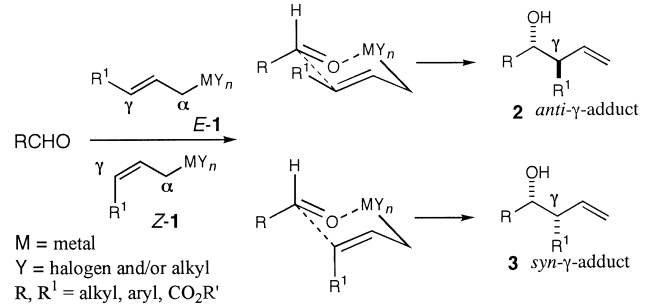
New Route to α-Adducts of Homoallylic Alcohols by an Acid-Catalyzed Stereospecific Allyl-Transfer Reaction from γ-Adducts

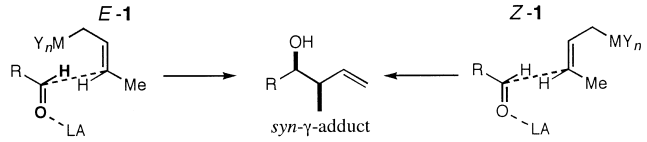
Junzo Nokami,* Laurence Anthony, and Shin-ichi Sumida[a]

Abstract: Allylation of aldehydes by an allyl-transfer reaction from the γ-adducts of homoallylic alcohols has been successfully carried out to give the corresponding α-adducts regiospecifically. The reaction proceeds via a hemiacetal (**11**), derived from an aldehyde and the homoallylic alcohol, followed by a six-membered cyclic transition state (2-oxonia[3.3]-sigmatropic rearrangement) in the presence of a Lewis acid. Moreover, the γ-adducts are restructured into the corresponding α-adducts via a similar transition state by an acid catalyst, in which chirality in both *anti*- and *syn*-γ-adducts is stereospecifically transferred to the corresponding *E*- and *Z*-α-adducts, respectively, with >98 % *ee*.

Keywords: alcohols · allylations · allyl complexes · allyl-transfer · homoallylic alcohols · reaction mechanisms



Scheme 1.



Scheme 2.

Introduction

One of the most fundamental and important reactions for constructing carbon–carbon bonds is the allylation of aldehydes and ketones (carbonyls) with allylic organometallic reagents.[1] For example, Grignard and Barbier-type reactions have been widely utilized for the allylation of carbonyls, in which chemo-, regio-, and stereoselectivities of the desired homoallylic alcohols are highly dependent on the nature of the metals employed. For example, the *E* and *Z* crotylmetals **1** ($R^1 = CH_3$; $MY_n = Cp_2TiBr$,[2] $CrCl_2$,[3] $AlEt_2$,[4] $B(OR)_2$,[5] etc) react with an aldehyde to give selectively the *anti*-γ-adduct **2** and *syn*-γ-adduct **3**, respectively, via a six-membered cyclic transition state (Scheme 1). Moreover, Lewis acid promoted reactions of less reactive crotylmetals, such as but-2-enyltributyltin (**4**),[6] with an aldehyde afford the *syn*-γ-adduct **2** selectively via an acyclic transition state (Scheme 2).

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These facts clearly indicate that allylic metals commonly react with carbonyls at the γ-position to afford γ-adducts of homoallylic alcohols predominantly, although a few exceptions have been reported.[7]

Discussion

α-Selective allylation of aldehydes using allylic metals: Much effort has been devoted to synthesize regioselectively α-adducts using allylic metals. It has been discovered that the allylic metals used for the synthesis of γ-adducts are also useful for the synthesis of α-adducts when they are used together with some additives. For example, but-2-enyltributyltin (**4**)/Bu_2SnCl_2,[8] **4**/$BuSnCl_3$,[9] **4**/$AlCl_3$–*i*PrOH,[10] but-2-enylmagnesium chloride/$AlCl_3$,[11] but-2-enyllithium/$CeCl_3$,[12] **4**/$CoCl_2$,[13] but-2-enyltrimethyltin/$SnCl_4$,[14] **4**/$SnCl_4$,[15] *Z*-**4**/$BuSnCl_3$,[16] etc[17] react with aldehydes to give the corresponding α-adducts of homoallylic alcohols selectively. For some of these reactions, it is assumed that the reaction will proceed by transmetalation of the allylic functionality from the less reactive allylic metal **4** to the corresponding additive **5** to give the γ-adduct of the allylic metal (**6**), which is more reactive than **4**. This, in turn, reacts with aldehyde at its γ-position to give the α-adduct **7** (Scheme 3). However, one of

