JOC Article

Direct Preparation of Allylic Indium(III) Reagents from Allylic Alcohols via a Reductive Transmetalation of π-Allylnickel(II) with Indium(I) Iodide

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InI-mediated direct allylation of carbonyl compounds with allylic alcohols proceeded smoothly with catalytic amounts of $Ni(acac)_2$ and PPh_3 to give the corresponding homoallylic alcohols in high yields. Allylindium compounds were shown to be the real allylating agents in the present system. Substituted allylic alcohols gave branched homoallylic alcohols with syn-selectivity irrespective of the geometry of the starting allylic alcohols, whereas high anti-selectivity was observed when a bulky substituent is present in the allylic alcohols. The outcome of the diastereoselectivity is discussed on the basis of the reaction mechanism, comparing with the corresponding Pd-catalyzed version. Another distinct behavior between the Ni- and Pd-catalyzed allylation was demonstrated in the reaction of hex-1,5-diene-3,4-diol derivatives: the Pd catalyst did not give any coupling product, whereas the Ni-catalyzed InI-mediated reaction with benzaldehyde afforded the 1:1 and 1:2 adduct diols selectively depending on the reaction conditions.

Introduction

Allylation of carbonyl compounds with a variety of allylmetal reagents has been widely studied for carbon−carbon bond formation.[1] Among them, allylindium reagents have received much attention in the past decade, because they are water-tolerant reagents.[2] Allylindium reagents are easily prepared from allylic bromides or allylic iodides with metallic indium in polar solvents including water. Recently, we developed Pd-catalyzed InI-mediated allylation of aldehydes,[3] where various allylic compounds including allylic alcohols are used as the allylic source.[3a] Although Pd-catalyzed allylation of carbonyl compounds with allylic alcohols has hitherto been achieved by using $SnCl_2$ and Et_3B as reductants for the intermediate π-allylpalladium, it usually requires a longer time compared with the reaction employing allylic halides.[4] The Pd-catalyzed In-mediated allylation also proceeds slowly and there remains a need to develop efficient methods for the preparation of allylating agents from allylic alcohols. The direct use of allylic alcohol is advantageous in view of synthetic efficiency and green chemistry; it facilitates the access to a broad range of allylindium reagents without transformation to allylic alcohol derivatives bearing a wasteful leaving group. We report here that allylindium reagents can be prepared directly from allylic alcohols via reductive transmetalation of a π-allylnickel intermediate with InI by the use of $Ni(acac)_2$ and PPh_3. The coupling in situ with carbonyl compounds gave the corresponding homoallylic alcohols in a much shorter time than that involving the Pd catalyst.

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(2) (a) Cintas, P. *Synlett* **1995**, 1087. (b) Marshall, J. A. *Chemtracts: Org. Chem.* **1997**, *10*, 481. (c) Li, C.-J.; Chan, T.-H. *Tetrahedron* **1999**, *55*, 11149. (d) Araki, S.; Hirashita, T. In *Main Group Metals in Organic Synthesis*; Yamamoto, H., Oshima, K., Eds.; Wiley-VCH: Weinheim, Germany, 2004; Vol. 1, pp 323−386.

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(4) (a) Takahara J. P.; Masuyama Y.; Kurusu, Y. *J. Am. Chem. Soc.* **1992**, *114*, 2577. (b) Kimura, M.; Tomizawa, T.; Horino, Y.; Tanaka, S.; Tamaru, Y. *Tetrahedron Lett.* **2000**, *41*, 3627.

Results and Discussion

By using allyl acetate as a representative allylic component, Barbier-type nickel-catalyzed indium-mediated allylations of benzaldehyde were examined under various conditions. $Ni(cod)_2$ and $Ni(acac)_2$ gave the corresponding homoallylic alcohol **1a** in moderate yields in 1,3-dimethyl-2-imidazolidinone (DMI) (Table 1, entries 1 and 2). With heating, the yield was increased to 82% yield (entry 3). The use of the triphenylphosphine ligand accelerated the reaction and quantitative yields of **1a** were attained (entries 4−6).

