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Allylation of Carbonyl Compounds with Catalytic Amount of Indium

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Synopsis. Allylation of aldehyde and ketone, and prenylation of 2-chlorobenzoquinone were achieved by using a combination of a catalytic amount of indim(III) chloride and metallic aluminium or zinc.

We recently reported that organoindium compounds are useful reagents in organic synthesis.[1] In particular, allylic indium sesquihalides, which are readily accessible from indium metal and allyl halides, enable several organic transformations conveniently and highly selectively; i.e. allylation of carbonyl compounds,[2] reduction of allylic halides to 1-propenes,[2c] and synthesis of 1,5-dienes.[3] Although allylation of carbonyl compounds with various allylmetal compounds is known,[4] our indium-based procedure on aldehyde,[2a] ketone,[2a] acid anhydride,[2b] imide,[2c] and quinone[2d] shows some unique features. However, these reactions require stoichiometric amounts of indium. Indium metal and simple indium salts are not very expensive; nevertheless, if the reactions can be done with catalytic amounts of indium, its usefulness and versatility in organic synthesis should markedly be increased.[5] We describe here the allylation of aldehydes and quinones by using catalytic amounts of indium(III) chloride in combination with aluminium or zinc metal.

Results and Discussion

1. Allylation of Aldehyde and Ketone. A mixture of benzaldehyde (2 mmol) and allyl bromide (3.2 mmol) in a tetrahydrofuran (THF)–water mixture was stirred with aluminium powder (3.2 mmol) and indium(III) chloride (0.2 mmol) at room temperature for 50 h. Chromatographic separation yielded 1-pheny-3-buten-1-ol (**1a**) in 88% yield and a small amount (4%) of the starting benzaldehyde was recovered. The reaction did not occur in the absence of indium(III) chloride. Table 1 summarized the results of the influence of the amount of indium(III) chloride on the yield of the product. It shows that 4—6 mol% of the catalyst are sufficient for obtaining the maximum yield. Table 2 lists the results of the indium-catalyzed allylation of aldehydes and ketones under the standard conditions, which show the following features: (i) both aromatic and aliphatic aldehydes gave high yields of the corresponding homoallylic alcohols, whereas ketone gave a lower yield of the product, (ii) α,β-unsaturated aldehyde afforded a 1,2-addition product exclusively, (iii) crotylation of benzaldehyde gave only the γ-addition product, 2-methyl-1-phenyl-3-buten-1-ol (**1f**), the erythro : threo ratio of which was 70 : 30. These features correspond very well to the previously reported allylation mediated by stoichiometric indium,[2a] suggesting that the active species in the present reaction is allylindium and metallic aluminium (or zinc) acts as a reductant for In(III) to In(0). A plausible mechanism is illustrated in Scheme 1.

When the reaction was carried out in anhydrous THF, the yield of **1** dropped to 61%, and 4-phenyl-1,6-heptadien-4-ol (20%) and benzyl alcohol (19%) were

Table 1. Al–$InCl_3$–Mediated Allylation of Benzaldehyde[a)]

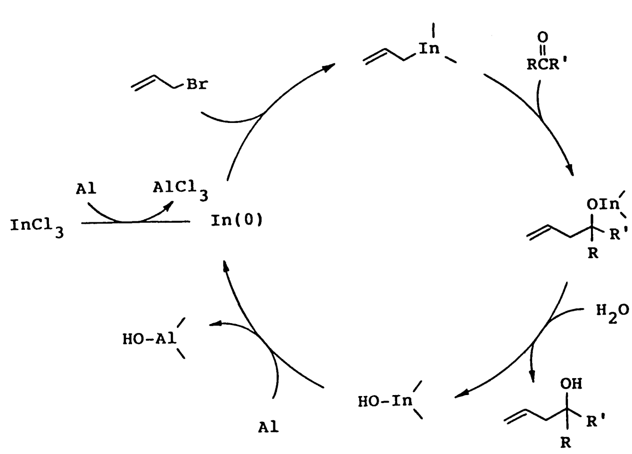
mol% of $InCl_3$[b)]	Yield of 1-phenyl-3-buten-1-ol/%	Recovered benzaldehyde/%
0	0	81
2	12	72
4	82	7
6	91	5
10	88	4
50	94	2
100	93	0

a) Reactions were carried out with benzaldehyde (2 mmol), allyl bromide (3.2 mmol), aluminium (3.2 mmol), and indium(III) chloride in THF–H_2O (5 : 2) at room temperature for 50 h. b) To the amount of benzaldehyde used.