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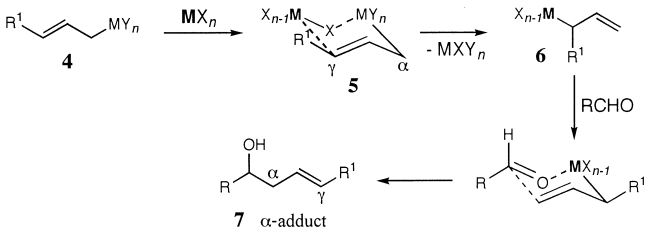
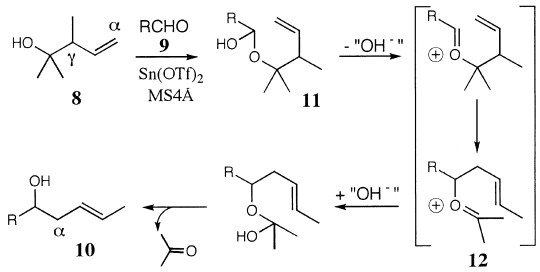


Scheme 3. Reaction of **4** to give the homoallylic alcohol **7.**

the main problems with this explanation is that it does not account for cases in which the product has *Z* selectivity.

One further allylation reaction is the reaction of allylic barium compounds discovered by H. Yamamoto,[7] which is very different from those described above in that it gives the α-adducts rather than γ-adducts of homallylic alcohols selectively without any additives.

α-Selective allylation of aldehydes by an allyl-transfer reaction of homoallylic alcohols from ketones to aldehydes: We have reported a conceptually new allylation of aldehydes:[18] an allylic functionality of the homoallylic alcohol **8**, derived by allylation of acetone, is transferred to the aldehyde **9** to give specifically the corresponding α-adduct **10** of the homoallylic alcohol in the presence of a *catalytic amount* of $Sn(OTf)_2$. We have also proposed a plausible reaction mechanism via the hemiacetal **11** and then the oxycarbenium ion **12**, that is, a 2-oxonia[3.3]-sigmatropic rearrangement (Scheme 4).[19]

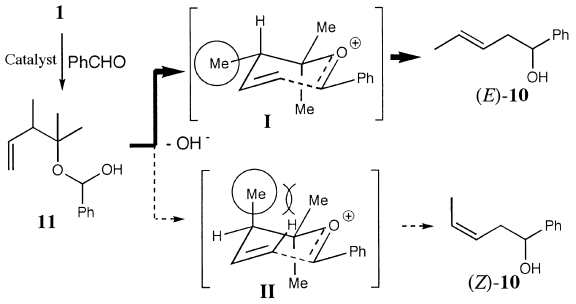


Scheme 4. Plausible mechanism for the conversion of homoallylic alcohol **8** to α-adduct **10.**

Abstract in Japanese:

アリル型金属化合物によるアルデヒドのアリル化反応は炭素延長反応の一つとして重要である。しかし、バリウムを除くすべての場合優先的にγ-付加体ホモアリルアルコールが生成する。(A): ルイス酸などの添加物を加えてα-付加体を得る反応が見出され、トランスメタル化を経由するものと理解されてきた。(B): これに対してわれわれは、γ-付加体ホモアリルアルコールをアリル供与体とする新しいα-付加体ホモアリルアルコールの合成法を見出した。この allyl-transfer 反応は、酸触媒によるヘミアセタール、続いて oxycarbenium ion 形成の後、6 員環遷移状態を経てγ-付加体ホモアリルアルコールからアルデヒドへ直接アリル基が移動する 2-oxonia[3.3]-sigmatropy 転位で進行する。(C): この反応を応用すればγ-付加体ホモアリルアルコールをα-付加体ホモアリルアルコールに変換できる。しかも、この反応は 6 員環遷移状態を経由して立体特異的に進行する。(D): この反応に有効な触媒系は (A) に有効な添加物とよく一致することから、(A) の多くはγ-付加体を経由する (C) の反応と見直すべきかも知れない。そうすれば、(A) の反応で *Z* 体が生成する場合も、*syn*-γ-付加体を経由するものとして合理的に説明できる。

