

Allylation of Alcohols and Carboxylic Acids with Allyl Acetate Catalyzed by $[\text{Ir}(\text{cod})_2]^+\text{BF}_4^-$ Complex

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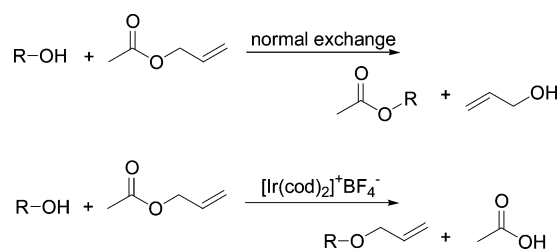
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A facile method for the synthesis of allyl alkyl ethers from alcohols with allyl acetate was developed by the use of $[\text{Ir}(\text{cod})_2]^+\text{BF}_4^-$ complex. For instance, the reaction of allyl acetate with *n*-octyl alcohol in the presence of a catalytic amount of $[\text{Ir}(\text{cod})_2]^+\text{BF}_4^-$ complex afforded allyl octyl ether in quantitative yield. Allyl carboxylates were also prepared by the exchange reaction between carboxylic acids and allyl acetate in good yields. The $[\text{Ir}(\text{cod})_2]^+\text{BF}_4^-$ complex catalyzed the reaction of alkyl and aromatic amines with allyl acetate to lead to the corresponding allylamines in fair to good yields.

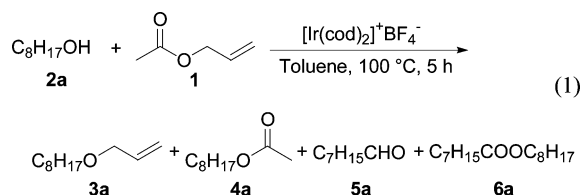
Allyl ethers are frequently used important compounds as monomers for the production of polymer materials and as starting materials for Claisen rearrangement.¹ A variety of methods have been developed for the synthesis of allyl ether using palladium complexes,² but only a limited number of papers have appeared for the synthesis of allyl ethers from allylic acetates and simple alcohols.³ It is because the normal exchange reaction between allyl acetate and alcohols except for phenols affords an equilibrium mixture of allyl alcohols and alkyl acetate, and no allyl ethers are formed (Scheme 1). Takeuchi et al. have reported allylic alkylation and allylic amination by Ir complexes;⁴ however, the allylation of alcohols with allyl acetate by Ir complexes has not yet been performed so far.

SCHEME 1



Recently, we have reported that $[\text{IrCl}(\text{cod})]_2$ complex catalyzes a very unique exchange reaction between vinyl acetate and alcohols, which provides useful vinylation method of a wide variety of vinyl ethers,⁵ but this catalytic system does not promote the allylation of alcohols with allyl acetate. In continuation of our study to develop a facile method for allyl ether synthesis using Ir complexes, we found that an iridium cation complex, $[\text{Ir}(\text{cod})_2]^+\text{BF}_4^-$, catalyzes the allylation of alcohols with allyl acetate. This method appears to provide an alternative facile synthetic method for allyl ethers using ally acetate as allylic source.

To confirm an optimum reaction condition for allylation of alcohols (**2**) with allyl acetate (**1**), the reaction of 1-octanol (**2a**) with **1** was chosen as a model reaction and allowed to react under various conditions using several iridium complexes (eq 1 and Table 1).



A stoichiometric reaction of **1** with **2a** afforded allyl octyl ether (**3a**) (23%), octyl acetate (**4a**) (1%), octanal (**5a**)

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TABLE 1. Reaction of **2a** with **1** Catalyzed by $[\text{Ir}(\text{cod})_2]^+\text{BF}_4^-$ ^a

run	1 (equiv)	conv (%)		yield (%)			
		2a	1	3a	4a	5a	6a
1	1	84	76	23	1	1	16
2	2	87	50	56	1	1	11
3	5	96	24	86	4	4	2
4	10	>99	27	99	n.d.	n.d.	n.d.
5 ^b	10	5	3	trace	n.d.	n.d.	n.d.
6 ^c	10	3	1	n.d.	1	n.d.	n.d.
7 ^d	10	19	11	7	11	n.d.	n.d.
8 ^e	10	99	21	4	13	n.d.	74
9 ^f	10	49	15	27	trace	n.d.	n.d.

