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Ruthenium-Catalysed Coupling of Allyl Alcohol With Alkynes : A New Route to γ,δ-Unsaturated Acetals and Aldehydes

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ABSTRACT : γ,δ-Unsaturated acetals and aldehydes have been obtained *via* a new ruthenium-catalysed coupling of allyl alcohol with alkynes. The branched isomer is regioselectively formed. Comparative studies of catalyst precursors have shown that (C_5Me_5)Ru(IV) derivatives favours the formation of acetals and that, with (C_5Me_5)Ru(II) moieties, the reaction can be carried out either in water or without solvent at room temperature. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

During the last years, the use of ruthenium catalysts for selective organic synthesis has known a tremendous development[1]. Especially very simple ruthenium complexes have allowed the discovery of new carbon-carbon bond forming reactions such as cyclopropanation[2], cyclic olefin ring opening metathesis polymerisation[3,4] and the reverse ring and C=C bond formation from non-conjugated dienes[5,6], formal insertion of alkenes or alkynes into C-H bonds of arenes[7] or conjugated alkenes[8] or carbonylation of diynes into phenols[9]. However, it is in the field of selective transformations of alkynes that ruthenium catalysts have recently brought important innovations. It is now well established that ruthenium-vinylidenes, resulting from activation of terminal alkynes, are key-intermediates in catalytic synthesis of alkenylcarbamates[10], enynes[11] and butatrienes[12] by alkyne dimerisation, or α,β-unsaturated ketones by coupling of alkynes with allylic alcohols[13,14]. Some examples of ruthenium-promoted selective carbon-carbon coupling of C≡C and C=C bonds have also been reported to occur *intermolecularly* to produce cyclobutenes[15], dienes[16], γ,δ-unsaturated ketones[17], butenolides[18] and *intramolecularly* in 1,6- and 1,7-enynes to generate cyclic olefins with skeleton rearrangement[5c,19].

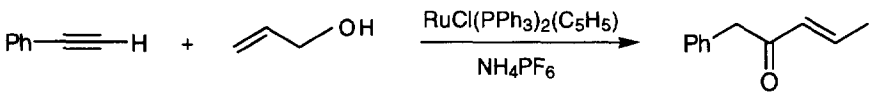
The concept of *electrophilic* activation of alkynes by ruthenium(II) complexes to promote nucleophilic addition at the C≡C bond of alkynes[1c,10] led us to study the influence of ruthenium(IV) derivatives, expected to act as stronger electrophilic promoters, for the addition of the alkene bond of allyl alcohol to alkynes.

We now describe, following our preliminary report[20], (i) a new one-step synthesis of branched γ,δ-unsaturated acetals or aldehydes *via* ruthenium-catalysed regioselective carbon-carbon coupling of allyl alcohol and alkynes and (ii) the comparative study of catalyst precursors containing (C_5Me_5)Ru(IV) and (C_5Me_5)Ru(II) moieties that are efficiently operating either in water or without solvent.

RESULTS AND DISCUSSION

Carbon-carbon coupling of alkynes with allyl alcohol with ruthenium(IV) catalysts

The reaction of phenylacetylene and allyl alcohol used as a solvent was attempted at 90 °C in the presence of 5% of either $RuCl_2(\eta^3\text{-}CH_2CHCH_2)(C_5H_5)$ **I**[21] or $RuCl_2(\eta^3\text{-}CH_2CMeCH_2)(C_5Me_5)$ **II**[21] as ruthenium(IV) catalyst precursor. These catalyst precursors did not lead to the unsaturated ketone derivative resulting from the ruthenium-vinylidene activated species as previously shown in the presence of $RuCl(PPh_3)_2(C_5H_5)$ catalyst and NH_4PF_6 (Eq. 1)[13], but to the formation of unsaturated acetals **1a** and **2a** (Scheme 1).



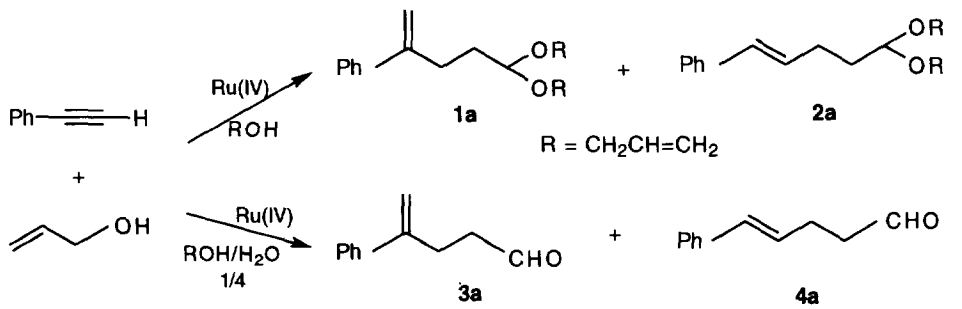
(eq.1)

With the precursor **I**, only 20% of conversion of the alkyne was reached after 22 h at 90 °C and **1a/2a** were produced in low yield in the ratio 33/67. With the catalyst **II** containing the bulkier and more electron-releasing C_5Me_5 ligand the same reaction led to the complete conversion of the alkyne after only 4 h at 90 °C and acetals **1a/2a** were isolated in 60% yield, but with the opposite regioselectivity (67/33) with respect to that offered by **I**. The direct formation of the acetals **1a/2a** suggested that the ruthenium(IV) catalyst **II** plays two roles : the promotion of the carbon-carbon coupling and the activation of the resulting aldehydes toward alcohol to form the acetals.

The same reaction with catalyst **II** but performed in an allyl alcohol/degassed water (1/4) mixture at 90 °C led to the aldehydes **3a/4a** (68/32) isolated in 58% yield (Scheme 1). As expected, the presence of water inhibited the formation of acetals but at the same time accelerated the conversion of the alkyne which was completed after only 2 h at 90 °C.