Next, allylic compounds with different leaving groups were subjected to this allylation (Table 2). Allyl methyl sulfide afforded **1a** in moderate yield in 24 h with catalytic amounts of $Ni(acac)_2$ (5 mol %) and PPh_3 (20 mol %) (entry 1). Allyl chloride, allyl phenyl ether, and even allyl alcohol (**2a**) gave **1a** in high yields in only 1 h (entries 2−4). The reaction of **2a** in THF or CH_2Cl_2 also proceeded smoothly to give **1a** in high yields (entries 5

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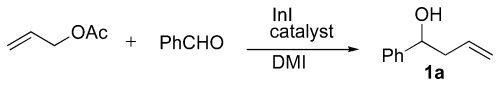
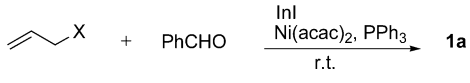
TABLE 1. Ni-Catalyzed In-Mediated Reaction of Allyl Acetate with Benzaldehyde[a]



entry	catalyst (mol %)	conditions	yield, %
1	$Ni(cod)_2$ (10)	rt, 20 h	34
2	$Ni(acac)_2$ (10)	rt, 20 h	50
3	$Ni(acac)_2$ (10)	70 °C, 3 h	82
4	$Ni(acac)_2$ (5), PPh_3 (20)	rt, 1 h	97
5	$NiBr_2(PPh_3)_2$ (10)	rt, 2 h	98
6	$Ni(PPh_3)_4$ (10)	rt, 1 h	100

[a] All reactions were carried out with allyl acetate (1.0 mmol) and benzaldehyde (0.50 mmol) in DMI (3 mL).

TABLE 2. Allylation with Various Allylic Compounds in Different Solvents[a]



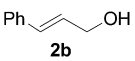
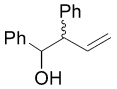
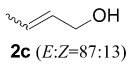
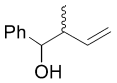
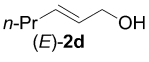
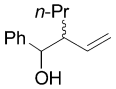
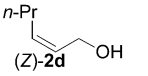
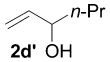
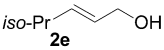
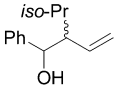
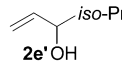
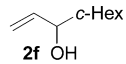
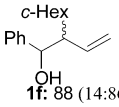
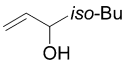
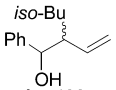
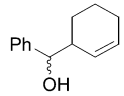
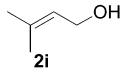
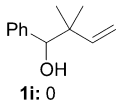
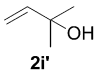
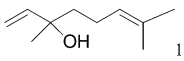
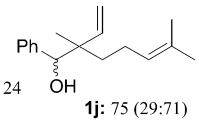
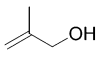
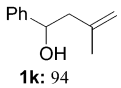
entry	X	solvent	*t*, h	yield, %
1	SMe	DMI	24	77
2	Cl	DMI	1	96
3	OPh	DMI	1	97
4	OH	DMI	1	96
5	OH	THF	5 (13)[b]	97 (76)[b]
6	OH	CH_2Cl_2	5	95
7	OH	DMI−H_2O	3	trace

[a] All reactions were carried out with allyl compound/benzaldehyde/InI = 2/1/2, $Ni(acac)_2$ (5 mol %), and PPh_3 (20 mol %) at room temperature. [b] $Pd(PPh_3)_4$ (5 mol %) was used in place of $Ni(acac)_2$.

and 6). It is noted that the present Ni-catalyzed allylation with allyl alcohol (**2a**) proceeded much faster than that with the Pd catalyst. The allylation did not proceed in aqueous DMI due to a decomposition of the nickel catalyst (entry 7). These results show that DMI is the best solvent regarding the reaction time.