^a **2a** (1 mmol) was allowed to react with **1** in the presence of $[\text{Ir}(\text{cod})_2]^+\text{BF}_4^-$ (0.01 mmol) in toluene (1 mL) at 100 °C for 5 h. ^b $[\text{IrCl}(\text{cod})_2]$ (0.01 mmol) was used as a catalyst. ^c $[\text{IrCl}(\text{CO})(\text{P}-\text{Ph}_3)_2]$ (0.01 mmol) was used as a catalyst. ^d $[\text{Rh}(\text{cod})_2]^+\text{BF}_4^-$ (0.01 mmol) was used as a catalyst. ^e Na_2CO_3 (0.03 mmol) was added. ^f At 90 °C.

(1%), and octyl octanoate (**6a**) (16%) which is thought to be formed through the Tishchenko-type reaction of the resulting aldehyde **5a** (run 1). The reaction of a 1:2 mixture of **2a** and **1** afforded **3a** in 56% yield and Tishchenko product **6a** (11%), but the yields of **4a** and **5a** were the same as those of the stoichiometric reaction (run 2). Previously, we reported that Ir complexes such as $[\text{IrCl}(\text{cod})_2]$ catalyzes the hydrogen transfer reaction of α,β -unsaturated ketones with alcohols to form saturated ketones rather than allylic alcohols.⁶ This shows that alkenes serve as a good hydrogen acceptor from alcohols. In the present reaction, it is probable that allyl acetate **1** was hydrogenated to propyl acetate by an Ir-dihydride complex which is formed as a transient intermediate in the course of the reaction. To depress the formation of aldehyde **5a**, the reaction must be carried out in the presence of excess **1** toward alcohol **2a**. The reaction of **2a** with **1** (5 equiv) under the influence of $[\text{Ir}(\text{cod})_2]^+\text{BF}_4^-$ (1 mol %) in toluene at 100 °C for 5 h afforded allyl octyl ether (**3a**) (86%) along with small amounts of octyl acetate (**4a**) (4%), octanal (**5a**) (4%), and octyl octanoate (**6a**) (2%) (run 3). When **1** (10 equiv) toward alcohol **2a** was employed, **3a** was obtained in almost quantitative yield (>99%) (run 4). It is interesting to note that $[\text{Ir}(\text{cod})_2]^+\text{BF}_4^-$ catalyst promotes the allylation rather than the usual ester exchange reaction, since esters react usually with alcohols to form ester exchange products (Scheme 1).

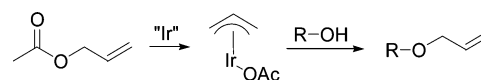
Under the same conditions, however, $[\text{IrCl}(\text{cod})_2]$ did not promote the present allylation at all (run 5). Similarly, $[\text{IrClCO}(\text{PPh}_3)_2]$ was inert for the allylation of **2a** with **1** (run 6). It is known that the cationic complex is more active than the neutral one, since the coordination of the cationic complex to the substrate smoothly takes place compared with the neutral complex.⁷ It was found

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SCHEME 2

that $[\text{Rh}(\text{cod})_2]^+\text{BF}_4^-$ promotes the normal ester exchange reaction between **1** and **2a** rather than the allylation to give **4a** (11%) in preference to **3a** (7%) (run 7). It was found that **6a** was obtained in good yield (74%) when a small amount of Na_2CO_3 (3 mol %) was added to the catalytic solution involving $[\text{Ir}(\text{cod})_2]^+\text{BF}_4^-$. The reaction at 90 °C resulted in a considerable decrease of allyl ether **3a** (run 9). This shows that the present allylation calls for higher temperature than 90 °C. The reaction seem to proceed through the formation of π -allyl iridium complex, followed by nucleophilic attack of alcohol (Scheme 2).

On the basis of these results, a variety of alcohols were allowed to react with **1** under the same conditions as run 4 in Table 1. These results are shown in Table 2.

Like **2a**, primary alcohol 1-butanol (**2b**) reacted smoothly with **1** under these conditions to form allyl butyl ether (**3b**) in excellent yield (98%) (run 1). However, secondary and tertiary alcohols such as 2-octanol (**2c**) and 1-adamantanol (**2d**) are less reactive than primary alcohols. As a result, although the reaction must be prolonged from 5 h for primary alcohols to 15 or 20 h for secondary and tertiary alcohols, **2c** and **2d** afforded the corresponding allyl ethers **3c** and **3d** in 85 and 62% yields along with 2-octanone (8%) and 1-adamantyl acetate (9%), respectively, as side products (runs 2 and 3). Benzyl alcohol (**2e**) gave allyl benzyl ether (**3e**) in 82% yield (run 4).