The favoured formation of the branched isomers **1a** or **3a** led us to consider that the reaction did not proceed *via* a ruthenium-vinylidene intermediate as in Trost's reaction (Eq. 1)[13], as such an intermediate should involve the coupling of the electrophilic terminal carbon of the alkyne with the oxygen atom or the C=C double bond of the allyl alcohol. This observation led to the hypothesis that the major branched isomer should result

from an oxidative coupling of the C≡C and C=C multiple bonds at the ruthenium site. Such an oxidative coupling cannot be envisaged to take place at a Ru(IV) center and it was postulated that the Ru(IV) catalyst precursor **II** was reduced to a Ru(II) species in the reaction either by reductive elimination of methallyl chloride or by reduction with allyl alcohol. These hypotheses led us to study several ruthenium(II) catalysts, containing the C_5Me_5 ligand expected to be responsible for the activity increase and the control of regioselectivity with respect to C_5H_5. Thus, catalyst precursors $[RuCl_2(C_5Me_5)]_n$ **III**[22], $[RuCl(C_5Me_5)]_4$ **IV**[23] and $RuCl(cod)(C_5Me_5)$ **V**[24] have been investigated.



Scheme 1

Ruthenium(II)-catalysed synthesis of γ,δ-unsaturated aldehydes in water

We first studied these catalyst precursors containing the $(C_5Me_5)Ru$ moiety in neat allyl alcohol. The catalytic coupling of phenylacetylene and allyl alcohol used as a solvent at 90 °C with 5% of catalysts **III**, **IV** and **V** led to the results summarized in Table 1.

i) The polymeric complex **III** containing Ru(III) species led to a mixture of acetals **1a/2a** (60%) and aldehydes **3a/4a** in 15% yield.

ii) The tetrameric ruthenium(II) species **IV** directly afforded the aldehydes **3a/4a** (50%). This result was analogous to that obtained with catalyst **II** in allyl alcohol/water (Scheme 1, Table 1).

iii) The catalyst **V**, obtained by reaction of **IV** with cycloocta-1,5-diene (cod)[24] but containing a labile cod ligand[15], appeared to be by far the best catalyst. In the absence of water catalyst **V** led to the aldehydes **3a/4a** (75/25) obtained in 70% yield without the formation of acetals.

This observation supports the idea that the ruthenium(IV) complex **II** was responsible for the transformation of aldehydes into acetals, a role that the ruthenium(II) complex **V** could not play. Indeed, when the mixture of **3a/4a** was reacted with allyl alcohol in the presence of 7 mol% of ruthenium(IV) complex **II** the

aldehydes were converted in their acetals **1a/2a** in 50% yield, after 3 h at 95 °C. From the same reaction but in the presence of the ruthenium(II) complex **V** the aldehydes **3a/4a** were recovered unchanged after 24 h at 95 °C.

Table 1. Synthesis in Allyl Alcohol of γ,δ-Unsaturated Acetals **1a/2a** and Aldehydes **3a/4a**

Catalyst	Reaction time	Products (yield)[a]	Selectivity
II	4 h	Acetals (60%)	**1a** / **2a** : 67/33
III	4 h	Acetals (60%) +	**1a** / **2a** : 71/29
		Aldehydes (15%)	**3a** / **4a** : 72/28
IV	2 h	Aldehydes (50%)	**3a** / **4a** : 73/27
V	1 h	Aldehydes (70%)	**3a** / **4a** : 75/25

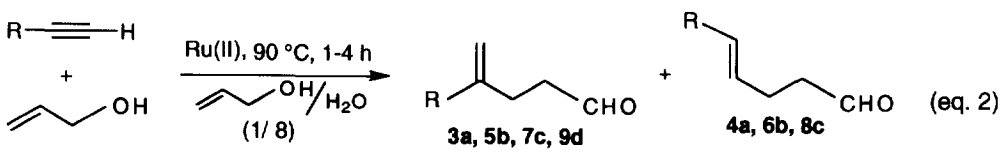
(a) Conditions : 2.5 mmol of phenylacetylene, 5 mL of allyl alcohol, 5 mol% of Ru catalyst, 90 °C

II : $RuCl_2(\eta^3\text{-}CH_2CMeCH_2)(C_5Me_5)$ **III** : $[RuCl_2(C_5Me_5)]_n$

IV : $[RuCl(C_5Me_5)]_4$ **V** : $RuCl(cod)(C_5Me_5)$

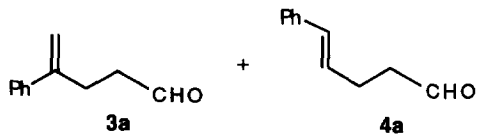
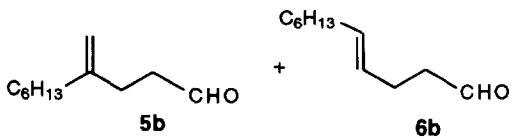
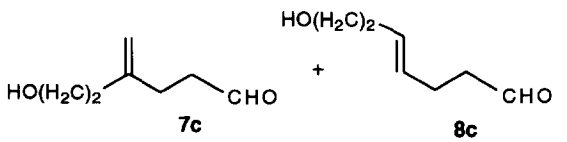
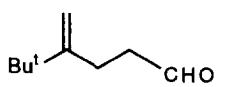
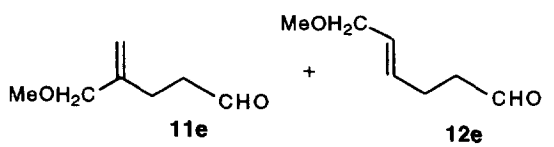
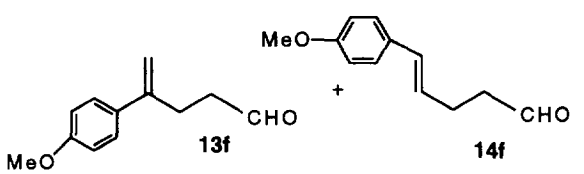
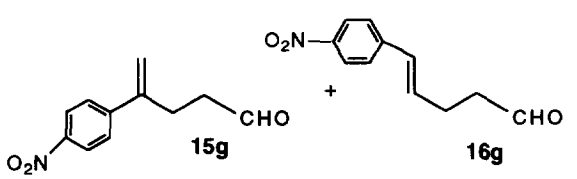
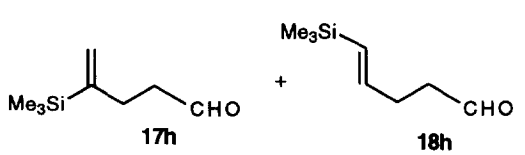
The addition of water to allyl alcohol led us to find the best conditions for catalyst **V** to operate. In allyl alcohol/water (1/8) with catalyst **V**, the yield in isolated aldehydes **3a/4a** significantly increased to reach 85% with the same regioselectivity (75/25). The ratio water/alcohol (8/1) could not be increased for otherwise catalyst **V** was not soluble and the conversion decreased.