Various allylic alcohols were then examined for the coupling with benzaldehyde in DMI and the results are summarized in Table 3. A cinnamylindium reagent, prepared from cinnamyl alcohol, gave the corresponding branched homoallylic alcohol **1b** exclusively in moderate yield (entry 1). The yield was easily improved by increasing the amount of $Ni(acac)_2$ (entry 2). Again, high efficiency of the Ni-catalyzed cinnamylation was observed compared with the Pd-catalyzed one (entry 3). Crotyl alcohol also gave the branched alcohol **1c** with syn-selectivity (entries 3 and 4). The secondary allylic alcohol **2c′** is usable for the present allylation (entry 5). Almost coincident diastereoselectivities were observed in the reactions of the isomeric allylic alcohols (entries 3−5). Both (*E*)- and (*Z*)-**2d** gave the corresponding homoallylic alcohol **1d** with coincident syn-diastereoselectivity (entries 6 and 7). Interestingly, the reaction of (*Z*)-**2d** proceeded more quickly than that of (*E*)-**2d**. Again, the corresponding secondary allyl alcohol **2d′** gave **1d** with syn-selectivity (entry 8). In contrast, the allylic alcohols bearing α-branched groups gave the anti-adducts selectively (entries 9−11). The reaction with isobutyl-substituted allylic alcohol **2g** afforded **1g** with similar syn-selectivity to **2c**−**d** (entry 12). The cyclic allylic alcohol **2h** gave the coupling product **1h** in poor yield (entry 13).

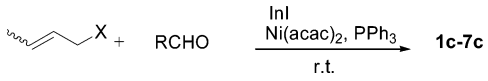
TABLE 3. Allylation of Benzaldehyde with Various Allylic Alcohols[a]

entry	allylic alcohol	$Ni(acac)_2$ (mol%)	*t*, h	product and yield, %[b]
1	 **2b**	5	24	 **1b:** 56 (0:100)
2	"	10	15 (24)[c]	**1b:** 98 (15:85) (31 (0:100))[c]
3	 **2c** (*E*:*Z*=87:13)	5	24	 **1c:** 19 (86:14)
4	"	15	3	**1c:** 84 (80:20)
5	 **2c'**	10	2	**1c:** 95 (81:19)
6	 (*E*)-**2d**	15	15	 **1d:** 90 (74:26)
7	 (*Z*)-**2d**	15	5	**1d:** 88 (82:18)
8	 **2d'**	10	5	**1d:** 95 (78:22)
9	 **2e**	20	22	 **1e:** 4 (11:89)
10	 **2e'**	20	19	**1e:** 54 (8:92)
11	 **2f**	20	22	 **1f:** 88 (14:86)
12	 **2g**	20	18	 **1g:** 100 (73:27)
13	 **2h**	10	20	 **1h:** 21 (93:7)
14	 **2i**	20	17	 **1i:** 0
15	 **2i'**	10	20	**1i:** 93
16	 **2j**	15	24	 **1j:** 75 (29:71)
17	 **2k**	20	4	 **1k:** 94

[a] All reactions were carried out with allylic alcohol (1.0 mmol), PhCHO (0.50 mmol), and InI (1.0 mmol) in DMI at room temperature. [b] Numbers in parentheses show syn:anti ratios. [c] With $Pd(PPh_3)_4$ in place of $Ni(acac)_2/PPh_3$.

Prenylindium cannot be prepared from **2i** even with an increasing amount of the nickel catalyst (entry 14).

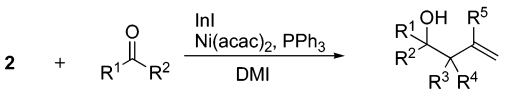
TABLE 4. Diastereoselectivity in the Crotylation of Various Aldehydes[a]



entry	crotyl compod X	crotyl compod *E*:*Z*	R	$Ni(acac)_2/PPh_3$, mol %	conditions	yield, % (syn:anti)[b]
1	OAc	86:14	Ph	15/60	DMI, 4 h	**1c**: 90 (75:25)
2	Cl	85:15	Ph	15/60	DMI, 1 h	**1c**: 100 (80:20)
3	OAc	86:14	Ph	15/60	THF, 6 h	**1c**: 63 (59:41)
4	Cl	85:15	Ph	10/40	THF, 20 h	**1c**: 94 (70:30)
5	OH	0:100	Ph	20/80	DMI, 2 h	**1c**: 81 (79:21)
6	OAc	0:100	Ph	20/80	DMI, 2 h	**1c**: 84 (81:19)
7	OH	84:16	$PhCH_2CH_2$	40/160	DMI, 6 h	**3c**: 87 (54:46)
8	OH	84:16	*n*-C_6H_{13}	40/160	DMI, 6 h	**4c**: 82 (50:50)
9	OH	84:16	*c*-C_6H_{11}	40/160	DMI, 5.5 h	**5c**: 55 (81:19)
10	OH	84:16	Me_2CH	40/160	DMI, 6 h	**6c**: 56 (72:28)
11	OH	84:16	PhMeCH	40/160	DMI, 3 h	**7c**: 88 (8:70:4:18)[c]

[a] All reactions were carried out in a ratio of crotyl compound/RCHO/InI = 2/1/2. [b] Determined by ^1H NMR. [c] Diastereomeric ratio.

