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LETTERS

Tandem reaction by using compatible catalysts: cross-metathesis reaction and hydrogenation

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Abstract—A one-pot tandem cross-metathesis/hydrogenation procedure was achieved at room temperature, under one atmosphere of hydrogen, in the presence of ruthenium catalyst **II** and PtO_2 showing the compatibility of the two catalysts. © 2002 Elsevier Science Ltd. All rights reserved.

The 'ideal synthesis' of functionalized compounds requires the development of one-pot successive reactions from commercially available and cheap starting materials and/or catalysts.[1] Organometallics that are able to catalyze distinct reactions directly or by simple modifications should be developed.[2] Sequential reactions by using compatible catalysts which will be able to achieve reactions with different rates could be a second way for obtaining efficient synthetic processes. It has been demonstrated recently that Grubbs' catalyst **I**[3] (Fig. 1) could be used in a sequential cross-metathesis/hydrogenation procedure for the rapid construction of small molecules.[4] However, this two-step sequential procedure was achieved under high pressure of hydrogen (70 bars) and by heating the reaction mixture up 100°C.

Here, we would like to demonstrate that cross-metathesis can be faster than the hydrogenation of olefins, and that a tandem cross-metathesis/hydrogenation reaction can take place between an olefin and α,β-unsaturated carbonyl or carboxylic compounds[5] in the presence of ruthenium complex **II**[4d,e] (Fig. 1) and PtO_2, under one atmosphere of hydrogen and at room temperature.

When the cross-metathesis reaction of allyl-triphenylsilane with ethyl acrylate **1** was conducted in the presence of catalyst **II** under one atmosphere of hydrogen for 12 h and at room temperature, the cross-metathesis product **6′** was obtained in 80% yield and only a trace of the expected saturated ester **6** was observed (Table 1, entry 1). This result means that complex **II** was probably not converted to a ruthenium hydride complex and consequently could not catalyze the reduction of the double bond of the cross-metathesis product. To induce the formation of compound **6**, ethyl acrylate **1** (3 equiv.) and allytriphenylsilane (1 equiv.) were treated with ruthenium catalyst **II** (0.05 equiv.) and Pd/C (0.05 equiv.) in CH_2Cl_2 at room temperature under one atmosphere of hydrogen (Table 1, entry 2). Under these conditions, the saturated ester **6** was formed in 30% yield as well as the cross-metathesis compound **6′** (20%) and propyltriphenylsilane **11** (49%). The formation of compound **11** in good yield means that the hydrogenation of the allyltriphenylsilane, induced by Pd/C, was faster than the cross-metathesis reaction. On the contrary, by replacing Pd/C by PtO_2 (0.05 equiv.), compound **6** was obtained in good yield (80%) an propyltriphenylsilane was obtained in only 10% yield

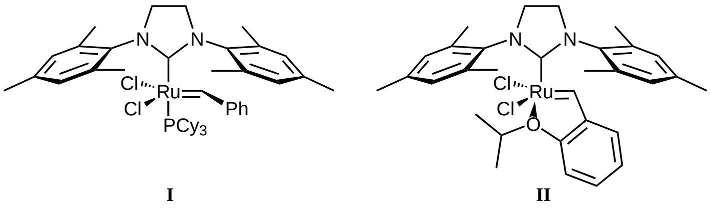

Figure 1.

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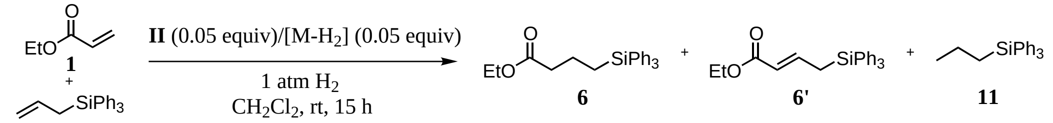
Table 1.

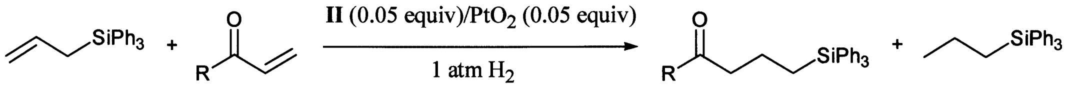


Entry	$[M-H_2]$	Yield in **6** (%)	Yield in **6′** (%)	Yield in **11** (%)
1	–	–	80	–
2	Pd/C 5%	30	20	49
3	PtO_2	80	–	10

