DOI: 10.1002/adsc.200606162

Efficient Access to Conjugated Dienones and Diene-diones from Propargylic Alcohols and Enolizable Ketones: A Tandem Isomerization/Condensation Process Catalyzed by the Sixteen-Electron Allyl-Ruthenium(II) Complex [Ru(η^3-2-C_3H_4Me)(CO)(dppf)][SbF_6]

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Received: April 5, 2006; Accepted: July 11, 2006

In memoriam of our friend and colleague Prof. Dr. Marcial Moreno-Mañas.

Supporting information for this article is available on the WWW under http://asc.wiley-vch.de/home/.

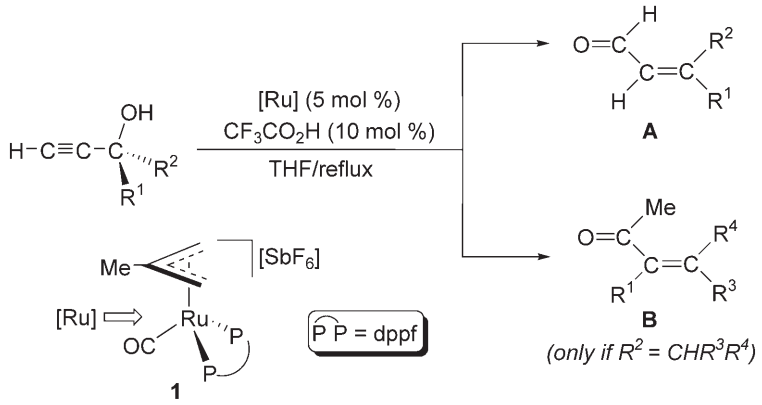
Abstract: A large variety of conjugated dienones $R^1R^2C{=}CHCH{=}C(R^3)C(=O)R^4$ and diene-diones $R^1R^2C{=}CHCH{=}C\{C(=O)R^3\}C(=O)R^4$ have been synthesized in high yields by reacting terminal propargylic alcohols $HC{\equiv}CCR^1R^2(OH)$ with enolizable ketones $R^3CH_2C(=O)R^4$ and β-dicarbonyl compounds $R^3C(=O)CH_2C(=O)R^4$, respectively. The process, which is catalyzed by the 16e$^-$ (η^3-allyl)-ruthenium(II) complex [Ru(η^3-2-C_3H_4Me)(CO)(dppf)][SbF_6] associated with CF_3CO_2H, involves the initial isomerization of the propargylic alcohol into the corresponding α,β-unsaturated aldehyde $R^1R^2C{=}CHCHO$ (Meyer–Schuster rearrangement) and subsequent aldol-type condensation.

Keywords: aldol condensation; dienones; enals; isomerization; propargylic alcohols; ruthenium

