A New Route to 2(5*H*)-Furanones *via* Ruthenium-catalysed Oxidative Cyclocarbonylation of Allylic Alcohols

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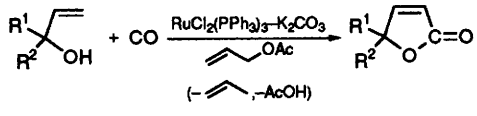
Several 2(5*H*)-furanones are readily prepared in moderate to high yields by ruthenium-catalysed oxidative cyclocarbonylation of 1,1-disubstituted allyl alcohols.

The scope and understanding of carbonylation has grown to such an extent that it can be regarded as one of the more generally useful techniques of synthetic organic chemistry.[1] Recently, the preparation of five-membered lactones has been one of the most intensively studied areas of carbonylation chemistry[2] in view of the widespread occurrence of lactone rings in natural compounds.[3] However, as for the synthesis of 2(5*H*)-furanones, the examples are limited to carbonylations of propynyl alcohols,[4] acetylenes[5] and/or vinyl halides.[6] In the carbonylation of allylic alcohols, saturated γ-butyrolactones were generally obtained[4] and direct oxidative cyclocarbonylation of allylic alcohols to 2(5*H*)-furanones has never been reported.

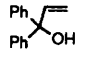
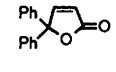
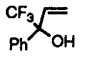
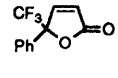
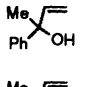
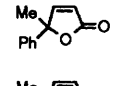
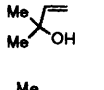
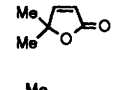
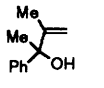
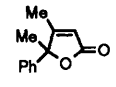
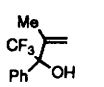
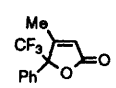
Here, we report the first example of ruthenium-catalysed oxidative cyclocarbonylation of allylic alcohols for direct synthesis of 2(5*H*)-furanones [eqn. (1)].



(1)

Representative results are summarized in Table 1. For example, the oxidative cyclocarbonylation of 1,1-diphenyl-2-propen-1-ol in the presence of a catalytic amount of $RuCl_2(PPh_3)_3$ afforded the corresponding 2(5*H*)-furanone in 77% yield (run 1). Under the optimized reaction conditions (at 200 °C under 10 kgcm^{-2} of initial carbon monoxide),† several 2(5*H*)-furanones were also obtained in moderate to high yields from the oxidative cyclocarbonylation of 1,1-disubstituted allyl alcohols (runs 2–6). However, when 1-monosubstituted allyl alcohols, such as 1-phenyl-2-propen-1-ol, were treated under the same reaction conditions, no carbonylation occurred and only isomerization proceeded to give propiophenone quantitatively.‡

Table 1 Ruthenium-catalysed synthesis of 2(5*H*)-furanones from 1,1-disubstituted allyl alcohols[a]

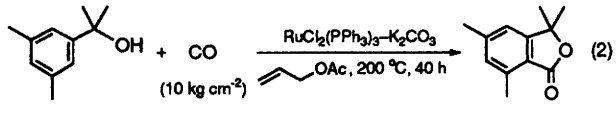
Run	Allylic alcohol	Product	Yield (%)[b]
1			77
2			46
3			31
4			15
5			68
6			32

[a] A mixture of 1,1-disubstituted allyl alcohol (4.0 mmol), allyl acetate (30 mmol), $RuCl_2(PPh_3)_3$ (0.20 mmol), K_2CO_3 (10 mmol) and THF (8.0 ml) in a 50 ml stainless steel autoclave was heated at 200 °C under CO (10 kg cm^{-2}) for 15 h. [b] Determined by GLC.

The present oxidative cyclocarbonylation was characteristic of ruthenium catalysts, especially $RuCl_2(PPh_3)_3$ complex. Other ruthenium catalyst systems such as $Ru_3(CO)_{12}$ and $RuCl_3 \cdot nH_2O$ combined with triaryl- or trialkyl-phosphines also promoted the carbonylation, but a considerable amount of saturated γ-lactones as well as 2(5*H*)-furanones were obtained. However, other group 8–10 metal catalysts such as $NiBr_2(PPh_3)_2$, $RhCl(PPh_3)_3$, $PdCl_2(PPh_3)_2$ and $PtCl_2(PPh_3)_2$ were totally ineffective and no carbonylation proceeded.

Addition of allyl acetate was essential for the selective synthesis of 2(5*H*)-furanones. In the absence of allyl acetate or in the presence of other hydrogen acceptors such as acetone, cyclohexene and diphenylacetylene, no carbonylated product was obtained. Further, when propynyl acetate or allyl methyl carbonate was employed as a hydrogen acceptor, the corresponding saturated γ-lactones were obtained as the major product. After the reaction of run 5, a stoichiometric amount of propylene was evolved into a gas phase, and we consider that only allyl acetate could operate as an effective hydrogen acceptor as in our previous work.[8] There exists the possibility that the product 2(5*H*)-furanones would be obtained by carbonylation or carboxylation by K_2CO_3 as a carbonyl source, and we examined the reaction using ^{13}C-labelled K_2CO_3 (*i.e.* $K_2{}^{13}CO_3$) under ^{12}CO. However, the carbonyl group in the generated 2(5*H*)-furanone was only $^{12}C{=}O$ derived from external ^{12}CO. Thus, K_2CO_3 operates only as a base for trapping acetic acid generated by hydrogenolysis of allyl acetate.

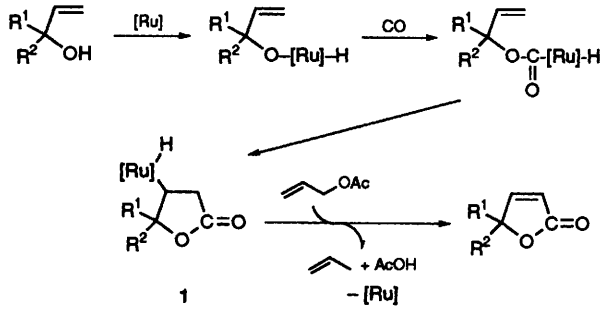
In addition, the present oxidative cyclocarbonylation can be applied to the synthesis of phthalides from 1,1-disubstituted benzyl alcohols. For example, 2-(3,5-xylyl)propan-2-ol was transformed into the corresponding phthalide in 49% yield [eqn. (2)].



(2)

49 %

A tentative reaction pathway is illustrated in Scheme 1.



Scheme 1

Oxidative addition of the hydroxy group in allylic alcohol to an active ruthenium centre firstly occurs and insertion of carbon monoxide into a O–[Ru] bond proceeds, followed by insertion of an olefin to give the intermediate **1**. Subsequent β-hydride elimination affords 2(5*H*)-furanone together with regeneration of an active ruthenium species *via* removal of hydrogen by hydrogen transfer (hydrogenolysis) to allyl acetate.

In conclusion, this novel oxidative cyclocarbonylation reveals one of the most intriguing transformations of allylic compounds by ruthenium catalysts.[8–10]

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Footnotes

† The present reaction also proceeded at 180 °C, but at 150 °C, no carbonylation proceeded. Further, both higher (30 kg cm^{-2}) and lower (5 kg cm^{-2}) CO pressure leads to low yields of the products.

‡ Similar ruthenium-catalysed redox isomerization of allyl alcohols has recently been reported by Trost *et al.*[7]

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