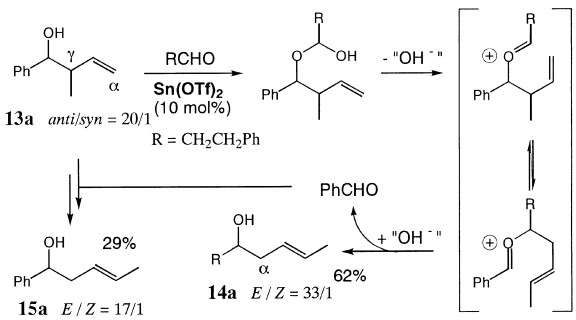
The reaction mechanism (proposed in Scheme 4) can be substantiated further by the high *E* selectivity of the product. This can be explained by the cyclic chairlike transition states **I** and **II** (see Scheme 5). That is, the transition state **I** is



Scheme 5. Proposed chairlike transition states **I** and **II** in the reaction of **1** to give **10**.

preferable to **II** due to the minimization of 1,3-diaxial repulsion between the methyl substituent and the hydrogen atom of the terminal olefin. Although the reaction mechanism is not completely clear, we can assume that the reaction is accelerated to give i) more stable cations, ii) sterically less hindered homoallylic alcohols, and iii) thermodynamically more stable olefins.

Conversion of γ-adducts of homoallylic alcohols to the corresponding α-adducts: Recently, we investigated the allyl-transfer reaction further using 2-methyl-1-phenyl-3-buten-1-ol (**13a**) as an allyl donor. Based on the hypotheses i)–iii) above, reaction of **13a** with an alkanal should give the corresponding α-adduct. The reaction of **13a** (*anti*/*syn* 20/1) with 3-phenylpropanal gave selectively the desired product 1-phenyl-5-hepten-3-ol (**14a**) (*E*/*Z* 33/1) in 62% yield, although 1-phenyl-3-penten-1-ol (**15a**) (*E*/*Z* 17/1) was also obtained in 29% yield. Formation of the undesired product **15a** suggested that benzaldehyde, formed during the reaction of **13a** with 3-phenylpropanal, will also react with **13a** competitively (Scheme 6). This fact prompted us to find a



Scheme 6.

more efficient design to give the α-adducts selectively from the corresponding γ-adducts by an allyl-transfer reaction, that is, γ to α conversion. A very successful approach was to restructure the γ-adducts into the corresponding α-adducts by treatment with a small amount (10 mol%) of the corresponding aldehyde in the presence of a catalytic amount of $Sn(OTf)_2$. In this case, *anti* diastereoisomers (Table 1) gave

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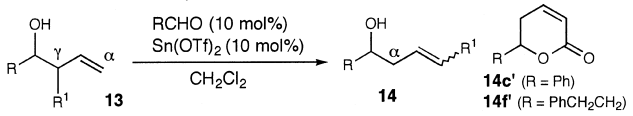
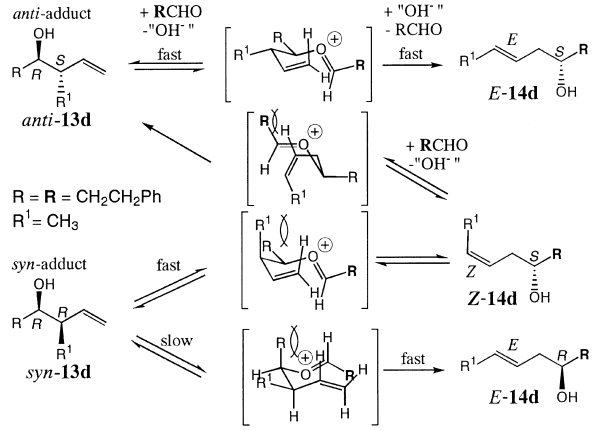
Table 1. Conversion of γ-adducts to α-adducts.[a]