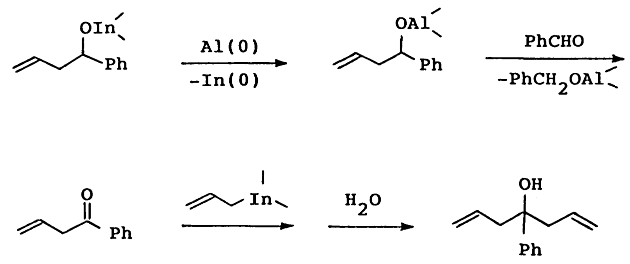
Table 2. Allylation of Carbonyl Compounds by Al–$InCl_3$ or Zn–$InCl_3$[a)]

Allyl bromide	Carbonyl compound	Metal	Product	Yield/%
CH_2=$CHCH_2Br$	PhCHO	Al–$InCl_3$	$PhCH(OH)CH_2CH$=CH_2 (**1a**)	88
CH_2=$CHCH_2Br$	$Me(CH_2)_6CHO$	Al–$InCl_3$	$Me(CH_2)_6CH(OH)CH_2CH$=CH_2 (**1b**)	81
CH_2=$CHCH_2Br$	*p*-$MeOC_6H_4CHO$	Al–$InCl_3$	*p*-$MeOC_6H_4CH(OH)CH_2CH$=CH_2 (**1c**)	81
CH_2=$CHCH_2Br$	PhCH=CHCHO	Al–$InCl_3$	$PhCH$=$CHCH(OH)CH_2CH$=CH_2 (**1d**)	69
CH_2=$CHCH_2Br$	MeCOPh	Al–$InCl_3$	$MeCPh(OH)CH_2CH$=CH_2 (**1e**)	55
$MeCH$=$CHCH_2Br$	PhCHO	Al–$InCl_3$	$PhCH(OH)CH(Me)CH$=CH_2 (**1f**)	72[b)]
CH_2=$CHCH_2Br$	PhCHO	Zn–$InCl_3$	**1a**	67
CH_2=$CHCH_2Br$	$Me(CH_2)_6CHO$	Zn–$InCl_3$	**1b**	82

a) Reactions were carried out with carbonyl compound (2 mmol), allylic bromide (3.2 mmol), Al (or Zn) (3.2 mmol), and $InCl_3$ (0.2 mmol) in THF–H_2O (5 : 2) at room temperature for 50 h.
b) Erythro : threo ratio=70 : 30.



Scheme 1.



Scheme 2.

formed in addition. The formation of these by-products could be rationalized by Scheme 2. Indium(III) 1-phenyl-3-buten-1-olate, resulting from allylindium and benzaldehyde, is considered to be reduced by aluminium metal to give the corresponding aluminium(III) alcoholate and In(0). Meerwein–Ponndorf reduction of benzaldehyde with the aluminium alcoholate gives aluminium benzylate and 1-phenyl-3-buten-1-one, which is further allylated to furnish 4-phenyl-1,6-heptadien-4-ol.

2. **Prenylation of 2-Chloronaphthoquinone.** As we reported, the reaction of 2-chloronaphthoquinone with prenylindium sesquibromide in *N,N*-dimethylformamide (DMF) gave 2-prenyl-1,4-naphthoquinone (**2**) and 2,3-dihydro-2,2-diprenyl-1,4-naphthalenedione (**3**) in 53% and 37% yield, respectively. On the other hand, zinc-mediated prenylation of the same quinone in THF gave chlorine-containing products, 2-chloro-3-prenyl-1,4-naphthoquinone (**4**) and 2,3-dihydro-3-chloro-2,2-diprenyl-1,4-naphthalenedione (**5**).[6] Therefore, the prenylation of 2-chlorobenzoquinone with Zn–InCl$_3$ is considered to be a suitable probe for determining whether the active species of this indium-catalyzed reaction is prenylindium or prenylzinc. Results in two different solvent systems (dry THF and THF–H$_2$O) are summarized in Table 3. In dry THF, indium-mediated reaction gave **2** and **3**, in good accord with the reaction in DMF.[2d] With Zn–InCl$_3$ a product mixture of four possible compounds (**2**—**5**) was obtained; indicating that the prenylation proceeded via both prenylindium and prenylzinc in this medium. In THF–H$_2$O, InCl$_3$-catalyzed reaction gave **2** and **3**, but with zinc alone no reaction occurred. This shows that in the indium-catalyzed prenylation, the quinone was prenylated only by prenylindium and zinc metal is considered to serve to regenerate In(0) species from In(III); prenylzinc, which is more basic than prenylindium, is probably not tolerable with water in the solvent.