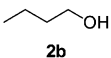
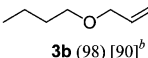
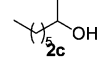
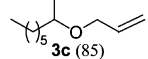

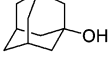
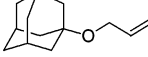
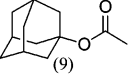
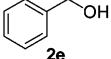
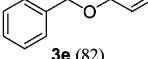
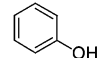
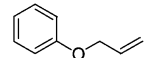
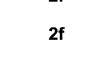
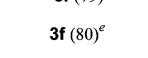
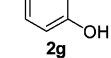
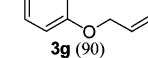
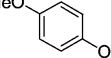
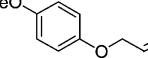

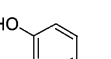
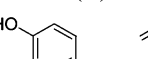
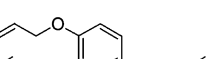
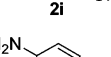
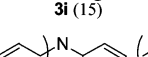
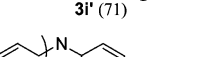
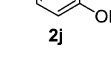
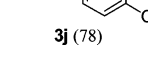
We next tried the reaction of various phenols with **1** (runs 5–10). Phenol (**2f**) reacted with **1** at 100 °C to form allyl phenyl ether (**3f**) in 79% yield, but the same reaction at 120 °C produced **3f** (80%) and Claisen rearrangement product *o*-allylphenol (8%) (runs 5 and 6). *p*-Cresol (**2g**) and *p*-methoxyphenol (**2h**) were also allylated with **1** in almost the same extent to form the corresponding allyl ethers **3g** and **3h** (runs 7 and 8). Under these conditions, hydroquinone (**2i**) afforded a mixture of mono- and diallylated products **3i** and **3i'** in fair yields (run 9). In the reaction of *p*-aminophenol (**2j**), the amino group was preferentially allylated rather than phenolic one to lead to *p*-diallylaminophenol (**3j**) and allyl *p*-diallylamino-phenyl ether (**3j'**) (run 10). In a similar manner as **2j**, *p*-hydroxybenzoic acid (**2k**) was allylated with **1** to give double-allylated product (**3k'**) along with a small amount of monoallylated products (**3k**) (run 11). This shows that the allylation of the carboxyl group in **2k** takes place more easily than that of the hydroxyl one.

It is interesting to note that 1-hexanethiol (**2l**) was smoothly allylated by the use of $[\text{Ir}(\text{cod})_2]^+\text{BF}_4^-$ (1 mol %) at 100 °C, since thiols easily coordinate to transition metal complexes such as Pd to prevent their catalysis (run 12). This is the first successful allylation catalyzed by iridium complex.⁸

Table 3 shows the results for the preparation of allyl carboxylates by the exchange reaction of carboxylic acids with **1** by the same catalytic system. It was found that the reaction of carboxylic acids with **1** takes place more easily than that of alcohols allyl acetates in good yields.

The exchange reaction between aliphatic carboxylic acids such as heptanoic acid (**7a**) or 2-ethylhexanoic acid

TABLE 2. Reaction of Alcohols and Thiols with **1** Catalyzed by $[\text{Ir}(\text{cod})_2]^+\text{BF}_4^-$ ^a

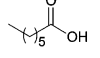
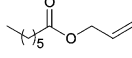
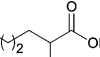
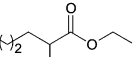
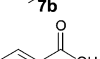
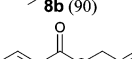
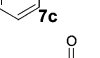
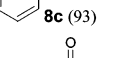
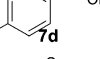
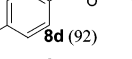
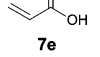
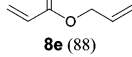
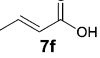
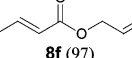
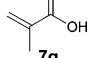
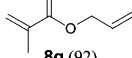
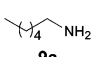
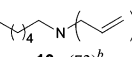
Run	Substrate	Time, Conv. (h, %)	Product (Yield / %)
1		5, 99	 3b (98) [90] ^b
2		15, 94	 3c (85) 
3 ^c		20, 71	 3d (62) 
4		10, 99	 3e (82)
5 ^c		20, 82	 3f (79)
6 ^{c,d}	2f	20, 95	3f (80) ^e
7 ^c		15, 92	 3g (90)
8 ^c		18, 98	 3h (93)
9 ^{c,d}		20, 99	 3i (15)  3i' (71)
10 ^e		15, 99	 3j (78)  3j' (18)
11 ^{c,d}		15, 99	 3k (6)  3k' (88)
12		24, 92	 3l (89) ^f