Entry		γ-adduct **13** R	R^1	(*anti*/*syn*)[b]	*T* °C	*t* h	α-adduct **14** yield [%][c]	(*E*/*Z*)[b]
1	**a**	Ph	Me	(20/1)	0	2	78	(49/1)[d]
2	**b**	Ph	Ph	(35/1)	0	0.5	76	(*E*)[e]
3	**c**	Ph	CO_2Et	(1/1.7)	40	40	11	(*E*)[f,g]
4	**d**	$PhCH_2CH_2$	Me	(33/1)	0–25	3	89	(25/1)
5	**d**	$PhCH_2CH_2$	Me	(1/7.5)	25	2	90	(1/5.3)[h]
6	**e**	$PhCH_2CH_2$	Ph	(14/1)	25	1	82	(*E*)[i]
7	**f**	$PhCH_2CH_2$	CO_2Et	(1/1.3)	40	24	41	(*E*)[j]
8	**g**	$CH_3(CH_2)_8$	Me	(12/1)	0	2	72	(11/1)
9[k]	**g**	$CH_3(CH_2)_8$	Me	(12/1)	−25–0	9	91	(11/1)

[a] All reactions were performed with **13** (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 spectroscopy. [c] Yield of isolated product. [d] 4% (*anti*/*syn* 1/1) of **13a** was recovered. [e] 8% (*anti*/*syn* 2/1) of **13b** was recovered. [f] The *Z* isomer was obtained as the lactone **14c′** (33%). [g] 19% (*anti*/syn 14/1) of **13c** was recovered. [h] 3% (*syn*) of **13d** was recovered. [i] 6% (*anti*/*syn* 1/23) of **13e** was recovered. [j] The *Z* isomer was obtained as the lactone **14f′** (51%). [k] Performed with $Sn(OTf)_2$ (0.15 mmol).

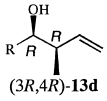
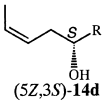
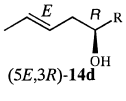
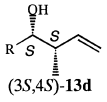
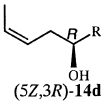
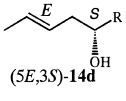
E olefins and *syn* diastereoisomers gave *Z* olefins predominantly. The former reaction rate seemed to be faster than the latter, as *syn* isomer was recovered predominantly when a mixture of *syn* and *anti* was used for the reaction. The difference in selectivity between *anti* and *syn* is well explained by the six-membered cyclic transition state model, as shown in Scheme 7. The transition state model, including the chirality,



Scheme 7. Stereochemistry of allyl transfer as explained by the formation of a six-membered transition state. The absolute configurations (*R* and *S*) are shown as $R = CH_2CH_2Ph$ and $R^1 = Me$.

was confirmed by employing optically pure *anti*- and *syn*-γ-adducts, (3*R*,4*S*)- and (3*R*,4*R*)-1-phenyl-4-methyl-5-hexen-3-ol (**13d**) ($R^1 = CH_3$, $R = CH_2CH_2Ph$ in Scheme 7). The reaction of the *anti* isomer (3*R*,4*S*)-**13d** with 10 mol% of 3-phenylpropanal and $Sn(OTf)_2$[20] gave (5*E*,3*S*)-1-phenyl-5-hepten-3-ol ((5*E*,3*S*)-**14d**) in 82% yield with >98 % *ee* as a single product. A similar treatment of the *syn* isomer (3*R*,4*R*)-**13d** gave a mixture of (5*Z*)-1-phenyl-5-hepten-3-ol ((5*Z*)-**14d**), (5*E*)-1-phenyl-5-hepten-3-ol ((5*E*)-**14d**), and unreacted (3*R*,4*R*)-**13d** in the ratio of about 18/1/1 (by ^1H NMR spectroscopy). The chiral HPLC analysis of the mixture using DAICELL CHIRALCELL OD showed that enantiomeric purities of both α-adducts, (5*Z*,3*S*)-**14d** and (5*E*,3*R*)-**14d**, were >98 % *ee*. However, it is noteworthy that, in this allyl-transfer reaction from *syn*-**13d** to α-adducts **14d**, the ratios of (5*E*)-**14d** were increased with diminishing the enantiomeric purities of (5*E*)-**14d** (Table 2; Figure 1).[21] This shows the *Z* product, (5*Z*)-**14d**, was not very stable under the reaction conditions.