Table 3. Prenylation of 2-Chloro-1,4-naphthoquinone[a]

Metal	Solvent	Product (yield/%)
In	THF	**2**(26), **3**(4)
Zn	THF	**4**(34), **5**(7)
Zn–InCl$_3$[b]	THF	**2**(29), **3**(10), **4**(24), **5**(3)
Zn	THF–H$_2$O[c]	No reaction
Zn–InCl$_3$[b]	THF–H$_2$O[c]	**2**(32), **3**(14)

a) Reactions were carried out with the quinone (2 mmol), prenyl bromide (3 mmol), and metal (3.2 mmol) at room temperature for 4 h. b) Zn (3.2 mmol) and InCl$_3$ (0.2 mmol) were used. c) THF : H$_2$O=5 : 2.

In summary, by using the bimetallic system (Al–InCl$_3$ or Zn–InCl$_3$) allylic indium species were found to allylate carbonyl compounds catalytically. In these reactions, solvent system is important; the presence of water is effective to suppress undesired side reactions.

Experimental

General. Mass spectra (MS) were recorded on a Hitachi M-2000 instrument with electron impact ionization at 70 eV using a direct inlet system. Infrared (IR) spectra were recorded on a JASCO A-102 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were obtained for solutions in CDCl$_3$ on a Hitachi R-90 (90 MHz) and Varian XL-200 (50 MHz) spectrometers, respectively, with Me$_4$Si as internal standard. All chemicals used in this work were purchased from Nacalai Tesque Co., Ltd.

Allylation of Carbonyl Compounds with Al(or Zn)–InCl$_3$. The following allylation of benzaldehyde represents the typical procedure. To a mixture of aluminium powder (86 mg, 3.2 mmol) and indium(III) chloride (44 mg, 0.2 mmol) in THF (5 ml)–water (2 ml), were added allyl bromide (387 mg, 3.2 mmol) and benzaldehyde (212 mg, 2 mmol). The mixture was stirred at room temperature for 50 h under argon. The reaction was quenched with dilute hydrochloric acid, and the product was extracted with ether. The extracts were dried over anhydrous Na$_2$SO$_4$ and the solvent was removed under reduced pressure. The residue was subjected to column chromatography (silica gel, CH$_2$Cl$_2$) to give 1-phenyl-3-buten-1-ol (**1a**) (259 mg, 88%) and benzaldehyde (8.5 mg, 4%).

Other carbonyl compounds were similarly allylated, and the structures of the products (**1a**—**f**) were deduced by comparison of their spectral data (^{1}H NMR and IR) with those of the authentic samples.[2a,5] When benzaldehyde was allylated in anhydrous THF, were obtained **1a** (61% yield), benzyl alcohol (19%), and 4-phenyl-1,6-heptadien-4-ol[7] (20%): Colorless oil; MS (rel. intensity): *m/z* 189 (M$^+$, 1), 171 (M$^+$−H$_2$O, 18), 148 (76), 126 (70), 78 (100); IR (neat, cm^{-1}) 3500, 3023, 2880, 2805, 1622, 1421, 1320, 1016, 985, 902, 668; ^{1}H NMR δ=2.17 (s, 1H, OH), 2.36—2.82 (m, 4H, CH$_2$), 5.06 (d, J=9 Hz, 2H, olefinic H), 5.07 (d, J=17 Hz, 2H, olefinic H), 5.41—5.87 (m, 2H, olefinic H), and 7.14—7.45 (m, 5H, Ph); ^{13}C NMR δ=46.8 (t), 75.2 (s), 119.4 (t), 125.6 (d), 126.8 (d), 128.2 (d), 133.7 (d), 146.1 (s).

Reactions of 2-Chloro-1,4-naphthoquinone with Prenyl Bromide. The following reaction with Zn–InCl$_3$ in anhydrous THF is representative. To a mixture of zinc powder (209 mg, 3.2 mmol), indium(III) chloride (44 mg, 0.2 mmol) and 2-chloro-1,4-naphthoquinone (385 mg, 2 mmol) in THF (5 ml), was added prenyl bromide (447 mg, 3 mmol). The mixture was stirred at room temperature for 4 h under argon. The reaction was quenched by the addition of dil hydrochloric acid and the products were extreacted with ether. The extracts were dried (Na_2SO_4) and the solvent was evaporated. The residue was chromatographed on silica gel (pentane:CH_2Cl_2=1:1) to give products **2** (129 mg, 29%), **3** (60 mg, 10%), **4** (124 mg, 24%), and **5** (15 mg, 3%). These compounds are known,[2d,6] and were identified by their spectral data.

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