TABLE 5. Allylation of 3-Phenylpropanal and Acetophenone with Various Allylic Alcohols[a]



3a: R^1=$PhCH_2CH_2$, R^2=R^3=R^4=R^5=H
3c: R^1=$PhCH_2CH_2$, R^2=H, R^3=Me, R^4=R^5=H
3d: R^1=$PhCH_2CH_2$, R^2=H, R^3=*n*-Pr, R^4=R^5=H
3i: R^1=$PhCH_2CH_2$, R^2=H, R^3=R^4=Me, R^5=H
3k: R^1=$PhCH_2CH_2$, R^2=R^3=R^4=H, R^5=Me
8a: R^1=Ph, R^2=Me, R^3=R^4=R^5=H
8c: R^1=Ph, R^2=Me, R^3=Me, R^4=R^5=H
8k: R^1=Ph, R^2=Me, R^3=R^4=H, R^5=Me

entry	**2**	R^1	R^2	*t*, h	yield, %	syn:anti[b]
1	**2a**	$PhCH_2CH_2$	H	1	**3a**: 95	–
2	**2c**[c]	$PhCH_2CH_2$	H	20	**3c**: 63	52:48
3	**2c′**	$PhCH_2CH_2$	H	6	**3c**: 90	52:48
4	(*Z*)-**2d**	$PhCH_2CH_2$	H	22	**3d**: 27	*d*
5	**2d′**	$PhCH_2CH_2$	H	24	**3d**: 48	59:41[e]
6	**2i′**	$PhCH_2CH_2$	H	22	**3i**: 29	–
7	**2k**	$PhCH_2CH_2$	H	16	**3k**: 92	–
8	**2a**	Ph	Me	8	**8a**: 84	–
9	**2c**[c]	Ph	Me	17	**8c**: 55	87:13
10	**2c′**	Ph	Me	8	**8c**: 56	86:14
11	**2k**	Ph	Me	24	**8k**: 30	–

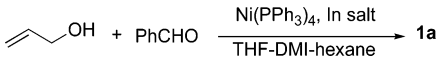
[a] All reactions were carried out with **2** (0.50 mmol), 3-phenylpropanal (0.25 mmol) or acetophenone, InI (0.50 mmol), $Ni(acac)_2$ (20 mol %), and PPh_3 (80 mol %) in DMI (3 mL). [b] Determined by ^1H NMR. [c] *E*:*Z* = 84:16. [d] Not determined. [e] Determined by GC analysis of the corresponding acetate.

However, **2i′**, an allylic isomer of **2i**, gave the corresponding branched homoallylic alcohol **1i** in high yield (entry 15). Even the sterically demanding tertiary allylic alcohol, linalool (**2j**), underwent allylation efficiently to give **1j** in good yield (entry 16). Methallyl alcohol (**2k**) afforded **1k** in high yield (entry 17).

The unique syn-selective crotylation of benzaldehyde observed in Table 3 prompted us to investigate the reaction of a variety of crotyl compounds. The reaction of *E*-rich crotyl acetate and crotyl chloride in place of crotyl alcohol gave **1c** also syn-selectively (Table 4, entries 1 and 2). The corresponding Pd-catalyzed reaction with crotyl chloride afforded **1b** with a slight anti-selectivity (46:54). In THF the syn-selectivity was decreased (entries 3 and 4). (*Z*)-Crotyl alcohol and (*Z*)-crotyl acetate also gave **1c** syn-selectively (entries 5 and 6), indicating that the stereochemical outcome of the present Ni-catalyzed crotylation is independent from the geometry of the starting allylic compounds, and suggesting that the crotylation proceeds via the same intermediate. To examine the generality of the syn-selectivity, crotylation of a variety of aliphatic aldehydes was studied (entries 7−11). The reaction of 3-phenylpropanal with crotyl alcohol gave **3c** in high yield. A larger amount (40 mol %) of $Ni(acac)_2$ was required to complete the reaction in comparison with the case of benzaldehyde (entry 7). Heptanal gave **4c** in high yield (entry 8). The syn-selectivity was not observed for these linear aliphatic aldehydes. On the contrary, cyclohexanecarboxaldehyde afforded **5c** syn-selectively, albeit in moderate yield (entry 9). 2-Methylpropanal also afforded **6c** syn-selectively (entry 10). 2-Phenylpropanal selectively gave one diastereomer **7c** of the possible four isomers (entry 11).