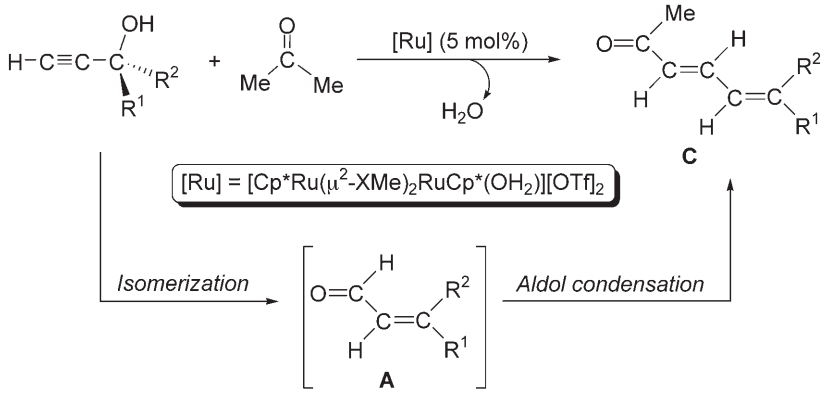
Introduction

Over the last decade the interest in ruthenium-catalyzed reactions directed to organic synthesis has spectacularly increased and a large number of new highly efficient synthetic approaches are nowadays well documented.[1–3] Among them, those proceeding in an atom economical manner, that is, all atoms of the reactants end up in the final product,[4] are probably the most promising.[1f] Isomerization reactions are typical examples of atom economical transformations since no by-products are generated. In this context, we have reported that the 16e$^-$ (η^3-allyl)-ruthenium(II) complex [Ru(η^3-2-C_3H_4Me)(CO)(dppf)][SbF_6] [dppf = 1,1′-bis(diphenylphosphino)ferrocene] (**1**),[5] associated with CF_3CO_2H, is a highly efficient catalyst for the isomerization of readily available terminal propargylic alcohols $HC{\equiv}CCR^1R^2(OH)$ into synthetically useful α,β-unsaturated carbonyl compounds (see Scheme 1).[6] Moreover, this catalytic system has proven to be highly chemoselective since it leads to the exclusive formation of enals **A** (Meyer–Schuster-type rearrangement) or enones **B** (Rupe-type rearrangement) depending on the nature of the propargylic alcohol substituents.[7]

Quite recently, Nishibayashi and co-workers have found that the treatment of terminal propargylic alcohols with acetone in the presence of a catalytic amount of the dinuclear species [Cp*Ru(μ^2-XMe)$_2$RuCp*(OH_2)][OTf]$_2$ (X = S, Se, Te) does not result in the expected propargylic substitution reaction,[8] leading instead to the formation of conjugated dienones **C** (see Scheme 2).[9] These highly unsaturated species result from the initial isomerization of the propargylic alcohol into the corresponding α,β-unsaturated aldehyde (**A**; Meyer–Schuster rearrangement), followed by aldol condensation between **A** and acetone. Nevertheless, it should be noted that, despite the great interest of catalytic tandem processes in synthesis,[10] the practical application of this unpre-



Scheme 1. Ru-catalyzed isomerization of propargylic alcohols.



Scheme 2. Coupling reaction of propargylic alcohols with acetone catalyzed by ruthenium.

cedented coupling process shows serious drawbacks mainly due to the low yields (<54%), the very limited scope of substrates, and the extremely long reaction times (*ca.* 70 h).[9] Apparently, all these limitations seem to arise from the low activity of the catalysts in the initial isomerization step, i.e., using 5 mol% of $[Cp^*Ru(\mu^2\text{-}SMe)_2RuCp^*(OH_2)][OTf]_2$ (10 mol% in Ru) HC≡CCHPh(OH) is isomerized into PhHC=CHCHO in only 15% yield after 20 h (1,2-dichloroethane, 60 °C).[9] This result contrasts with the behaviour shown by the $16e^-$ complex, $[Ru(\eta^3\text{-}2\text{-}C_3H_4Me)(CO)(dppf)][SbF_6]$ reported by us, which catalyzes the quantitative isomerization of HC≡CCHPh(OH) into PhHC=CHCHO after only 3.5 h in refluxing THF.[6]

With all these precedents in mind, and as part of our ongoing interest in the catalytic applications of the allyl-ruthenium(II) complex $[Ru(\eta^3\text{-}2\text{-}C_3H_4Me)(CO)(dppf)][SbF_6]$, we have investigated the potential of our catalytic system for the tandem isomerization/aldol condensation coupling processes. Thus, herein we describe a general and highly efficient synthetic approach to conjugated dienones $R^1R^2C{=}CHCH{=}C(R^3)C(=O)R^4$ and diene-diones $R^1R^2C{=}CHCH{=}C\{C(=O)R^3\}C(=O)R^4$ starting from readily accessible terminal propargylic alcohols HC≡$CCR^1R^2(OH)$ and commercially available enolizable ketones $R^3CH_2C(=O)R^4$ and β-dicarbonyl compounds $R^3C(=O)CH_2C(=O)R^4$, respectively.