Thus catalyst **V** and the latter conditions for the formation of **3a/4a** were selected to study the activation of a variety of terminal alkynes [RC≡CH : R = C_6H_{13} (**b**) ; CH_2CH_2OH (**c**) ; Bu^t (**d**)] (Eq. 2). In each case, the aldehydes were obtained and the branched isomer favoured : **5b/6b** (80/20) (80%) ; **7c/8c** (58/42) (70%) and with the bulky tert-butyl group the branched aldehyde **9d** (50%) was the only product formed. The low isolated yield was due to its volatility (Eq. 2).



Alkyne	Selectivity branched/linear	Yield (%)
a R = Ph	**3a** / **4a** : 75/25	85
b R = C_6H_{13}	**5b** / **6b** : 80/20	80
c R = $(CH_2)_2OH$	**7c** / **8c** : 58/42	70
d R = Bu^t	**9d** / - : 100/ -	50

Table 2. Synthesis of γ,δ-Unsaturated Aldehydes Without Solvent[a]

Alkyne	Products	Yield (%)	Selectivity branched/linear
a	 **3a** + **4a**	85	75/25
b	 **5b** + **6b**	83	80/20
c	 **7c** + **8c**	75	58/42
d	 **9d**	60	100/-
e	 **11e** + **12e**	70	76/24
f	 **13f** + **14f**	82	68/32
g	 **15g** + **16g**	80	83/17
h	 **17h** + **18h**	50	27/73

(a) Conditions : 0.125 mmol of V (5 mol%) dissolved in 0.5 mL (7.5 mmol) of allyl alcohol and then addition of the alkyne (2.5 mmol) at room temperature. Reaction time : 10-15 min.

Ruthenium(II)-catalysed coupling of alkynes with allyl alcohol without solvent

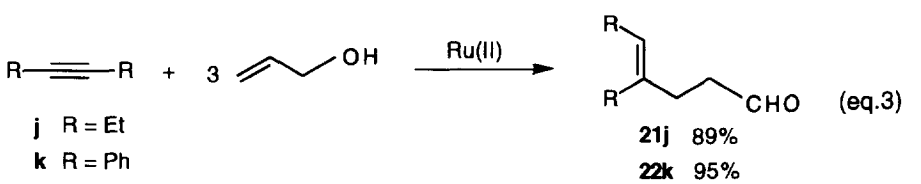
While studying the influence of the components of the reaction, the catalyst **V** was first dissolved in the minimum of allyl alcohol and on addition of the alkyne the catalytic reaction proceeded very quickly without water. This observation led us to put in action an efficient catalytic procedure *without solvent* using 5 mol% of catalyst with respect to the alkyne. Thus, 0.125 mmol of RuCl(cod)(C_5Me_5) **V** (5 mol%) was dissolved in 0.5 mL of allyl alcohol (7.5 mmol) under an inert atmosphere of argon. Then the alkyne (2.5 mmol) was added to the stirred mixture and the reaction was usually completed in 10-15 min at room temperature. The aldehydes were directly isolated after purification on a short chromatography column of silica-gel. With this procedure, a turnover number of about 120 h^{-1} was obtained.

The results are displayed in Table 2. With alkynes **a**, **b**, **c** and **d** the yields obtained in 15 min at room temperature were similar or slightly improved with respect to those obtained in water under the conditions of equation 2 (90 °C/1-4 h) but with the same regioselectivity.

From the alkynes RC≡CH [R = $MeOCH_2$ (**e**), *p*-$MeOC_6H_4$ (**f**), *p*-$NO_2C_6H_4$ (**g**), Me_3Si (**h**)] the aldehydes were obtained in 70% [**11e/12e** (76/24)], 82% [**13f/14f** (68/32)], 80% [**15g/16g** (83/17)] and 50% [**17h/18h** (27/73)] yields, respectively. The reaction led to the major branched isomer except from trimethylsilylacetylene (**h**) for which the reaction did not take place at room temperature but at 50 °C for 24 h.

From the unsymmetrical alkyne PhC≡CMe (**i**) a mixture of both aldehydes (*Z*)-MeCH=C(Ph)CH_2CH_2CHO/(*E*)-PhCH=C(Me)CH_2CH_2CHO **19i/20i** (72/28) was obtained in 85% yield.

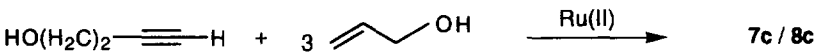
The reaction performed with symmetrically disubstituted alkynes (R = Et, Ph) led to the formation at 25 °C of high isolated yields of **21j** (89%) and **22k** (95%) after 15 min and 24 h respectively, showing the drastic influence of an aryl group with respect to the alkyl group (Eq. 3). Thus this reaction applied to symmetrically substituted alkynes constitutes an excellent route to the selective formation of one isomer of γ,δ-unsaturated aldehydes.



In an attempt to bring information on the reaction mechanism, the alkyne $HOCH_2CH_2C{\equiv}CH$ (**c**) was reacted with catalyst **V** in 3 equivalents of allyl alcohol at various temperature and the conversion of the alkyne was measured after 10 min. The results (Table 3) show that at 20 °C, the conversion was excellent (75%) but

improved at 0 °C (100%) to give **7c/8c** (64/36), whereas the conversion decreased at higher (60 °C) or lower temperature (- 30 °C).

