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Ruthenium-catalyzed carbonylation of allene: direct synthesis of methacrylates and methacrylamides

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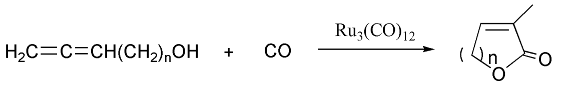
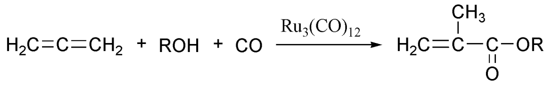
Carbonylation reactions of allene in alcohols and amines in the presence of a ruthenium carbonyl catalyst under mild conditions gave methacrylates and methacrylamides, respectively, in good yields with an atom economy of 100%.

Carbonylations of unsaturated hydrocarbons have provided practical methods for the production of a variety of carbonyl compounds such as aldehydes and carboxylic acid derivatives.[1] There is still continuous interest in the development of new carbonylation systems in both academic and industrial fields. The development is essentially dependent on finding new metal catalysts effective for carbonylations. It is well known that group 9 metals such as cobalt and rhodium show efficient catalytic activities towards several types of carbonylation reactions of alkenes and alkynes.[2,3] On the other hand, few carbonylations of 1,2-alkadienes (allenes) are known,[4–6] although there are many reports on transformation reactions of allene catalyzed by group 10 metals such as nickel and palladium.[6,7] Recently we reported a new type of carbonylation in which a ruthenium complex acts as an effective catalyst for cyclocarbonylation of allenyl alcohols giving lactones (eqn. (1)).[8] Now we have found a new ruthenium-catalyzed alkoxycarbonylation of allene which gives methacrylates in a high yield with an atom economy of 100% (eqn. (2)).



(1)



$$H_2C{=}C{=}CH_2 + ROH + CO \xrightarrow{Ru_3(CO)_{12}} H_2C{=}C(CH_3){-}C({=}O){-}OR \qquad (2)$$

R = Me, Et, ${}^{n}Bu$, ${}^{t}Bu$, Bz etc.

1

Poly(methacrylate)s are one of the common polymers which have a wide range of applications. Practical syntheses of the monomer, alkyl methacrylates, have been extensively studied, and nowadays in industry methacrylates are produced mainly by three methods[4] consisting of several tansformation steps which involve oxidation and condensation with undesirable formation of wastes. One might expect the alkoxycarbonylation of allene to give methacrylates directly. Indeed, several efforts have been made so far to find effective catalysts for the direct synthesis of methacrylates from allene. The first carbonylation of allene was reported by Jenner and Lindsey[5a] using a Pt–Sn binary catalyst in 1959, however it needs extremely severe reaction conditions. Mori and Tsuji[5b] in 1972 and Grigg *et al.*[6] recently reported the syntheses of methacrylates by $Fe(CO)_5$- and Pd-catalyzed carbonylations, respectively, of allene. The former system, however, showed a low activity for the carbonylation and the latter is limited to the synthesis of aryl methacrylates such as phenyl and naphthyl methacrylates. Now we have successfully applied our ruthenium system, which is active towards the cyclocarbonylation of allenyl alcohols as mentioned above, to intermolecular alkoxycarbonylation of allene giving directly methacrylates. Thus, allene was reacted with carbon monoxide (15 atm) in the presence of a catalytic amount of $Ru_3(CO)_{12}$ in ethanol at 100 °C for 3 h to give ethyl methacrylate **1** (R = Et, EMA) in 88% yield (eqn. (2)).† Polymeric products were not detected at all.[9] Reactions at higher (120 °C) or lower (80 °C) temperature resulted in a decrease in the yield of EMA. Use of solvents such as THF and dioxane also decreased the yield. $Co_2(CO)_8$ and $Rh_6(CO)_{16}$ catalysts did not give EMA under the same reaction conditions, but instead led to the formation of oligo- and poly-ketones.[9] $RuCl_3$ itself showed a moderate activity and using tertiary amine additives such as Et_3N and α-picoline improved the yield of EMA to *ca.* 70%, suggesting ruthenium catalysts to exhibit a distinctive activity towards the present alkoxycarbonylation of allene.