Results and Discussion

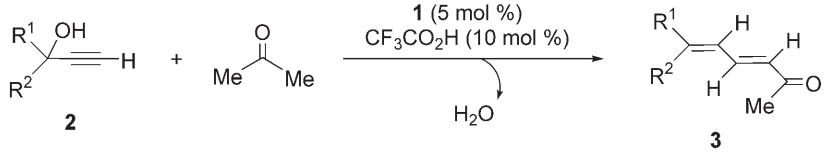
Tandem Isomerization/Aldol Condensation of Propargylic Alcohols with Enolizable Ketones: Synthesis of Conjugated Dienones

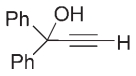
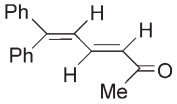
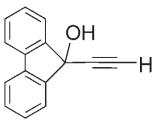
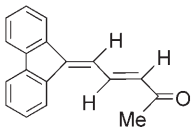
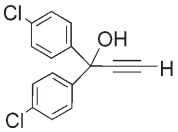
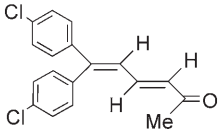
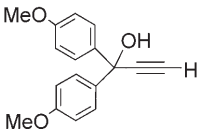
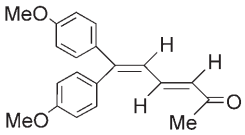
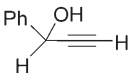
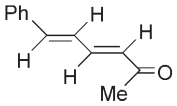
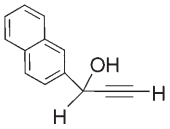
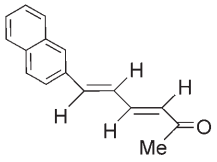
Following the optimal experimental conditions to promote the catalytic Meyer–Schuster isomerization of terminal propargylic alcohols HC≡$CCR^1R^2(OH)$ into enals $R^1R^2C{=}CHCHO$ by $[Ru(\eta^3\text{-}2\text{-}C_3H_4Me)(CO)(dppf)][SbF_6]$ (**1**) (i.e., 1.0 M solutions of the substrate in refluxing THF (undistilled) and a [substrate]:[**1**]:$[CF_3CO_2H]$ ratio = 20:1:2)[6] we have studied the reaction in the presence of 10 equivalents of acetone. Thus, in a preliminary experiment it was found that 1,1-diphenyl-2-propyn-1-ol (**2a**) is converted into (*E*)-6,6-diphenyl-3,5-hexadien-2-one (**3a**) in *ca.* 70% yield after 50 h. A significant rate enhancement was observed working without solvent (THF) and raising the

temperature to 75 °C (sealed tube). Thus, under these optimized reaction conditions ([**2a**]:[acetone]:[**1**]:[CF_3CO_2H] ratio = 20:200:1:2), an almost quantitative transformation of **2a** into dienone **3a** was achieved after 24 h (91 % isolated yield; see entry 1 in Table 1). The high catalytic activity shown by [Ru(η^3-2-C_3H_4Me)(CO)(dppf)][SbF_6]/CF_3CO_2H (5 mol % in Ru) contrasts with that of the dinuclear species [Cp*Ru(μ^2-XMe)$_2$RuCp*(OH_2)][OTf]$_2$ (X = S, Se, Te), i.e., using [Cp*Ru(μ^2-SMe)$_2$RuCp*(OH_2)][OTf]$_2$ (10 mol % in Ru) HC≡CCPh_2(OH) (**2a**) was transformed into (*E*)-Ph_2C=CHCH=C(H)COMe (**3a**) in only 53 % yield after 70 h in refluxing acetone (to be compared with entry 1).[9] It is also worthy of note that, in the absence of the ruthenium catalyst **1**, the treatment of isolated Ph_2C=CHCHO with acetone in the presence of 10 mol % of CF_3CO_2H gives (*E*)-6,6-diphenyl-3,5-hexadien-2-one (**3a**) in much lower yield after 24 h, i.e., 20 % *vs.* 91 % (entry 1 in Table 1). This fact clearly indicates that Lewis acid-ruthenium species, formed *in situ* from **1** and CF_3CO_2H, are the actual catalytic active species in the aldol condensation step.[11]

Other 1,1-diaryl (**2b–d**) and 1-aryl (**2e**, **f**) substituted propargylic alcohols also reacted with acetone, in the presence of **1**/CF_3CO_2H, to afford the corresponding conjugated (*E*)-dienones **3b–f** in moderate to good yields (59–91 %) after 20–72 h (see entries 2–6 in Table 1).[12] All the processes are chemo- and stereoselective since no propargylic substitution by-products, namely HC≡CCR^1R^2(CH_2COMe),[13] or *Z*-stereoisomers were observed by GC and NMR spectroscopy (see the Supporting Information). The stereoselectivity of this coupling process is in complete accord with the *E*-stereochemistry previously reported by