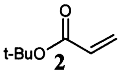
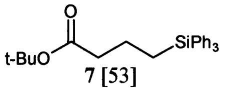
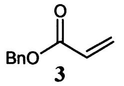
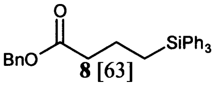
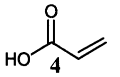
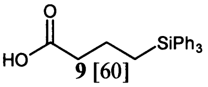
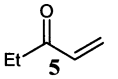
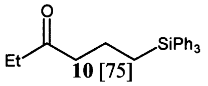
(Table 1, entry 3). Among the hydrogenation catalysts, only PtO_2 was compatible with ruthenium catalyst **II** in this cross-metathesis/hydrogenation tandem reaction. The tandem cross-metathesis/hydrogenation reaction is general.[6] As shown in Table 2, excellent yields of various saturated γ-silyl carboxylic and γ-silyl carbonyl compounds were obtained by using a convenient and mild 'one-pot' tandem catalysis procedure involving two catalysts. The unsaturated ester **2** was transformed to the corresponding saturated *tert*-butyl ester **7** in 53% yield (Table 2, entry 1). Furthermore, this one-pot tandem Ru-catalyzed cross-metathesis/PtO_2 hydrogenation reaction is chemoselective as benzyl acrylate **3** was transformed to the benzyl saturated ester **8** in 63% yield (Table 2, entry 2). Under these conditions the benzyl ester was not cleaved. We have to point out that the relative rate of the cross-metathesis reaction and the hydrogenation depends on the steric hindrance of the ester functionality as the yield of **11** decreases when the steric hindrance of the ester group is decreased. In the case of acrylic acid **4**, the saturated acid **9** was isolated in 60% yield (Table 2, entry 3) and similarly, we found that the mixture of catalysts **II**/PtO_2 was also excellent for the synthesis of ketone **10** from vinylketone **5** as **10** was obtained with a yield of 75% (Table 2, entry 4). The reactivity of acrolein with allyltriphenylsilane in the presence of ruthenium complex **II** and PtO_2 under one atmosphere of hydrogen was also examined. When the reaction was performed at room temperature for 15 h, a mixture of three products, aldehyde **12** (22%), triphenylsilylpropane **11** (45%) and alcohol **13** (32%) was obtained. As aldehyde **12** was reduced to alcohol **13** (85%) in the presence of PtO_2 and under one atmosphere of hydrogen, the cross-metathesis/hydrogenation reaction was conducted over a period of 160 h with the aim of increasing the yield of alcohol **13**. By using these conditions, alcohol **13** was formed in 50% yield and product **11** in 39% yield (Scheme 1). In contrast to the α,β-unsaturated esters **1**–**3**, acid **4** and ketone **5**, the yield of the cross-metathesis/hydrogenation products involving acrolein was lower, due probably to the hydrogenation of acrolein in the presence of PtO_2 which consequently consumes acrolein with a corresponding increase in the yield of **11**.

We have shown here, that the cross-metathesis reaction of α,β-unsaturated ketones, acids and esters with allyltriphenylsilane is faster than the hydrogenation of double bonds when the ruthenium complex **II** and PtO_2 are

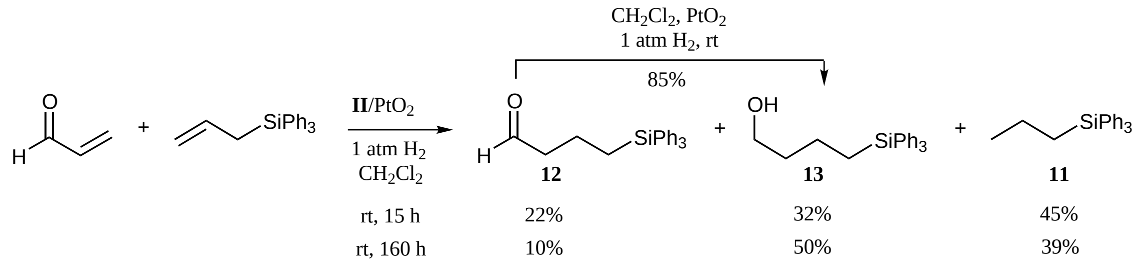
Table 2.



2 - 5 **7 - 10** **11**

Entry	Starting material	Product [Yield (%)]	Yield in **11** (%)
1	 **2**	 **7** [53]	46
2	 **3**	 **8** [63]	17
3[a]	 **4**	 **9** [60]	14
4[a]	 **5**	 **10** [75]	17

[a] When H_2 was bubbled through CH_2Cl_2 before the reaction, the saturated acid **9** was obtained in 45% yield and the saturated ketone **10** was obtained in 51% yield. On the other hand, triphenylsilane **11** was obtained in 50% yield.



Scheme 1.

used as catalysts at room temperature under one atmosphere of hydrogen. This tandem reaction is performed under very mild conditions and without purification of the intermediates.[7] The tandem cross-metathesis/hydrogenation reaction is general and applicable to various synthetic objectives which will be reported in due course.

Acknowledgements

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6. Typical procedure for tandem cross-metathesis/hydrogenation reaction: A solution of α,β-unsaturated carbonyl compound (3 equiv.) and allyltriphenylsilane (1 equiv.) in CH_2Cl_2 (0.2 M) was degassed under vacuum, purged with H_2 and then catalyst **II** and PtO_2 were introduced. The reaction mixture was degassed again under vacuum and then stirred under one atmosphere of hydrogen. After 15 h at rt, the solvent was evaporated and the residue was purified by flash chromatography to produce the corresponding γ-silylated carbonyl compound.
7. When the cross-metathesis products were isolated and then the hydrogenation was carried out, yields of γ-silylated carbonyl compounds were comparable to those of the one step process, but the purification of the cross-metathesis compounds was necessary.