Table 3. Temperature Influence



Reaction temperature	60 °C	20 °C	0 °C	- 30 °C
Alkyne conversion at t = 10 min	30%	75%	100%	49%

Mechanism

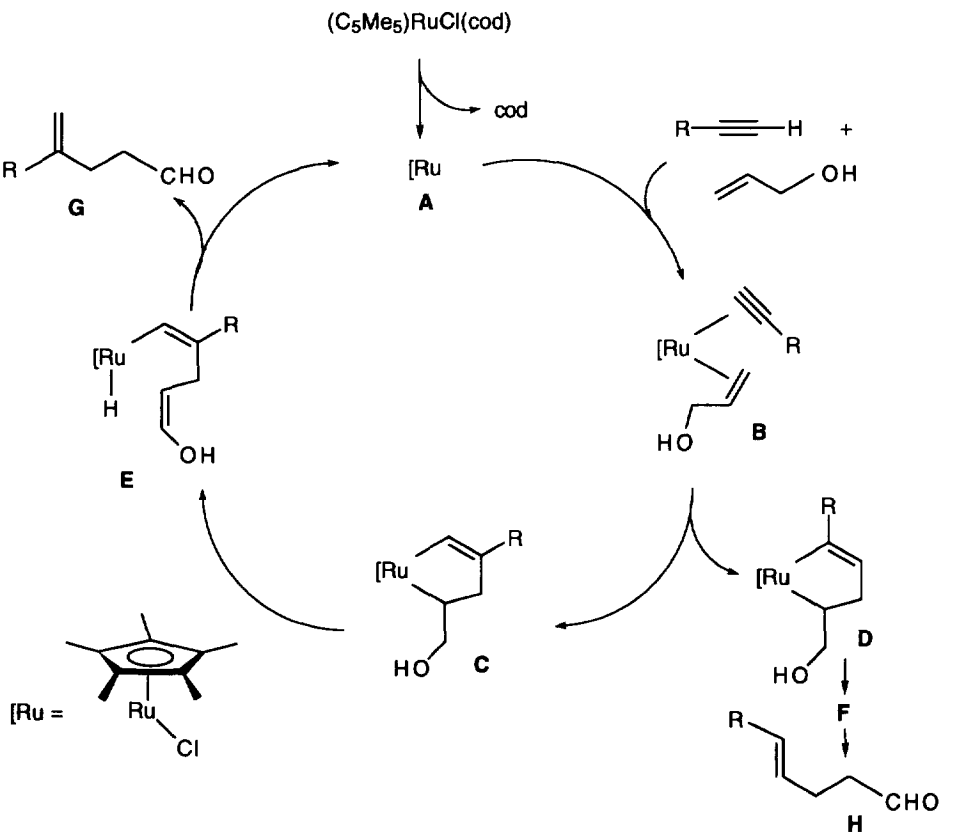
As the linear derivatives are never the major isomers, the activation of the alkyne *via* the vinylidene intermediate cannot be the main process[13]. The ruthenium(II) complex $(C_5Me_5)RuCl(cod)$ appearing to be the best catalyst precursor to produce the branched isomer as the major product, a regioselective oxidative coupling of the C≡C and C=C bonds of the reagents seems the most likely process (Scheme 2).

Indeed, it is well known that $CpRuCl(cod)$[16-18], and even in one instance $(C_5Me_5)RuCl(cod)$[15], very easily loose their cod ligand. Thus, the 14-electron species "$(C_5Me_5)RuCl$" **A** is likely to be more easily generated from catalyst **V** than from the tetramer **IV**. By addition of the alkyne and double bond to species **A**, the coordinatively saturated species **B** is expected to give the oxidative coupling into the ruthenium(IV) moieties **C** and **D**. Indeed the comparison of $(C_5Me_5)Ru(II)$ and $(C_5H_5)Ru(II)$ complexes by cyclic voltammetry has shown that the C_5Me_5 ligand is a strong electron-releasing ligand and thus favours the oxidation of the ruthenium(II) metal site with respect to C_5H_5[25].

The bulkiness of both C_5Me_5 and R groups should favour the formation of the intermediate **C** rather than **D**. From the 16-electron species **C**, β–elimination of one hydrogen of the exocyclic $CH_2(\beta)$ should lead to the alkenyl hydrido ruthenium species **E**, directly affording the major isomer **G** and species **A** by reductive elimination. Analogously, the minor species **D** should lead to **F**, similar to **E**, and then to **H** and **A**. It is noteworthy that the β-elimination involving an exocyclic $C_\beta H_2Y$ group with a free C_α-C_β rotation is easier than the $C_\beta H_2$ group involved in a strained metallacyclopentene, as the M-C_α-C_β-H bonds are away from the coplanarity with the relative *syn* positions of the M-C_α and C_β-H bonds.

It is noteworthy that a related catalytic reaction was already observed by Trost et al.[17] for the synthesis of γ,δ-unsaturated ketones *via* the C-C coupling of alkynes but with *1-substituted* allylic alcohols. The catalyst

$RuCl(cod)(C_5H_5)/NH_4PF_6$ (10%) operated at 100 °C in DMF-H_2O and led to the linear γ,δ-unsaturated ketone as the major isomer and, according to the nature of the allylic alcohol substituent, the selectivity in the formation of linear/branched isomers could reach the ratio 3/1. Thus in the formation of aldehydes (Eq. 2, Scheme 2) the use of $RuCl(cod)(C_5Me_5)$ in allyl alcohol without NH_4PF_6 salt led to the reverse selectivity in the coupling of the C≡C and C=C bonds (branched/linear : 4/1). At this stage we can suggest that the highest activity of $RuCl(cod)(C_5Me_5)$ with respect to $RuCl(cod)(C_5H_5)$ is due to its higher electron-richness favouring the oxidative coupling (step **B** → **C**) and that the selective formation of the branched isomer **G** is due to the steric effect of the C_5Me_5 ligand with respect to the C_5H_5 ligand, thus favouring the formation of the ruthenium(IV) species **C**, rather than **D**, to decrease the steric interaction of C_5Me_5 and R groups. This is consistent with the observation that the bulkiest ^tBu group led to the sole formation of the branched isomer **9d**.