Next, the allylation of 3-phenylpropanal and acetophenone with various allylic alcohols was investigated and the results were summarized in Table 5. The reaction of **2a** gave **3a** in high yield (entry 1). Although crotyl alcohol (**2c**) gave **3c** in only 63% yield, its isomer **2c′** afforded **3c** in 90% yield in a shorter time (entries 2 and 3). The same tendency was observed in the reaction of (*Z*)-**2d** and **2d′** (entries 4 and 5). Again, the diastereoselectivity was lower than that with benzaldehyde (entries 3−8 in Table 3). Although the prenylation of benzaldehyde with the

TABLE 6. Nickel-Catalyzed Allylation of Benzaldehyde in the Presence or Absence of Indium Salts[a]



entry	$Ni(PPh_3)_4$, mol %	In salt, mol %	*t*, h	yield, %
1	200	none	6	0
2	200	$InCl_3$ (200)	6	0
3	200	$In(OH)_3$ (200)	6	0
4	10	InI (200)	1	100

[a] All reactions were carried out with PhCHO, allyl alcohol (200 mol %), and InI (200 mol %) in THF−DMI−hexane (2:1:1) at room temperature.

tertiary alcohol **2i′** proceeded smoothly, the reaction of 3-phenylpropanal gave **3i** in lower yield (entry 6). β-Substituted allylic alcohol **2k** afforded the corresponding product **3k** in high yield (entry 7). The allylation of acetophenone also proceeded smoothly in the presence of $Ni(acac)_2$ (20 mol %) giving **8a** in high yield (entry 8). The allyl alcohols substituted by a methyl group at the α, β, or γ position gave the corresponding homoallylic alcohols **8c** and **8k** syn-selectively in moderate yields (entries 9−11).

Mechanistic Consideration. π-Allylnickel halides are known as nucleophilic reagents; for example, dimeric π-allylnickel bromide reacts with carbonyl compounds to give the corresponding homoallylic alcohols.[5] This fact raises a question about the real allylating agent in the present reaction. There is a possibility that π-allylnickel directly reacts with the aldehyde, where InI simply plays a role as a reductant for Ni(II) to Ni(0), and the resulting In(III) salt acts as a Lewis acid to promote the reaction. To examine this possibility, we carried out the reaction of allyl alcohol with benzaldehyde in the presence of an equimolar amount of a Ni(0) catalyst without InI: thus, $Ni(PPh_3)_4$ was prepared by treatment of a mixture of $Ni(acac)_2$ and PPh_3 with DIBAL and the reaction was performed in the presence or absence of InX_3 (X = Cl or OH, 200 mol %). The results are summarized in Table 6. The reactions without InI did not give homoallylic alcohol **1a** (Table 6, entries 1−3). In contrast, the reaction proceeded smoothly in the presence of InI (200 mol %) and $Ni(PPh_3)_4$ (10 mol %) to give **1a** quantitatively (entry 4). These results clearly indicate that the key nucleophilic intermediate in the present allylation is not an allylnickel species but allylindium compounds. The most plausible reaction mechanism involving allylindium is depicted in Scheme 1. A Ni(0) catalyst is preformed from $Ni(acac)_2$ and InI. A π-allylnickel intermediate, generated from allylic alcohol and the Ni(0) catalyst, undergoes a reductive transmetalation with InI to afford an allylindium reagent, which allylates benzaldehyde.