Table 2. Enantioselectivity of *E* adducts from *syn* adducts.

syn-**13d**	recovery [%]	α-adduct total yield [%]	*Z* (>98 % *ee*)	*Z*/*E*	*E*-**14d** [% *ee*]
 (3*R*,4*R*)-**13d**	4	81	 (5*Z*,3*S*)-**14d**	18/1	 (5*E*,3*R*)-**14d** 99
	2	90		14/1	67
	1	80		11/1	53
 (3*S*,4*S*)-**13d**	2	80	 (5*Z*,3*R*)-**14d**	18/1	 (5*E*,3*S*)-**14d** 98
	1	80		7/1	26

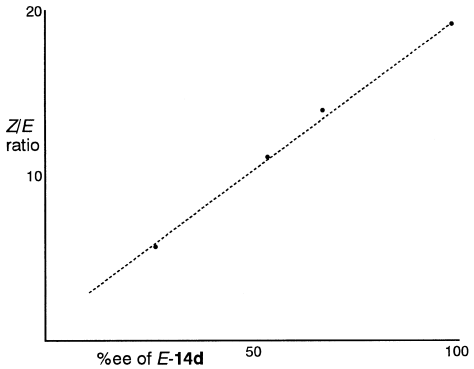
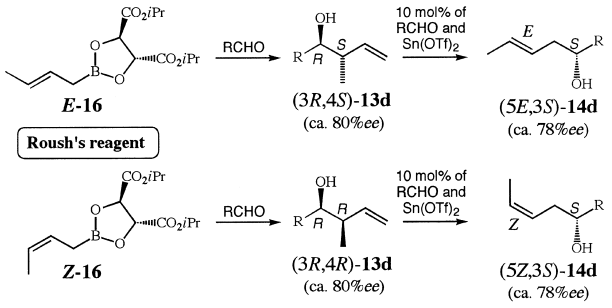


Figure 1. Plot of relationship between *E*/*Z* and enatiomeric excess of *E* adducts. The absolute configurations (*R* and *S*) are shown as $R = CH_2CH_2Ph$.

From the above results, it can be seen that a γ-specific highly enantioselective allylation by Roush's reagent **16**[22] is very useful for the enantioselective synthesis of α-adducts by this stereospecific allyl-transfer reaction (Scheme 8). For

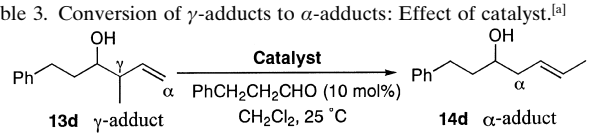


Scheme 8. Enantioselective α-allylation using Roush's reagent. The absolute configurations (*R* and *S*) are shown as $R = CH_2CH_2Ph$.

example, the reaction of *E*-**16** and *Z*-**16** with 3-phenylpropanal gave optically active (3*R*,4*S*)-**13d** (*anti*) and (3*R*,4*R*)-**13d** (*syn*), respectively, with good enantioselectivities (ca. 80 % *ee*). These, in turn, gave (5*E*,3*S*)-**14d** and (5*Z*,3*S*)-**14d**, respectively with > 78 % *ee* by the allyl-transfer reaction using 10 mol % of 3-phenylpropanal and $Sn(OTf)_2$.[20]

An alternative reaction mechanism for the α-selective allylation of aldehydes accomplished by using an allylic metal together with additive: Further investigation of the catalyst for this γ to α conversion reaction made it clear that many Lewis acids, such as $Cu(OTf)_2$, AgOTf, $AlCl_3$, $SnCl_4$, $(iPrO)_2TiCl_2$, $BF_3 \cdot Et_2O$ were effective, as well as hydrogen chloride (Table 3).[23] However, $BaCl_2$ was ineffective. Some of the

Table 3. Conversion of γ-adducts to α-adducts: Effect of catalyst.[a]



