Catalytic synthesis of 3-vinyl-2,5-dihydrofurans from yne-enes promoted by photochemically activated metal–allenylidene $L_nRu{=}C{=}C{=}CR_2$ complex

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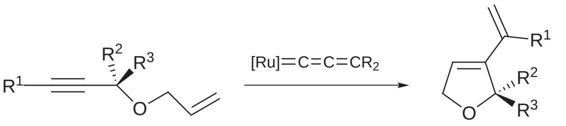
The ruthenium(II)–allenylidene salt [(*p*-cymene)(PCy$_3$)-ClRu=C=C=CPh$_2$]PF$_6$ acts as an olefin metathesis catalyst precursor for the yne-ene transformation of the mixed propargylic allyl ethers HC≡C–CR$_2$OCH$_2$CH=CH$_2$ into 3-vinyl-2,5-dihydrofurans; initial photochemical irradiation efficiently promotes the catalytic activity.

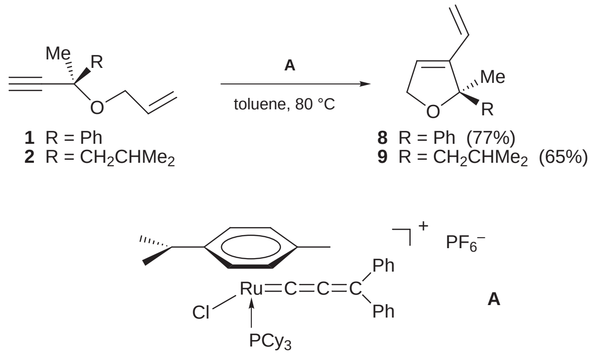
3-Vinyl-2,5-dihydrofurans have potential as Diels–Alder dienes and for access to optically active derivatives *via* asymmetric catalysis.[1] To the best of our knowledge, no direct preparation of these compounds has been reported, whereas a stereoselective route to 3-vinyltetrahydrofuran derivatives from cyclic allylsiloxanes has just been found.[2] However, it appears that the 3-vinyl-2,5-dihydrofuran structure **II** should be reached, in a straightforward way, from oxygenated yne-enes of type **I** *via* catalytic ring closing metathesis (RCM) reaction (Scheme 1). Indeed, since the pioneering work of Katz,[3] carbocycles have been made by RCM reactions using tungsten[3] or chromium[4] carbene catalysts. Recently, neutral 16-electron ruthenium carbenes (PCy$_3$)$_2$Cl$_2$Ru=CHR (R = CH=CPh$_2$, Ph), which tolerate functional groups, have been shown to efficiently promote access to N- and O-containing heterocycles, *via* ring closing metathesis.[5,6] However, these Ru=CHR complexes appear to be less efficient for the ring closing metathesis of yne-ene derivatives containing a terminal C≡CH bond.[5,7]



I **II**

Scheme 1

We now report (i) a general method for the preparation of new 3-vinyl-2,5-dihydrofurans of type **II** directly from mixed propargylic allyl ether derivatives **I**, *via* a RCM reaction in the presence of a novel olefin metathesis catalyst, the 18-electron cationic ruthenium allenylidene complex [(arene)(PCy$_3$)Cl-Ru=C=C=CPh$_2$]PF$_6$, which has just been shown to perform the ring closing metathesis of 1,6- to 1,20-dienes,[8] and (ii) that the catalytic species formation is favoured by photochemical activation of the catalyst precursor.



1 R = Ph
2 R = CH$_2$CHMe$_2$

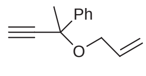
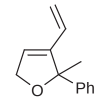
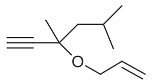
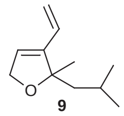
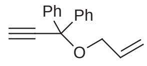
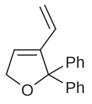
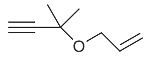
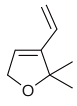
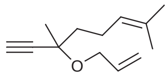
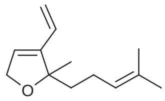
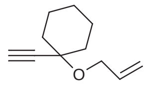
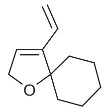
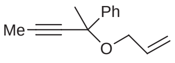
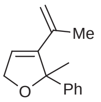
8 R = Ph (77%)
9 R = CH$_2$CHMe$_2$ (65%)