We examined the scope of the present carbonylation of allene with respect to alcohols and the results obtained are summarized in Table 1. Reactions in methanol, butanol and 2-ethylhexanol afforded corresponding the methacrylates in a good yield, while use of *tert*-butyl and benzyl alcohols gave a lower yield of methacrylates (entries 4 and 6). Increase of carbon monoxide pressure improved the efficiency of the carbonylation and the reaction in benzyl alcohol under a CO pressure of 30 atm at 80 °C gave benzyl methacrylate in 73% yield. Phenol did not give the corresponding methacrylate under the same reaction conditions,[6] while 1,2-addition product **2** was formed as a major product (40% yield). Diols like ethylene glycol gave the

Table 1 Carbonylation of allene in alcohols or amines[a]

Entry	Alcohol or amine	Product	Yield[c] (%)
1	MeOH	CH_2=C(Me)–COOMe	84
2	EtOH	CH_2=C(Me)–COOEt	88 (71)[d]
3	BuOH	CH_2=C(Me)–COOBu	57
4	^{t}BuOH	CH_2=C(Me)–COO^{t}Bu	27 (36)[e]
5	$Me(CH_2)_3CH(Et)CH_2OH$	CH_2=C(Me)–$COOCH_2CH(Et)(CH_2)_3Me$	73
6	$PhCH_2OH$	CH_2=C(Me)–$COOCH_2Ph$	27 (73)[e]
7	$HOCH_2CH_2OEt$	CH_2=C(Me)–$COOCH_2CH_2OEt$	80
8	$HNEt_2$[b]	CH_2=C(Me)–$CONEt_2$	80
9	$HNBu_2$[b]	CH_2=C(Me)–$CONBu_2$	89 (68)[d]
10	$H_2N(CH_2)_3NMe_2$[b]	CH_2=C(Me)–$COHN(CH_2)_3NMe_2$	10[f]

[a] *Reaction conditions*: allene 9 mmol; $Ru_3(CO)_{12}$ 0.063 mmol; alcohol 15 ml; CO 15 atm; 100 °C; 3 h. [b] *Reaction conditions*: allene 3.4 mmol; $Ru_3(CO)_{12}$ 0.014 mmol; amine 1.5 mmol; dioxane 15 ml; CO 13 atm; 100 °C; 18 h. [c] GC analysis. [d] Isolated yield. [e] CO 30 atm; 80 °C; 5 h. [f] A complex mixture of products.

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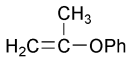
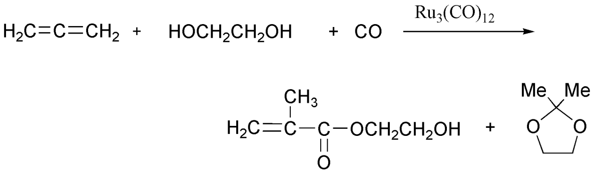


$H_2C{=}C(CH_3){-}OPh$

2

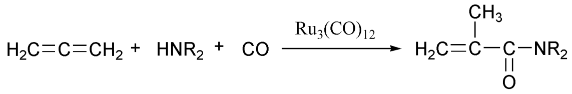
corresponding methacrylate, in which one of two hydroxyl groups remained free, in 8% yield along with uncarbonylated **3** as the major product (52% yield) (eqn. (3)).



$H_2C{=}C{=}CH_2 + HOCH_2CH_2OH + CO \xrightarrow{Ru_3(CO)_{12}} H_2C{=}C(CH_3){-}C({=}O){-}OCH_2CH_2OH + $ (3)

1 **3**

Interestingly, the present catalytic system is also active for the aminocarbonylation of allene yielding methacrylamides (eqn. (4)). Secondary amines gave methacrylamides in a good yield, but use of primary amines gave methacrylamides in a low yield along with several unidentified products (Table 1, entries 8–10).



$$H_2C{=}C{=}CH_2 + HNR_2 + CO \xrightarrow{Ru_3(CO)_{12}} H_2C{=}C(CH_3){-}C({=}O){-}NR_2 \qquad (4)$$

4

Methylacetylene, which is an isomer of allene and is carbonylated by the catalysis of palladium and platinum,[4,10] did not undergo carbonylation in the present catalytic system.

In summary, we have shown that ruthenium carbonyl effectively catalyzes intermolecular alkoxy- and amino-carbonylation of allene under mild conditions, which may provide a new simple and effective method for the production of a variety of methacrylates and methacrylamides directly from allene with an atom economy 100%.

Notes and references

† Carbonylation reactions were performed in a 100 ml stainless steel autoclave equipped with a stirrer bar and the following were placed in the autoclave in the order, $Ru_3(CO)_{12}$ (0.063 mmol, 40 mg), EtOH (15 ml), allene (9 mmol, 360 mg) and CO (15 atm). Reaction at 100 °C for 3 h gave ethyl methacrylate in 88% yield (GC). The reaction mixture was poured into water (60 ml) and extracted with diethyl ether. The fractional distillation gave 730 mg (71% yield) of ethyl methacrylate.

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