to give the *Z*-isomer of **6i** predominantly.

Stereochemistry in the Allyl Transfer from *anti*-γ to *E*-α. To confirm the stereospecificity shown in Scheme 4, optically pure (3*R*,4*S*)-**3i**[10] was separated by preparative HPLC and treated with 10 mol % of 3-phenylpropanal and $Sn(OTf)_2$ in CH_2Cl_2 for 3 h to give (*E*)-**6i** in 85% yield with >98% ee (determined by HPLC; DAISEL CHIRALCEL OD). The absolute configuration of **6i** derived from (3*R*,4*S*)-**3i** was determined to be *S* after hydrogenation of **6i** to (3*R*)-1-phenyl-3-heptanol **14** by identification with an authentic sample prepared as follows.

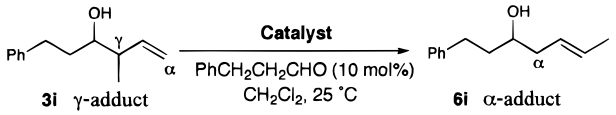
Preparation of Authentic Sample (*R*)-14. Ethyl 3-oxo-5-phenylpentanoate **9** was treated with Ru_2Cl_4(*S*-BINAP)$_2$·NEt_3 catalyst under 20 Kgf/cm^2 hydrogen atmosphere at 30 °C to give ethyl (3*S*)-3-hydroxy-5-phenylpentanoate **10**[11] (98%ee), which was in turn converted to *tert*-butyldimethylsilyl (TBDMS) ether **11** by treatment with TBDMS-Cl/imidazole in DMF. This was then converted to the corresponding aldehyde **12** by

Scheme 5[a]



[a] Key: (i) Ru_2Cl_4[(S)-BINAP]·$2Et_3N$ (cat.)/H_2 (20 atm, 30 °C); (ii) *t*-$BuMe_2SiCl$/imidazole/DMF; (iii) DIBAL/−78 °C/0.5 h/ether; (iv) $Ph_3P^+ - {}^-CHCH_3$/−78 °C/15 min; (v) Bu_4NF/3 h/0 °C/THF; (vi) H_2/Pd−C/ethanol/2 h.

Table 3. Conversion of γ-Adducts to α-Adducts: Effect of Catalysts[a]



run	catalyst/mol%	**3i** (anti/syn)[b]	time h	yield of **6i** %[c] (*E*/*Z*)[b]	recovery of **3i** %[c] (anti/syn)[b]
1	$Sn(OTf)_2$/10	23/1	2	88 (25/1)	N.D.[d]
2	$Sn(OTf)_2$/10	1/7.5	2	90 (1/5.3)	3 (*syn*)
3	$Sn(OTf)_2$/10	19/1	4	80 (20/1)	2 (2/1)
4	$Cu(OTf)_2$/10	17/1	48	72 (25/1)	16 (6/1)
5	Ag(OTf)/10	23/1	95	83 (25/1)	4 (3/1)
6[e]	$AlCl_3$/10	25/1	6	51 (50/1)	39 (10/1)
7	$AlCl_3$·$3Pr^iOH$/33	16/1	3	63 (20/1)	23 (12/1)
8[f]	$SnCl_4$/2	33/1	8	77 (23/1)	10 (4/1)
9[g]	Bu_2SnCl_2/100	25/1	24	56 (33/1)	35 (16/1)
10[g]	$CeCl_3$/100	1/1	24	37 (1.7/1)	51 (0.8/1)
11[h]	$CeCl_3$/100	16/1	36	44 (17/1)	15 (9/1)
12	$BaCl_2$/100	20/1	48	N.D.[d]	quant
13	CF_3SO_3H/10	18/1	2	89 (17/1)	1 (*syn*)
14	HCl/100	100/1	4	84 (100/1)	2 (*syn*)

[a] All reactions were performed with **3i** (0.5 mmol) and 3-phenylpropanal (0.05 mmol), in CH_2Cl_2 (2.5 mL) at 25 °C, unless otherwise noted. [b] Determined by ^1H NMR. [c] After isolation by column chromatography on silica gel. [d] Not detected. [e] Performed in ether (0.3 mL). [f] Performed at 0−25 °C. [g] Performed in refluxing CH_2Cl_2 (0.5 mL). [h] Performed in refluxing CH_3CN (0.3 mL). [i] Performed in refluxing CH_2Cl_2, CH_3CN, and THF.