Scheme 2

CONCLUSION

The reaction which is described here with the $[RuCl(C_5Me_5)]_4$ **IV** or $RuCl(cod)(C_5Me_5)$ **V** catalyst illustrates a new example of a drastic influence of a slight modification of a ruthenium catalyst on the improvement of the catalytic activity and of the regioselectivity. For practical uses it shows that ruthenium(IV) catalysts can be applied to produce acetals from aldehydes and that symmetrically disubstituted alkynes can be transformed into γ,δ-unsaturated aldehydes by a stereoselective coupling with allyl alcohol.

EXPERIMENTAL SECTION

All reactions were carried out under inert atmosphere in Schlenk tubes. Chemicals were obtained commercially and used as supplied. Complexes were prepared according to reported methods : $RuCl_2(\eta^3\text{-}CH_2CHCH_2)(C_5H_5)$ **(I)**[21], $RuCl_2(\eta^3\text{-}CH_2CMeCH_2)(C_5Me_5)$ **(II)**[21], $[RuCl_2(C_5Me_5)]_n$ **(III)**[22], $[RuCl(C_5Me_5)]_4$ **(IV)**[23], $RuCl(cod)(C_5Me_5)$ **(V)**[24].

^1H and ^{13}C NMR spectra were recorded on a Brucker AM 300 WB spectrometer. Infrared spectra were recorded on a Nicolet 205 spectrometer. Gas chromatography was performed on a Hewlett Packard 5890 series II chromatograph equipped with a HP FFAP (30 m x 0.53 mm) column. Products were isolated by silica gel (70-230 mesh) column chromatography. Elemental analyses were performed by "Le Service de Microanalyse du CNRS", Lyon, France and high resolution mass spectra by "Le Centre Régional de Mesures Physiques de l'Ouest", Université de Rennes 1, Rennes, France.

General procedure for the reactions in allyl alcohol :
Alkyne (2.5 mmol) was added to a mixture of ruthenium complex (0.125 mmol) and allyl alcohol (5 mL). The mixture was stirred and heated at 90 °C for 4 h. The solvent was evaporated under vacuum and the residue was extracted with Et_2O. The organic layer was evaporated and the products were isolated by column chromatography over silica gel with pentane/Et_2O mixtures as eluent.

General procedure for the reactions in water :
Degassed water (4 mL) was added to a mixture of ruthenium complex (0.125 mmol), allyl alcohol (7.5-15 mmol, 0.5-1 mL) and alkyne (2.5 mmol). The non homogeneous mixture was stirred and heated at 90 °C for 1-4 h. The cooled mixture was poured into water. The solution was extracted with Et_2O and the organic layer washed with H_2O, dried over $MgSO_4$ and evaporated. The products were purified by column chromatography over silica gel with pentane/Et_2O mixtures as eluent.

General procedure for the reactions without solvent :
The ruthenium complex $(C_5Me_5)RuCl(cod)$ (0.125 mmol) was dissolved in allyl alcohol (7.5 mmol, 0.5 mL) under argon and the alkyne (2.5 mmol) was added to the mixture. For most alkynes, the reaction was completed in 10-15 min. The products were isolated after column chromatography over silica gel (30 g) with pentane/Et_2O mixtures as eluent.

2-phenyl-5,5-diallyloxypent-1-ene, 1a. IR (film) ν/cm^{-1} 3082 (=CH_2), 3058, 3021, 1648 (CH=CH_2), 1628 (C=CH_2) ; ^{1}H NMR δ (300 MHz, $CDCl_3$) 7.33-7.16 (m, 5 H, Ph), 5.82 (ddt, 2 H, ^3J = 17.2 Hz, ^3J = 10.4 Hz, ^3J = 5.6 Hz, =CH), 5.20 (d, 1 H, ^2J = 1.2 Hz, C=CH_2), 5.19 (dm, 2 H, ^3J = 17.2 Hz, CH=$\underline{CH_2}$), 5.07 (dm, 2 H, ^3J = 10.4 Hz, CH=$\underline{CH_2}$), 5.00 (d, 1 H, ^2J = 1.2 Hz, C=CH_2), 4.55 (t, 1 H, ^3J = 5.7 Hz, O-CH-O), 4.00 (ddt, 2 H, ^2J = 12.7 Hz, ^3J = 5.6 Hz, ^4J = 1.4 Hz, OCH_2), 3.90 (ddt, 2 H, ^2J = 12.7 Hz, ^3J = 5.6 Hz, ^4J = 1.4 Hz, OCH_2), 2.51 (t, 2 H, ^3J = 7.7 Hz, $\underline{CH_2}CH_2$), 1.73 (dt, 2 H, ^3J = 5.7 Hz, ^3J = 7.7 Hz, $\underline{CH_2}CH$) ; ^{13}C NMR δ (75.5 MHz, $CDCl_3$) 147.73, 140.97, 134.65, 128.28, 127.39, 126.07, 116.68, 112.43, 101.64, 66.29, 31.99, 30.31. HRMS calcd for $C_{14}H_{17}O_2$ (M^+- C_3H_5) 217.1228, found 217.1227.

1-phenyl-5,5-diallyloxypent-1-ene, 2a. IR (film) ν/cm^{-1} 3023, 1648 (C=C) ; ^{1}H NMR δ (300 MHz, $CDCl_3$) 7.35-7.12 (m, 5 H, Ph), 6.31 (d, 1 H, ^3J = 15.8 Hz, =CH), 6.12 (dt, ^3J = 15.8 Hz, ^3J = 6.8 Hz, =CH), 5.83 (ddt, 2 H, ^3J = 17.2 Hz, ^3J = 10.4 Hz, ^3J = 5.4 Hz, $\underline{CH}$=CH_2), 5.21 (dm, 2 H, ^3J = 17.2 Hz, CH=$\underline{CH_2}$), 5.05 (dm, 2 H, ^3J = 10.4 Hz, CH=$\underline{CH_2}$), 4.56 (t, 1 H, ^3J = 5.7 Hz, O-CH-O), 4.04 (ddt, 2 H, ^2J = 12.7 Hz, ^3J = 5.4 Hz, ^4J = 1.4 Hz, OCH_2), 3.94 (ddt, 2 H, ^2J = 12.7 Hz, ^3J = 5.4 Hz, ^4J = 1.4 Hz, OCH_2), 2.20 (dt, 2 H, ^3J = 6.8 Hz, ^3J = 7.8 Hz, CH_2), 1.73 (dt, 2 H, ^3J = 5.7 Hz, ^3J = 7.8 Hz, CH_2) ; ^{13}C NMR δ (75.5 MHz, $CDCl_3$) 140.63, 134.13, 130.28, 129.75, 128.45, 126.90, 125.91, 116.73, 102.63, 66.23, 32.97, 28.22.