^a Reaction was run under the same conditions as shown in Table 1, run 4. ^b Isolated yield. ^c $[\text{Ir}(\text{cod})_2]^+\text{BF}_4^-$ (0.02 mmol) was used. ^d At 120 °C, and octane (1 mL) was used as a solvent. ^e *o*-Allylphenol (8%) was produced. ^f NMR yield.

(**7b**) and **1** (5 equiv) under the influence of $[\text{Ir}(\text{cod})_2]^+\text{BF}_4^-$ (1 mol %) afforded allyl heptanoate (**8a**) and 2-ethylhexanoic acid (**8b**) in good yields (runs 1 and 2). Benzoic acid (**7c**) and *p*-toluic acid (**7d**) afforded the corresponding allyl carboxylates, **8c** (93%) and **8d** (92%) (runs 3 and 4). α,β -Unsaturated carboxylic acids, like **7e**, **7f**, and **7g**, led to allyl esters, **8e**, **8f** and **8g**, in good yields, respectively (Runs 5–7).

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TABLE 3. Reaction of Carboxylic Acids and Amines with **1** Catalyzed by $[\text{Ir}(\text{cod})_2]^+\text{BF}_4^-$ ^a

Run	Substrate	Time Conv. (%)	Product (Yield)
1		5 96	 8a (90)
2		5 95	 8b (90)
3		5 99	 8c (93)
4		5 99	 8d (92)
5		5 91	 8e (88)
6		5 99	 8f (97)
7		5 93	 8g (92)
8		5 99	 10a (73) ^b
9		5 99	 10b (95)

^a Substrate (1 mmol) was allowed to react with **1** (5 mmol) in the presence of $[\text{Ir}(\text{cod})_2]^+\text{BF}_4^-$ (0.01 mmol) in toluene (1 mL) at 100 °C. ^b *N*-Hexylacetamide (**11a**) (20%) was produced.

Under the same conditions, an alkylamine such as hexylamine (**9a**) was also subjected to allylation with **1**, leading to diallylhexylamine (**10a**) (73%) and *N*-hexylacetamide (**11a**) (20%) which is formed by the noncatalytic reaction of **10a** with **1** (run 8). But, the aromatic amine, aniline (**9b**), reacted with **1** to give diallyl aniline (**10b**) in high selectivity without formation of amide (run 9).

In summary, we have developed a synthetic method for allyl ethers by the use of $[\text{Ir}(\text{cod})_2]^+\text{BF}_4^-$ complex using allyl acetate as allylic source. In addition, transallylation between carboxylic acid and allyl acetate was realized in good yields using the same system. Further studies for the optimization of the reaction conditions as well as for the reaction pathway are now in progress.

Experimental Section

All starting materials were commercially available and used without any purification. GLC analysis was performed with a flame ionization detector using a 0.2 mm × 25 m capillary column (OV-1). ¹H and ¹³C NMR were measured at 270 and 67.5 MHz, respectively, in CDCl₃ with Me₄Si as the internal standard.

Typical Reaction Procedure. To a mixture of $[\text{Ir}(\text{cod})_2]-\text{BF}_4$ (0.01 mmol) and toluene (1 mL) were added substrate (1 mmol) and **1** (10 mmol) under Ar. The reaction mixture was stirred at 100 °C for 5 h. The conversions and yields of products were estimated from the peak areas based on the internal

standard technique using GC. The products **3c**,⁹ **3d**,¹⁰ **3i**,¹¹ **3k**,¹² **3k'**,¹³ **3l**,¹⁴ **8b**,¹⁵ **8d**,¹⁶ and **10a**¹⁷ were reported previously. Compounds **3b**, **3e**, **3f**, **3g**, **3h**, **3i'**, **8a**, **8c**, **8e**, **8f**, **8g**, and **10b** were commercially available.

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