13d γ-adduct **14d** α-adduct

Run	Catalyst /mol%	**13d** *anti*/*syn*[b]	*t* h	Yield of **14d** [%][c]	(*E*/*Z*)[b]	Recovery of **13d** [%][c]	(*anti*/*syn*)[b]
1	$Sn(OTf)_2$/10	23/1	2	88	(25/1)	–[d]	
2	$Sn(OTf)_2$/10	1/7.5	2	90	(1/5.3)	3	(*syn*)
3	$Cu(OTf)_2$/10	19/1	4	80	(20/1)	2	(2/1)
4	$Zn(OTf)_2$/10	17/1	48	72	(25/1)	16	(6/1)
5	AgOTf/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	$AlCl_3$•3 *i*PrOH/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	$(iPrO)_2TiCl_2$/100	50/1	3	58	(100/1)	12	(20/1)
11	BF_3•Et_2O/10	1/1	24	73	(1/1)	–[d]	
12	CF_3SO_3H/10	18/1	2	89	(17/1)	1	(*syn*)
13	HCl/100	100/1	4	84	(100/1)	2	(*anti*)

[a] All reactions were performed with **13d** (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 spectroscopy. [c] Yield of isolated product. [d] Not detected. [e] Performed in diethyl ether (0.3 mL). [f] Performed at 0 – 25 °C. [g] Performed in refluxing CH_2Cl_2 (0.5 mL).

additives, used together with allylic metals for the apparently α-selective allylations described in **A**, are also effective for the γ to α conversion as described in **C**. Therefore, we propose an alternative reaction mechanism for the α-selective allylation by an allylic metal together with an additive (described in **A**). That is, the allylic metal reacts with aldehyde in the presence of an additive[24] to give the common γ-adducts of homoallylic alcohols *syn*- or *anti*-selectively. Then, the *syn*- and *anti*-γ-adducts are selectively transformed into the corresponding *Z*- and *E*-α-adducts, respectively, by the γ to α conversion described in **C**.

In conclusion, a new allylation reaction of aldehydes, in addition to the Grignard or Barbier-type reactions, was discovered. In the reaction, the allylic functionality of homoallylic alcohol γ-adducts is transferred to the aldehyde to give the α-adducts specifically, and the *E* olefin selectively via a six-membered cyclic transition state (2-oxonia [3.3]-sigmatropic rearrangement) in the presence of an acid catalyst. Conversion of the γ-adducts of homoallylic alcohols into the corresponding α-adducts is very successful, exclusively stereoselective (from *anti* to *E*, and from *syn* to *Z*), and enantiospecific. The reaction products also support an alternative mechanism to that previously proposed for several α-selective allylations utilizing usual allylic metals together with additives.[25]

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[17] α-Selective coupling reactions of allylic alcohols with aldehydes using: a) $Me_3SiCl/NaI/H_2O$-Sn: K. Kanagawa, Y. Nishiyama, Y. Ishii, *J. Org. Chem*. **1992**, *57*, 6988 – 6991; and b) $PdCl_2(PhCN)_2$ (cat.)/$SnCl_2$/ultrasonication: Y. Masuyama, A. Hayakawa, Y. Kurusu, *J. Chem. Soc. Chem. Commun*. **1992**, 1102 – 1103; c) Ref. [6c)].
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[19] The 2-oxonia[3.3]-sigmatropic rearrangement reaction was proposed as a plausible reaction mechanism in the $SnCl_4$-catalyzed reaction of 3,4-dihydroxy-1-alkene with aldehyde to give 3-acyltetrahydrofuran, though an alternative mechanism involving a Prins reaction was