4-phenylpent-4-enal, 3a[26]. IR (film) ν/cm^{-1} 3086 (=CH_2), 3058, 3030, 2720 ($\underline{CH}$O), 1725 (C=O), 1629 (C=C) ; ^{1}H NMR δ (300 MHz, $CDCl_3$) 9.65 (t, 1 H, ^3J = 1.5 Hz, CHO), 7.33-7.11 (m, 5 H, Ph), 5.25 (s, 1 H, =CH_2), 5.01 (m, 1 H, =CH_2), 2.77 (t, 2 H, ^3J = 7.5 Hz, CH_2), 2.52 (m, 2 H, CH_2) ; ^{13}C NMR δ (75.5 MHz, $CDCl_3$) 201.74, 146.54, 140.34, 128.42, 127.68, 126.03, 113.05, 42.35, 27.62.

(*E*)-5-phenylpent-4-enal, 4a[27]. IR (film) ν/cm^{-1} 3025, 2725 ($\underline{CH}$O), 1724 (C=O), 1687 (C=C) ; ^{1}H NMR δ (300 MHz, $CDCl_3$) 9.70 (t, 1 H, ^3J = 1.4 Hz, CHO), 7.30-7.10 (m, 5 H, Ph), 6.33 (d, 1 H, ^3J = 15.9 Hz, =CH), 6.10 (dt, 1 H, ^3J = 15.9 Hz, ^3J = 6.4 Hz, =CH), 2.54-2.41 (m, 4 H, CH_2CH_2) ; ^{13}C NMR δ (75.5 MHz, $CDCl_3$) 201.77, 137.14, 131.06, 128.49, 128.10, 127.19, 125.99, 43.26, 25.45.

4-(n-hexyl)pent-4-enal, 5b. IR (film) ν/cm^{-1} 3079 (=CH_2), 2720 ($\underline{CH}$O), 1729 (C=O), 1646 (C=C) ; ^{1}H NMR δ (300 MHz, $CDCl_3$) 9.68 (t, 1 H, ^3J = 1.7 Hz, CHO), 4.69 (m, 1 H, =CH_2), 4.62 (m, 1 H, =CH_2), 2.50 (tm, 2 H, ^3J = 7.5 Hz, CH_2), 2.27 (m, 2 H, =CH_2), 1.94 (tm, 2 H, ^3J = 7.3 Hz, CH_2), 1.4-1.15 (m, 8 H, CH_2), 0.80 (m, 3 H, CH_3). Anal. Calcd for $C_{11}H_{20}O$: C, 78.51 ; H, 11.98. Found : C, 78.38 ; H, 11.61.

(*E*)-undec-4-enal, 6b[28]. IR (film) ν/cm^{-1} 2720 ($\underline{CH}$O), 1728 (C=O), 1680 (C=C) ; ^{1}H NMR δ (300 MHz, $CDCl_3$) 9.67 (t, 1 H, ^3J = 1.7 Hz, CHO), 5.35 (m, 2 H, CH=CH), 2.40 (tm, 2 H, ^3J = 7.5 Hz, CH_2), 2.26 (m, 2 H, CH_2), 1.88 (tm, 2 H, ^3J = 7.6 Hz, CH_2), 1.4-1.15 (m, 8 H, CH_2), 0.80 (m, 3H, CH_3).

4-(2-hydroxyethyl)pent-4-enal, 7c. IR (film) ν/cm^{-1} 3420 (OH), 3079 (=CH_2), 2727 (CHO), 1722 (C=O), 1645 (C=C) ; ^{1}H NMR δ (300 MHz, $CDCl_3$) 9.72 (t, 1 H, ^{3}J = 1.5 Hz, CHO), 4.82 (d, 1 H, ^{2}J = 0.9 Hz, =CH_2), 4.78 (d, 1 H, ^{2}J = 0.9 Hz, =CH_2), 3.68 (t, 2 H, ^{3}J = 6.5 Hz, CH_2), 2.58 (td, 2 H, ^{3}J = 7.3 Hz, ^{3}J = 1.2 Hz, CH_2), 2.31 (t, 2 H, ^{3}J = 7.3 Hz, CH_2), 2.25 (t, 2 H, ^{3}J = 6.5 Hz, CH_2), 1.7 (sl, 1 H, OH) ; ^{13}C NMR δ (75.5 MHz, $CDCl_3$) 202.27, 144.15, 111.49, 60.20, 41.40, 39.06, 27.61. Anal. Calcd for $C_7H_{12}O_2$: C, 65.60 ; H, 9.44. Found : C, 65.29 ; H, 9.57.

(*E*)-7-hydroxyhept-4-enal, 8c. IR (film) ν/cm^{-1} 3428 (OH), 2727 (CHO), 1724 (C=O), 1680 (C=C) ; ^{1}H NMR δ (300 MHz, $CDCl_3$) 9.69 (t, 1 H, ^{3}J = 1.6 Hz, CHO), 5.53-5.34 (m, 2 H, CH=CH), 3.56 (t, 2 H, ^{3}J = 6.3 Hz, CH_2), 2.46 (td, 2 H, ^{3}J = 7.0 Hz, ^{3}J = 1.4 Hz, CH_2), 2.30 (dt, 2 H, ^{3}J = 6.3 Hz, ^{3}J = 7.0 Hz, CH_2), 2.19 (dt, 2 H, ^{3}J = 6.2 Hz, ^{3}J = 6.3 Hz, CH_2), 1.8 (sl, 1 H, OH) ; ^{13}C NMR δ (75.5 MHz, $CDCl_3$) 202.46, 148.63, 145.38, 60.28, 38.93, 36.10, 28.09. Anal. Calcd for $C_7H_{12}O_2$: C, 65.60 ; H, 9.44. Found : C, 65.09 ; H, 9.28.