It is interesting to note that the distinction between the nickel and palladium catalysts in the InI-mediated allylation is clearly marked by the diastereoselectivity. Syn products were formed predominantly from nickel-catalyzed reactions of benzaldehyde, except for the cases involving allylic alcohols with a bulky substitutent (Table 3, entries 1, 2, 9, 10, 11, and 15). In contrast, the diastereoselectivity of the Pd-catalyzed InI-mediated allylation can be controlled by a geometry of allylic alcohol derivatives: (*Z*)- and (*E*)-crotyl acetates react with benzaldehyde to give the corresponding syn- and anti-homoallylic alcohols, respectively.[3d] As the reaction of allylindium with aldehyde proceeds via a six-membered transition state, the syn preference in the nickel-catalyzed allylation suggests the existence of (*Z*)-allylic indium intermediates regardless of the geometry of starting allylic alcohols, unless a sterically demanding substitution is present. A π-crotylnickel complex is known to exist as an equilibrium of the syn- and anti-π-allyl isomers.[6] Therefore, it is reasonable to postulate the intermediacy of anti-π-allylic nickel complexes, which give upon transmetalation (*Z*)-allylic indium reagents more readily than syn isomers give (*E*)-allylic indium reagents.[7] The poor diastereoselectivity with 3-phenylpropanal and heptanal suggests that the energy difference is small between the two transition states, in which the alkyl group of the aldehydes occupies equatorial and axial positions.

Tandem Allylation with Hexa-1,5-diene-3,4-diol Derivatives. As a further example, hexa-1,5-diene-3,4-diol derivatives **9a**−**c** were subjected to the Ni-catalyzed InI-mediated allylation (Scheme 2). The reaction of diol **9a** with 2 equiv of benzaldehyde gave the 1:2 adduct **11** together with a small amount of **12** (Table 7, entry 1). When monoacetate **9b** was reacted with 3 equiv of the aldehyde, **11** was obtained in high yield with a small amount of **12** (entry 2). Addition of water increased the ratio of **12** (entry 3). In contrast, the reaction performed in carefully dried THF gave **11** exclusively (entry 4). The effect of water on the preference for **12** can be accounted for by the equilibrium of the intermediates **A** and **B**. As allylic indium reagents are coupled with carbonyl compounds at the γ-carbon, diols **11** and **12** are considered to come from **A** and **B**, respectively. The formation of **A** is favored by an intramolecular chelation, whereas water in the solvent may prevent the chelation of the alkoxide to indium and hence the acyclic intermediate **B** becomes more important. The use of a 2-fold amount of **9b** to the aldehyde led to an exclusive formation of the 1:1 adduct **10** (entry 5). Diacetate **9c** gave the 1:2 adduct **11** in 50% yield as a major product (entry 6). When the product diol **10** was subjected to the Ni-catalyzed InI-mediated reaction with benzaldehyde, **11** and **12** were formed in 47% and 28% yields, respectively. Again, addition of water reversed the ratio (**11**: 29%, **12**: 47%). In contrast, **9a**−**c** did not give any coupling product with $Pd(PPh_3)_4$. These results exhibit additional differences in the nature of the Pd- and Ni-catalyzed allylation. It is reported that the Ni-catalyzed allylation of diethylamine with allylic alcohols is much more efficient than the corresponding Pd-involving one.[8] This fact is in accord with the high

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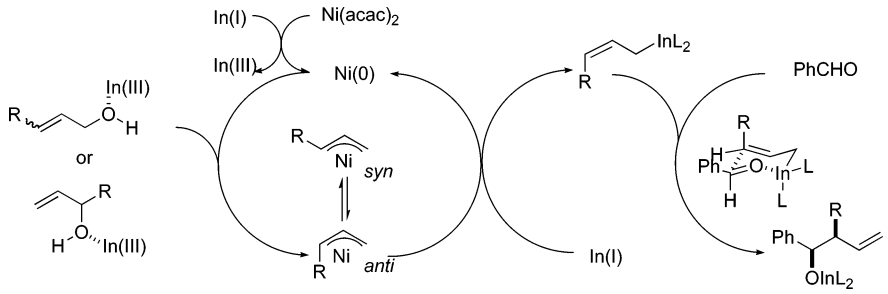
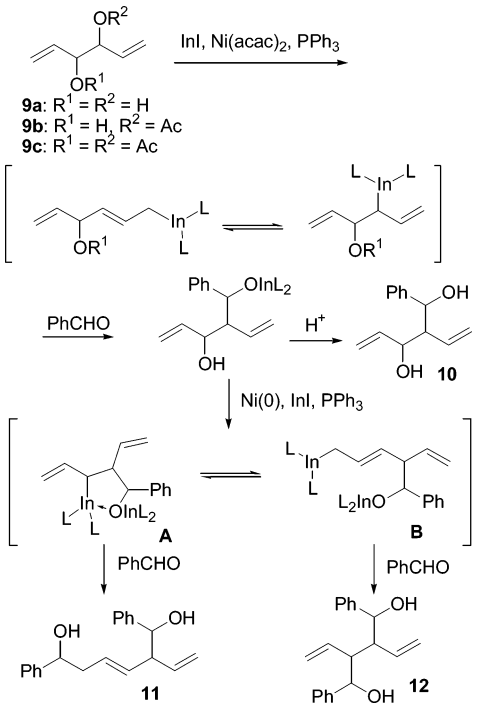
SCHEME 1