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proposed in a later paper (see below[19c]): a) M. H. Hopkins, L. E. Overman, *J. Am. Chem. Soc*. **1987**, *109*, 4748–4749. It was proved that the $SnCl_4$-induced π-cyclization reaction of methyl 2-acetoxy-2-(3-alken-1-oxy)acetate to five- and six-membered-ring ethers proceeds by a 2-oxonia [3.3]-sigmatropic rearrangement: b) L. D. M. Lolkema, C. Semeyn, L. Ashek, H. Hiemstra, W. N. Speckamp, *Tetrahedron*, **1994**, *50*, 7129–7140. Many other intramolecular C–C bond formation reactions that proceed by an intramolecular Prins reaction of an oxycarbenium ion with π-nucleophile have been investigated for the syntheses of five- and six-membered cyclic ethers: c) M. H. Hopkins, L. E. Overman, G. M. Rishton, *J. Am. Chem. Soc.*, **1991**, *113*, 5354–5365. d) W. H. Bunnelle, D. W. Seamon, D. L. Mohler, T. F. Ball, D. W. Thompson, *Tetrahedron Lett*. **1984**, *25*, 2653–2654; e) A. Boaretto, D. Furlani, D. Marton, G. Tagliavini, A. Gambaro, *J. Organomet. Chem.*, **1986**, *299*, 157–167; f) L. Coppi, A. Ricci, M. Taddei, *Tetrahedron Lett*. **1987**, *28*, 973–976; g) Z. Y. Wei, J. S. Li, D. Wang, T. H. Chan, *Tetrahedron Lett.*, **1987**, *28*, 3441–3444; h) A. Mekhalfia, I. E. Markó, H. Adams, *Tetrahedron Lett*. **1991**, *32*, 4783–4786; i) I. E. Markó, F. Chellé, *Tetrahedron Lett*. **1997**, *38*, 2895–2898; j) D. Hoppe, T. Krämer, C. F. Erdbrügger, E. Egert, *Tetrahedron Lett*. **1989**, *30*, 1233–1236; k) J. S. Panek, R. Beresis, *J. Org. Chem.*, **1993**, *58*, 809–811; l) R. W. Hoffman, V. Giesen, M. Fuest, *Liebigs*, *Ann. Chem.*, **1993**, 629–639; m) M. Nishizawa, T. Shigaraki, H. Takao, H. Imagawa, T. Sugihara, *Tetrahedron Lett.*, **1999**, *40*, 1153–1156.It is noteworthy that we also obtained a 4-chlorotetrahydropyrane derivative (by an intramolecular Prins reaction) together with an α-adduct of homoallylic alcohols, when a stoichiometric amount of $SnCl_4$ was used in our allyl-transfer reaction. Therefore, we assume that the Prins reaction will be favored by the electophilic addition of a reactive incipient oxycarbenium ion along with enough nucleophile (e. g. Cl^- from $SnCl_4$) to give chlorinated cyclic ethers, etc.

[20] The reaction conditions shown in Table 1 (entry 5) were applicable.

[21] Treatment using higher concentrations (0.5 M) and/or longer reaction times (4–5 h) resulted in an increase of (*E*)-**14d** with lower optical purity, and the incomplete consumption of the starting material, *syn*-**13d**.

[22] a) W. R. Roush, K. Ando, D. B. Powers, R. L. Halterman, A. D. Palkowitz, *Tetrhaedron Lett*. **1988**, *29*, 5579–5582; b) W. R. Roush, K. Ando, D. B. Powers, A. D. Palkowitz, R. L. Halterman, *J. Am. Chem. Soc*. **1990**, *112*, 6339–6348.

[23] Hydrogen chloride (1.0 M solution in anhydrous ether; purchased from Aldrich) was effective for this reaction.

[24] It seems reasonable that the additives would serve as a Lewis acid for the common allylation by an inactive allylic metal such as **4** to give the *syn*-γ-adduct **2** predominantly, and then as a catalyst for the allyl-transfer reaction from γ to α with *Z* selectively. However, the actual catalyst for the reaction is not completely clear, because a Brønsted acid such as HCl also served as a good catalyst, and will be easily formed from a Lewis acid with alcohol (substrate of the reaction) or moisture.

[25] Although the allyl-transfer reaction was carried out at 20–25 °C with 10 mol% of $Sn(OTf)_2$ to give good results, many of the previously reported α-allylation reactions (described in A) were performed at a lower temperature for shorter reaction times with more than stoichiometric amounts of additives. It should be noted, however, that the in situ formed γ-adduct (Lewis acid complex) derived from an aldehyde and an allylic metal with additive (Lewis acid), would be much more reactive than the corresponding alcohol used in our reaction. The complex would smoothly react with a large amount of unreacted aldehyde, existing in the reaction mixture before the reaction with allylic metal, to give the oxycarbenium ion. We believe that this allyl-transfer reaction will play an important role in many α-selective allylation reactions.