4-(1,1-dimethylethyl)pent-4-enal, 9d[26]. IR (film) ν/cm^{-1} 3100 (=CH_2), 2720 (CHO), 1726 (C=O), 1637 (C=C) ; ^{1}H NMR δ (300 MHz, $CDCl_3$) 9.73 (t, 1 H, ^{3}J = 1.5 Hz, CHO), 4.86 (s, 1 H, =CH_2), 4.57 (s, 1 H, =CH_2), 2.56 (t, 2 H, ^{3}J = 7.6 Hz, CH_2), 2.35 (t, 2 H, ^{3}J = 7.6 Hz, CH_2), 1.03 (s, 9 H, CH_3) ; ^{13}C NMR δ (75.5 MHz, $CDCl_3$) 202.34, 155.94, 106.55, 42.84, 36.14, 29.07, 23.22.

4-(methoxymethyl)pent-4-enal, 11e. IR (film) ν/cm^{-1} 3079 (=CH_2), 2727 (CHO), 1722 (C=O), 1652 (C=C) ; ^{1}H NMR δ (300 MHz, $CDCl_3$) 9.71 (t, 1 H, ^{3}J = 1.6 Hz, CHO), 4.98 (s, 1 H, =CH_2), 4.85 (s, 1 H, =CH_2), 3.81 (s, 2 H, CH_2O), 3.24 (s, 3 H, CH_3O), 2.56 (td, 2 H, ^{3}J = 7.6 Hz, ^{3}J = 1.6 Hz, CH_2), 2.34 (t, 2 H, ^{3}J = 7.6 Hz, CH_2) ; ^{13}C NMR δ (75.5 MHz, $CDCl_3$) 201.82, 144.06, 112.52, 75.50, 57.72, 41.57, 25.24. HRMS calcd for C_6H_8O (M^+- CH_4O) 96.0575, found 96.0572.

6-methoxyhex-4-enal, 12e. IR (film) ν/cm^{-1} 2727 (CHO), 1718 (C=O), 1684 (C=C) ; ^{1}H NMR δ (300 MHz, $CDCl_3$) 9.72 (t, 1 H, ^{3}J = 1.6 Hz, CHO), 5.67 (dtt, 1 H, ^{3}J = 15.5 Hz, ^{3}J = 6.2 Hz, ^{4}J = 1.2 Hz, =CH), 5.54 (dtt, 1 H, ^{3}J = 15.5 Hz, ^{3}J = 5.9 Hz, ^{4}J = 1.2 Hz, =CH), 3.80 (d, 2 H, ^{3}J = 6.1 Hz, CH_2O), 3.25 (s, 3 H, CH_3O), 2.50 (t, 2 H, ^{3}J = 7.0 Hz, CH_2), 2.37-2.32 (m, 2 H, CH_2).

4-(4-methoxyphenyl)pent-4-enal, 13f[26]. IR (film) ν/cm^{-1} 3093 (=CH_2), 3065, 3037, 2727 (CHO), 1715 (C=O), 1623 (C=C) ; ^{1}H NMR δ (300 MHz, $CDCl_3$) 9.68 (t, 1 H, ^{3}J = 1.5 Hz, CHO), 7.26-7.23 (m, 2 H, Ph), 6.80-6.76 (m, 2 H, Ph), 5.17 (s, 1 H, =CH_2), 4.92 (s, 1 H, =CH_2), 3.73 (s, 3 H, OCH_3), 2.73 (t, 2 H, ^{3}J = 7.7 Hz, CH_2), 2.55-2.51 (m, 2 H, CH_2) ; ^{13}C NMR δ (75.5 MHz, $CDCl_3$) 201.78, 159.18, 145.77, 132.63, 127.05, 113.69, 111.38, 55.15, 42.35, 27.57.

5-(4-methoxyphenyl)pent-4-enal, 14f[29]. IR (film) ν/cm^{-1} 3030, 2727 (CHO), 1722 (C=O), 1680 (C=C) ; ^{1}H NMR δ (300 MHz, $CDCl_3$) 9.72 (t, 1 H, ^3J = 1.4 Hz, CHO), 7.20-7.15 (m, 2 H, Ph), 6.77-6.72 (m, 2 H, Ph), 6.43 (d, 1 H, ^3J = 15.8 Hz, =CH), 5.96 (dt, 1 H, ^3J = 15.8 Hz, ^3J = 6.6 Hz, =CH), 3.71 (s, 3 H, OCH_3), 2.55-2.40 (m, 4 H, CH_2) ; ^{13}C NMR δ (75.5 MHz, $CDCl_3$) 201.86, 158.84, 130.36, 129.92, 127.05, 125.83, 113.84, 55.15, 43.33, 25.40.

4-(4-nitrophenyl)pent-4-enal, 15g. IR (film) ν/cm^{-1} 3100 (=CH_2), 3086, 3030, 2727 (CHO), 1722 (C=O), 1631 (C=C), 1518 (NO_2) ; ^{1}H NMR δ (300 MHz, $CDCl_3$) 9.79 (t, 1 H, ^3J = 1.2 Hz, CHO), 8.18 (m, 2 H, Ph), 7.54 (m, 2 H, Ph), 5.45 (s, 1 H, =CH_2), 5.26 (s, 1 H, =CH_2), 2.85 (td, 2 H, ^3J = 7.1 Hz, ^3J = 1.2 Hz, CH_2), 2.63 (t, 2 H, ^3J = 7.1 Hz, CH_2) ; ^{13}C NMR δ (75.5 MHz, $CDCl_3$) 200.86, 147.08, 147.02, 144.85, 126.77, 123.66, 116.35, 41.94, 27.01. Anal. Calcd for $C_{11}H_{11}NO_3$: C, 64.38 ; H, 5.40. Found : C, 64.13 ; H, 5.53.