treatment with DIBAH in ether at −78 °C. The resulting aldehyde **12** was combined with triphenylphosphoniumethylide in THF at −78 °C to give (5*S*)-5-*tert*-butyldimethylsilyloxy-7-phenyl-2-heptene **13**, which was then treated with tetrabutylammonium fluoride to afford (3*S*)-1-phenyl-5-heptene-3-ol **6i** (*E*/*Z* = 1/1.6). Finally, the authentic (3*R*)-1-phenylheptan-3-ol **14** was obtained by hydrogenation of (3*S*)-**6i**. Note that the reactions used above were not optimized (Scheme 5).

Stereochemistry in the Allyl Transfer from *syn*-γ to *Z*-α. Optically pure (3*R*,4*R*)-**3i**, isolated by preparative chiral HPLC purification of (3*R*,4*R*)-**3i** (79% ee) that was prepared according to the method reported by Roush,[10] was allowed to react with 10 mol % of 3-phenylpropanal and $Sn(OTf)_2$ in CH_2Cl_2 for 3 h to give **6i** in 80% yield (*E*/*Z* = 1/18). The enantiomeric excess of (*Z*)-**6i** was determined to be >98% ee, and the absolute con figuration of the major isomer was identified as *S* by comparison with the authentic sample (*R*)-**14** after hydrogenation of (*Z*)-**6i** to **14**. In addition, (*E*)-**6i**, obtained here from (3*R*,4*R*)-**3i** as a minor product, was shown to have an *R* configuration and enantiomeric excess >98% by chiral HPLC analysis. This clearly shows that in addition to **T1** the transition models **T2** and **T3** are also reasonable.

Effect of Catalysts. To clarify the effect of catalysts, further studies of the reaction of **3i** with 3-phenylpropanal to give **6i** were carried out in the presence of a variety of metal salts and acids. The results are listed in Table 3.

In addition to metal triflates, most of the mediators **4**, used for the previously reported α-selective allylations by the allylic metals, served as effective catalysts for this allyl-transfer reaction (entries 1−11). Surprisingly, Brønsted acids, trifluoromethanesulfonic acid, and hydrogen chloride catalyzed this γ to α conversion (entries 13 and 14).

Conclusion

The mehod described in this paper provides a new, efficient procedure for the synthesis of α-homoallylic alcohols **6** via allyl transfer from the normal γ-homoallylic alcohols **3**. The allylation of the anti and syn diastereomers of the γ-adducts **3** proceeds in a highly stereoselective manner via the six-membered cyclic transition states [**T**] to afford the *E*- and *Z*-α-adducts **6**, respectively. Moreover, the optical purities of both anti- and syn-γ-adducts **3** are also transferred to the corresponding α-adducts **6** with >98% ee. As compared with the previously reported methods for the α-selective allylation via transmetalation of allylic metal reagents **1** with mediators **4**, the present approach has several advantages. First, use of the γ-homoallylic alcohols **3** as allyl-transfer reagents is a noteworthy advance in synthetic methodology. Second, both the stereochemistry of the product olefins and the absolute configuration of the α-adducts **6** is easily deduced from the starting γ-adducts **3**. Finally, the allyl-transfer reaction proceeds smoothly under mild reaction conditions (at room temperature with catalytic amount of acids), and the reaction products are easily purified.

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Supporting Information Available: Complete experimental details, including characterization data for **3** and **6**, stereochemical correlations, and copies of ^1H and ^{13}C NMR spectra of **6d**, **6d′**, **6e**, **6k**, **6k′**, **10**, **12**, and **14** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) The absolute configuration of **3i** was determined by comparison with an authentic sample prepared by the reaction of 3-phenylpropanal with (*R*,*R*)-diisopropyl tartrate (*E*)-2-butenylboronate: (a) Roush, W. R.; Ando, K.; Powers, D. B.; Palkowitz, A. D.; Halterman, R. L. *J. Am. Chem. Soc.* **1990**, *112*, 6339. (b) Roush. W. R.; Ando, K.; Powers, D. B.; Halterman, R. L.; Palkowitz, A. D. *Tetrahedron Lett.* **1988**, *29*, 5579.

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