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Preliminary communication

Ruthenium complex catalyzed allylation of aldehydes with allylic acetates

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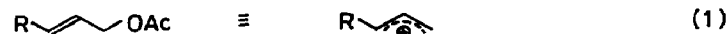
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Abstract

Ruthenium complexes such as $\text{Ru}_3(\text{CO})_{12}$ and $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ show high catalytic activity in the allylation of aldehydes by allylic acetates at 120°C to give homoallylic alcohols in good yields.

Extensive studies have been made on the π -allyl complexes [1], since they are often key intermediates in various homogeneous catalytic reactions [2]. In particular the palladium catalyzed allylation with allylic compounds represented by allylic acetates has been successfully applied to synthetic organic chemistry [3*]. In this process, the allylic acetates can be regarded as allylic cation synthons (eq. 1), which can react with nucleophiles.



Recently, more attention has been paid to the umpolung [4] of these electrophilic π -allylpalladium intermediates. Inanaga et al. [5] and Masuyama et al. [6] reported palladium-catalyzed allylation reaction of aldehydes and ketones with allylic acetates [5,6a] and alcohols [6b]. However, these reactions require a stoichiometric amount of SmI_2 [5] or SnCl_2 [6] to generate nucleophilic allylic species. Trost et al. reported the formation of a conjugated diene, and they claimed that the π -allylpalladium intermediate acted as a nucleophile rather than playing its normal role as an electrophile [7].

In the course of our study on ruthenium-catalyzed activation of formyl functionalities [8], we discovered a novel ruthenium catalysis in which allyl acetates react with aldehydes to give homoallylic alcohols (eq. 2). Noteworthy is that the reaction proceeds without the aid of additional metal compounds [5,6].

* Reference number with asterisk indicates a note in the list of references.

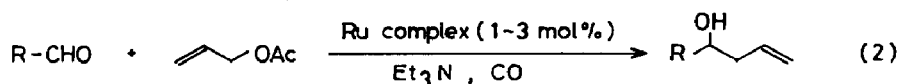
Table 1

Ruthenium complex catalyzed allylation of aldehydes with allylic compounds ^a

Run	Aldehyde	Allylic compound	Product	Yield (%) ^b
1	C ₆ H ₅ CHO	CH ₂ =CHCH ₂ OAc	C ₆ H ₅ CH(OH)CH ₂ CH=CH ₂	87
2	CH ₃ (CH ₂) ₅ CHO	CH ₂ =CHCH ₂ OAc	CH ₃ (CH ₂) ₅ CH(OH)CH ₂ CH=CH ₂	57
3	C ₆ H ₅ CH=CHCHO	CH ₂ =CHCH ₂ OAc	C ₆ H ₅ CH=CHCH(OH)CH ₂ CH=CH ₂	48
4	C ₆ H ₅ CHO	CH ₂ =CHCH(CH ₃)OAc	C ₆ H ₅ CH(OH)CH(CH ₃)CH=CH ₂	84
5 ^c	C ₆ H ₅ CHO	CH ₃ CH=CHCH ₂ OAc	C ₆ H ₅ CH(OH)CH(CH ₃)CH=CH ₂	64
6	C ₆ H ₅ CHO	CH ₂ =CHCH ₂ OCO ₂ CH ₃	C ₆ H ₅ CH(OH)CH ₂ CH=CH ₂	39
7	C ₆ H ₅ CHO	CH ₂ =CHCH ₂ Br	C ₆ H ₅ CH(OH)CH ₂ CH=CH ₂	38
8	C ₆ H ₅ CHO	CH ₂ =CHCH ₂ OH	—	0
9 ^d	C ₆ H ₅ CHO	CH ₂ =CHCH ₂ OAc	C ₆ H ₅ CH(OH)CH ₂ CH=CH ₂	91

^a Aldehyde (10 mmol), allylic compound (3.3 mmol), triethylamine (10 mmol), Ru₃(CO)₁₂ (0.033 mmol) and THF (8.0 ml) at 120 °C for 24 h under 10 kg cm⁻² of initial carbon monoxide pressure.

^b Determined by GLC based on the amount of allylic acetate charged. ^c At 140 °C. ^d RuCl₃·*n*H₂O (0.10 mmol) in place of Ru₃(CO)₁₂.



Aromatic, aliphatic, and α,β -unsaturated aldehydes are smoothly allylated with allylic acetates in good yields in the presence of a catalytic amount of Ru₃(CO)₁₂ (Table 1). When cinnamaldehyde was treated with allyl acetate, only the 1,2-addition product was obtained (run 3). 1-Methylallyl acetate and (*E*)-crotyl acetate gave a single regio- and the same diastereo- (*erythro*/*threo* 4/6) mixture as product (runs 4,5), indicating that the reaction proceeds via a π -allylruthenium [9] intermediate. The competitive allylation of benzaldehyde and acetophenone gave only the corresponding secondary homoallylic alcohol from benzaldehyde in 73% yield, while acetophenone was recovered in 80% yield.

Carbon monoxide was essential to the catalytic activity, and under an argon atmosphere, the reaction did not occur at all. Addition of base was also indispensable. Of the organic bases, triethylamine was most effective. Other tertiary amines such as *N*-methylpyrrolidine and tributylamine can be used. However, *N,N*-dimethylaniline, pyridine and K₂CO₃ were ineffective. The Effect of leaving groups of the allylic compounds was examined. Allyl carbonate and allyl bromide did not give high yields (runs 6 and 7). On the other hand, allyl alcohol [6b] did not react at all under the present reaction conditions (run 8).

In contrast to Ru(COD)(COT) or Ru(CO)₃(PPh₃)₂, RuCl₃·*n*H₂O also showed high catalytic activity (run 9). When RuCl₃·*n*H₂O was employed as the catalyst, RuCl·*n*H₂O was reduced to a ruthenium carbonyl species after the reaction, judging from FT-IR absorptions at 2020, 1968, and 1935 cm⁻¹. Under an argon atmosphere with RuCl₃·*n*H₂O, no carbonyl species was detected and the allylation reaction did not take place. Thus, the real catalyst species would be a low-valent ruthenium carbonyl, which is possibly anionic [10*]. Carbon monoxide pressure may be essential to stabilize such species.

The hydrogen source for the products is probably triethylamine, because it is well known that ruthenium [11] and other transition metal [12] complexes have high

catalytic ability in the transfer of hydrogen from amines under similar reaction conditions. Formally, this allylation reaction can be regarded as a catalytic umpolung of the π -allylruthenium intermediate. Further mechanistic studies, including the characterization of active catalyst species, are in progress.

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