5-(4-nitrophenyl)pent-4-enal, 16g. IR (film) ν/cm^{-1} 3030, 2727 (CHO), 1722 (C=O), 1680 (C=C), 1512 (NO_2) ; ^{1}H NMR δ (300 MHz, $CDCl_3$) 9.82 (t, 1 H, ^3J = 1.2 Hz, CHO), 8.13 (m, 2 H, Ph), 7.43 (m, 2 H, Ph), 6.44 (m, 2 H, CH=CH), 2.68-2.57 (m, 4 H, CH_2) ; ^{13}C NMR δ (75.5 MHz, $CDCl_3$) 201.04, 144.93, 143.65, 133.49, 129.35, 126.51, 123.93, 42.80, 25.48.

4-(trimethylsilyl)pent-4-enal, 17h[26]. IR (film) ν/cm^{-1} 3050 (=CH_2), 2720 (CHO), 1728 (C=O), 1616 (C=C) ; ^{1}H NMR δ (300 MHz, $CDCl_3$) 9.76 (t, 1 H, ^3J = 1.7 Hz, CHO), 5.52 (dt, 1 H, ^2J = 2.3 Hz, ^3J = 1.7 Hz, =CH_2), 5.36 (dt, 1 H, ^2J = 2.3 Hz, ^3J = 1.2 Hz, =CH_2), 2.54 (t, 2 H, ^3J = 7.0 Hz, CH_2), 2.44 (t, 2 H, ^3J = 7.0 Hz, CH_2), 0.09 (s, 9 H, $SiMe_3$).

5-(trimethylsilyl)pent-4-enal, 18h. IR (film) ν/cm^{-1} 2720 (CHO), 1728 (C=O), 1686 (C=C) ; ^{1}H NMR δ (300 MHz, $CDCl_3$) 9.75 (t, 1 H, ^3J = 1.7 Hz, CHO), 6.00 (dt, 1 H, ^3J = 18.6 Hz, ^3J = 5.7 Hz, =CH), 5.66 (dt, 1 H, ^3J = 18.6 Hz, ^3J = 1.5 Hz, =CH), 2.51 (t, 2 H, ^3J = 7.0 Hz, CH_2), 2.41 (t, 2 H, ^3J = 7.0 Hz, CH_2), 0.02 (s, 9 H, $SiMe_3$).

(*Z*)-4-phenylhex-4-enal, 19i. IR (film) ν/cm^{-1} 3058, 3022, 2727 (CHO), 1724 (C=O), 1645 (C=C) ; ^{1}H NMR δ (300 MHz, $CDCl_3$) 9.70 (t, 1 H, ^3J = 1.7 Hz, CHO), 7.38-7.23 (m, 3 H, Ph), 7.16-7.13 (m, 2 H, Ph), 5.61 (qt, 1 H, ^3J = 6.8 Hz, ^3J = 1.3 Hz, =CH), 2.68 (tm, 2 H, ^3J = 7.7 Hz, CH_2), 2.42 (tm, 2 H, ^3J = 7.7 Hz, CH_2), 1.55 (dt, 3 H, ^3J = 6.8 Hz, ^5J = 1.2 Hz, CH_3). Anal. Calcd for $C_{12}H_{14}O$: C, 82.72 ; H, 8.10. Found : C, 82.34 ; H, 7.85.

(*E*)-4-methyl-5-phenylpent-4-enal, 20i. IR (film) ν/cm^{-1} 3055, 3025, 2727 (CHO), 1722 (C=O), 1648 (C=C) ; ^{1}H NMR δ (300 MHz, $CDCl_3$) 9.84 (t, 1 H, ^3J = 1.7 Hz, CHO), 7.36-7.29 (m, 3 H, Ph), 7.24-7.15

(m, 2 H, Ph), 6.31 (s, 1 H, =CH), 2.66 (tm, 2 H, ^3J = 7.4 Hz, CH_2), 2.51 (tm, 2 H, ^3J = 7.4 Hz, CH_2), 1.86 (m, 3 H, CH_3). Anal. Calcd for $C_{12}H_{14}O$: C, 82.72 ; H, 8.10. Found : C, 82.11 ; H, 8.01.

4-ethylhept-4-enal, 21j[30]. IR (film) ν/cm^{-1} 2718 (CHO), 1728 (C=O), 1644 (C=C) ; ^1H NMR δ (300 MHz, $CDCl_3$) 9.71 (t, 1 H, ^3J = 1.7 Hz, CHO), 5.04 (t, 1 H, ^3J = 7.1 Hz, =CH), 2.46 (t, 2 H, ^3J = 7.4 Hz, CH_2), 2.27 (t, 2 H, ^3J = 7.4 Hz, CH_2), 2.01-1.90 (m, 4 H, CH_2), 0.91 (t, 3 H, ^3J = 7.6 Hz, CH_3), 0.87 (t, 3 H, ^3J = 7.5 Hz, CH_3).

4,5-diphenylpent-4-enal, 22k. IR (film) ν/cm^{-1} 3057, 3022, 2720 (CHO), 1721 (C=O), 1644 (C=C) ; ^1H NMR δ (300 MHz, $CDCl_3$) 9.74 (t, 1 H, ^3J = 1.5 Hz, CHO), 7.35-7.27 (m, 3 H, Ph), 7.17-7.14 (m, 2 H, Ph), 7.10-7.06 (m, 3 H, Ph), 6.94-6.91 (m, 2 H, Ph), 6.51 (s, 1 H, =CH), 2.85 (td, 2 H, ^3J = 7.5 Hz, ^3J = 1.8 Hz, CH_2), 2.54 (td, 2 H, ^3J = 7.5 Hz, ^3J = 1.5 Hz, CH_2). Anal. Calcd for $C_{17}H_{16}O$: C, 86.41 ; H, 6.82. Found : C, 86.49 ; H, 6.93.

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