A

Scheme 2

The allyl prop-2-yn-1-yl ethers of type **I** were conveniently prepared from the corresponding prop-2-yn-1-ols on treatment by NaH and allyl bromide in DMF at room temperature (60–97%). The derivatives **1** and **2** were first reacted with 2.5 mol% of [(*p*-cymene)(PCy$_3$)ClRu=C=C=CPh$_2$]PF$_6$ (**A**) in toluene at 80 °C. The conversion was completed after 24 h and 6.5

Table 1 Catalytic synthesis of 3-vinyl-2,5-dihydrofurans **8–14** with photochemically activated ruthenium–allenylidene catalyst **A**[a]

Substrate	Product	Heating period at 80 °C[a]/h	Isolated yield (%)[b]
 **1**	 **8**	4	84
 **2**	 **9**	1	62
 **3**	 **10**	23	67
 **4**	 **11**	63[c]	41
 **5**	 **12**	1	74
 **6**	 **13**	1	63
 **7**	 **14**	24	83

[a] Initial UV irradiation (300 nm) at room temperature for 0.5 h in toluene followed by heating at 80 °C until complete conversion of **1**–**7**. [b] Yields were obtained after distillation under reduced pressure. [c] Reaction performed in refluxing CH$_2$Cl$_2$ after irradiation.

h, respectively, and derivatives **8** (77%) and **9** (65%) were obtained as the sole reaction products (Scheme 2).

The 18-electron catalyst precursor is expected to give an active catalytic species after partial decoordination or loss of the arene ligand to generate a highly coordinatively unsaturated ruthenium species. In order to check this hypothesis and in the search for better activity, the previous reaction was performed under UV irradiation [Hg lamp, 300 nm] in order to displace the *p*-cymene ligand, as was suggested for (*p*-cymene)$RuCl_2(PR_3)$.[9] After 0.5 h irradiation at room temperature in toluene followed by thermal reaction at 80 °C for 4 h, the conversion of **1** was completed (*vs*. 24 h at 80 °C previously without initial irradiation) and the 3-vinyl dihydrofuran **8** was obtained in 84% yield. Similarly, the complete conversion of **2** was achieved after only 1 h at 80 °C instead of 6.5 h without irradiation, and **9** was obtained in 62% yield (Table 1).

Preliminary UV irradiation tremendously favours the generation of the active catalytic species as the period of heating at 80 °C was significantly reduced. The allyl ethers **3–5** were reacted under the latter conditions and the 3-vinyldihydrofurans **10–12** were isolated in 62–84% (Table 1). It is noteworthy that these 3-vinyl-2,5-dihydrofurans are stable in solution at moderate temperature (80 °C) but decompose rapidly when isolated as pure compounds.

The increasing of the steric hindrance at the ether carbon atom C1 slows down the conversion of the ether (**2** > **1** >> **3**). The RCM reaction applied to derivative **6**, easily made from cyclohexanone, led after 1 h at 80 °C to the spirodihydrofuran **13** (63%), and showed reactivity similar to that of the disubstituted derivative **2**. The transformation of compound **7** into the 3-isopropenyldihydrofuran **14** in 83% yield, after irradiation and 24 h of reaction at 80 °C, compared with that of compound **1** (4 h, 84%), indicates that the ring closing metathesis reaction of enynes involving a disubstituted C≡C triple bond is disfavoured. This contrasts with the RCM of yne-enes containing amido or tosylamido functional groups.[5,7] It is noteworthy that the formation of the bis(dihydrofuran) was obtained previously from the disubstituted yne-ene $CH_2{=}CHCH_2OCH_2C{\equiv}CCH_2OCH_2CH{=}CH_2$ and the $L_nRu{=}CHCH{=}CPh_2$ catalyst.[6]

The above results show the second use of (arene)-$Ru{=}C{=}C{=}CR_2$ complexes in catalysis.[8] They are not only able to promote non-conjugated diene metathesis, they are also efficient catalysts for the ring closing metathesis of terminal yne-enes. These results bring evidence for the first time that the (arene)$Ru{=}C{=}C{=}CR_2$ complex **A** can be photochemically activated for improved generation of the active catalytic species and that this catalyst tolerates the presence of a terminal C≡CH bond.

The authors are very grateful to Dr A. Fürstner for creative discussions.

Notes and References

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Received in Liverpool, UK, 24th July 1998; 8/06005C