SCHEME 2



efficiency of the present Ni-catalyzed allylation with allylic alcohols.

Conclusion

The umpolung of π-allylnickel with InI provides a new route for allylindium reagents by the direct use of allylic alcohols. The high availability of a wide range of allylic alcohols greatly enhances the usefulness of the present Ni-catalyzed reaction. High syn-selectivity is generally observed in the coupling with carbonyl compounds, regardless of the geometry of allylic alcohols. Further applications of this new process are currently underway.

Experimental Section

Typical Experimental Procedure (Table 2, entry 4). To a mixture of $Ni(acac)_2$, prepared by heating $Ni(acac)_2 \cdot 2H_2O$ (7.0 mg, 0.025 mmol) under reduced pressure, PPh_3 (26 mg, 0.1 mmol), and indium(I) iodide (0.24 g, 1.0 mmol) in DMI (1.5 mL) were added allyl alcohol (68 μL, 1.0 mmol) and benzaldehyde (52 μL, 0.50 mmol). The reaction mixture was stirred at room temperature under argon. The reaction was monitored by TLC. After 1.0 h, the benzaldehyde disappeared. Diluted hydrochloric acid (1 N) was added and the product was extracted with ether. The extracts were washed with water and dried over anhydrous sodium sulfate. The solvent was removed, and the residue was separated by chromatography on silica gel (EtOAc:hexane = 1:4) to give 1-phenylbut-3-en-1-ol (**1a**) (71 mg, 96%).

Products **1a**,[9] **1b**,[10] **1c**,[9] **1d**,[4a] **1e**,[11] **1f**,[12] **1h**,[9] **1i**,[9] **1j**,[9] **1k**,[9] **3a**,[9] **3c**,[9] **3i**,[9] **3k**,[9] **4c**,[13] **5c**,[9] **6c**,[14] **7c**,[15] **8a**,[4a] **8c**,[16] and **8k**[17] are all known compounds.

2-Isobutyl-1-phenylbut-3-en-1-ol (1g): ^{1}H NMR (300 MHz, $CDCl_3$) (syn isomer) δ 0.84 (dd, J = 12, 6.6 Hz, 6H), 1.09−1.37 (m, 2H), 1.42−1.67 (m, 1 H), 1.92 (br s, 1H), 2.26−2.61 (m, 1H), 4.60 (d, J = 5.6 Hz, 1H), 5.13−5.30 (m, 2H), 5.38−5.76 (m, 1H), 7.18−7.38 (m, 5H). ^{1}H NMR (300 MHz, $CDCl_3$) (anti isomer) δ 0.76 (dd, J = 18, 6.6 Hz, 6 H), 4.34 (d, J = 7.8 Hz, 1H), 4.96−5.13 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.1, 21.4, 24.0, 24.1 25.4, 38.9, 39.7, 49.3, 50.7, 117.1, 118.4, 126.5, 126.8, 127.1, 127.4, 127.7, 128.0, 138.8, 139.2, 142.1. IR (neat, cm^{-1}) 3400, 1635. Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.15; H, 10.10.

1-Phenyl-4-propylhex-5-en-3-ol (3d): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, J = 6.7 Hz, 3H), 1.12−1.49 (m, 4H), 1.63−1.95 (m, 2H), 1.99−2.20 (m, 1H), 2.55−2.94 (m, 2H), 3.42−3.54 (m, 1H), 5.02−5.20 (m, 2H), 5.47−5.71 (m, 1H), 7.15−7.32 (m, 5H). IR (neat, cm^{-1}) 3400, 1495. Anal. Calcd for $C_{15}H_{22}O$: C, 82.52; H, 10.16. Found: C, 82.28; H, 10.10.

1,2-Diethenyl-3-phenylpropan-1,3-diol (10): ^{1}H NMR (200 MHz, $CDCl_3$) (major isomer) δ 2.28 (br s, 2H), 2.26−2.38 (m, 1H), 4.20−4.29 (m, 1H), 4.90−5.35 (m, 5H), 5.69−6.07 (m, 2H), 7.21−7.35 (m, 5H). ^{1}H NMR (200 MHz, $CDCl_3$) (minor isomer) δ 2.47−2.60 (m, 1H). Elemental analysis was performed on the diacetate. Diacetate of **10**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.02−2.08 (m, 6H), 2.60−2.80 (m, 1H), 4.79−5.28 (m, 4H), 5.63−6.03 (m, 2H). Anal. Calcd for $C_{17}H_{20}O_4$: C,70.81; H, 6.99. Found: C, 71.07; H, 6.94.

2-Ethenyl-1,6-diphenylhex-3-en-1,6-diol (11): ^{1}H NMR (200 MHz, $CDCl_3$) (major isomer) δ 2.20−2.50 (m, 2H), 2.72 (br s, 2H), 2.94−3.08 (m, 1H), 4.37−4.66 (m, 2H), 4.78−5.86 (m, 3H), 7.10−7.38 (m, 10H). ^{1}H NMR (200 MHz, $CDCl_3$) (minor isomer) δ 3.37−3.58 (m, 1H). Elemental analysis was performed on the diacetate. Diacetate of **11**: ^{1}H NMR (200 MHz, $CDCl_3$) (major isomer) δ 2.02−2.06 (m, 6H), 2.42−2.72 (m, 2H), 3.09−3.26 (m, 1H), 4.77−5.20 (m, 2H), 5.22−5.44 (m,

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TABLE 7. Nickel-Catalyzed Reaction of Hexa-1,5-diene-3,4-diol Derivatives[a]

				yield, %, and diastereomeric ratio[b]		
entry	**9** (**9**:PhCHO)	solvent	*t*, h	**10**	**11**	**12**
1	**9a** (1:2)	DMI	3	0	65 (39:17:12:32)	6[c]
2	**9b** (1:3)	DMI	2.5	trace	61 (29:30:21:20)	17 (3:5:55:37)
3[d]	**9b** (1:3)	DMI	20	trace	34 (25:27:26:22)	27 (4:8:75:13)
4	**9b** (1:3)	THF	15	trace	61 (26:17:15:42)	0
5	**9b** (2:1)	DMI	22	84 (1:32:66:1)	0	0
6	**9c** (1:3)	DMI	1.5	0	50 (26:17:13:44)	11 (20:40:25:15)

[a] All reactions were performed on a 0.25-mmol scale of **9** in the presence of $Ni(acac)_2$ (20 mol %) and PPh_3 (80 mol %). [b] Yields and diastereomeric ratios were determined by GC analysis. [c] Diastereomeric ratio was not determined. [d] H_2O (3 mmol) was added.

2H), 5.50−5.81 (m, 3H). ^{1}H NMR (200 MHz, $CDCl_3$) (minor isomer) δ 3.44−3.56 (m, 1H). Anal. Calcd for $C_{24}H_{26}O_4$: C, 76.17; H, 6.92. Found: C, 75.86; H, 7.07.

2,3-Diethenyl-1,4-diphenylbutan-1,4-diol (12): ^{1}H NMR (300 MHz, $CDCl_3$) (major isomer) δ 1.90 (br s, 2H), 2.19 (t, J = 9.0 Hz, 2H), 4.42 (d, J = 9.0 Hz, 2H), 5.15 (dd, J = 17, 1.8 Hz, 2H), 5.41 (dd, J = 10, 1.8 Hz, 2H), 5.93 (dt, J = 17, 10 Hz), 7.03−7.13, 7.24−7.37 (m, 10H). ^{1}H NMR (300 MHz, $CDCl_3$) (minor isomer) δ 2.21 (t, J = 8.0 Hz, 2H), 4.50 (d, J = 8.4 Hz, 2H), 5.52−5.78 (m, 2H). Elemental analysis was performed on the diacetate. Diacetate of **12**: Anal. Calcd for $C_{24}H_{26}O_4$: C, 76.17; H, 6.92. Found: C, 76.04; H, 6.86.

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