Table 1. Tandem isomerization/condensation of propargylic alcohols **2** with acetone catalyzed by [Ru]/CF_3CO_2H: Synthesis of conjugated dienones **3**.[a]



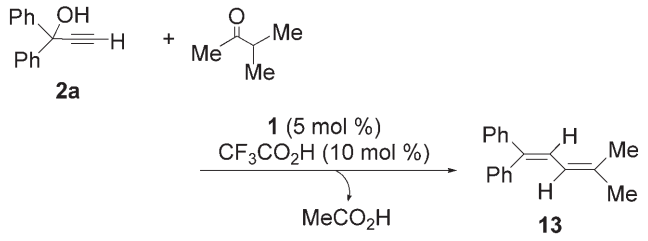
Entry	Substrate		Product		Time	Yield[b]
1		**2a**		**3a**	24 h	91 %[c]
2		**2b**		**3b**	24 h	89 %
3		**2c**		**3c**	20 h	86 %
4		**2d**		**3d**	72 h	90 %
5		**2e**		**3e**	24 h	64 %
6		**2f**		**3f**	24 h	59 %

[a] Reactions performed under N_2 atmosphere at 75 °C using 1 mmol of the corresponding propargylic alcohol and 10 mmol of acetone. [substrate]:[acetone]:[Ru]:[CF_3CO_2H] ratio = 20:200:1:2.
[b] Isolated yield.
[c] Dienone **3a** is obtained in 20 % yield when a 10 mol % of CF_3CO_2H is used in the absence of catalyst **1**.

Nishibayashi,[9] and with the stereoselective Meyer–Schuster rearrangement of monosubstituted propargylic alcohols observed by us.[6]

The following features are also worth noting: (*i*) As inferred by monitoring the reactions by GC, the rate-limiting step of this tandem process is in all cases the aldol condensation between the intermediate enal $R^1R^2C{=}CHCHO$ and acetone (the initial isomerization step proceeds quantitatively in 2–3 h). (*ii*) The nature of the aryl groups in the propargylic alcohol has a marked influence in the reaction rate, the introduction of an electron-releasing substituent in the aromatic ring slowing down the rate considerably (entry 4 *vs.* entries 1–3). And, (*iii*) although in all cases the complete consumption of the starting propargylic alcohol **2** as well as the intermediate enal has been observed by GC, some by-products are also formed starting from the monosubstituted alkynols **2e**, **f** decreasing the yields of dienones **3e**, **f** (entries 5 and 6 in Table 1).

In order to evaluate the scope of this catalytic tandem process, the behaviour of 1,1-diphenyl-2-propyn-1-ol (**2a**) towards a variety of enolizable ketones was explored under the standard reaction conditions described above ([**2a**]:[ketone]:[**1**]:[CF_3CO_2H] ratio = 20:200:1:2; 75 °C). Selected results are summarized in Table 2. Thus, both aromatic, i.e., acetophenones (entries 1–3) or propiophenones (entries 6–8), and aliphatic ketones, i.e., 2-butanone (entry 4), 3-pentanone (entry 5) or cyclohexanone (entry 9), were found to be suitable substrates for this transformation, the resulting dienones **4–12** being isolated in 79–94 % yield (quantitative conversions were in almost all cases observed by GC). As expected, when 2-butanone was used as substrate, the aldol condensation process between the intermediate 3,3-diphenyl-2-propenal and the ketone takes place selectively on the more activated CH_2 *vs.* CH_3 unit (entry 4). We also note that, as previously observed for **3a–f**, dienones **4–12** were in all cases stereoselectively obtained as the thermodynamically more stable *E* isomer.[12] The high yield formation of **4–12** clearly demonstrates the generality of this isomerization/aldol condensation tandem process. Nevertheless, it should be noted that attempts to generate $Ph_2C{=}CHCH{=}C(H)C(=O)$-*i*-Pr from propargylic alcohol $HC{\equiv}CCPh_2(OH)$ (**2a**) and $MeC(=O)$-*i*-Pr failed. Instead, following the same catalytic protocol, diene $Ph_2C{=}CHCH{=}CMe_2$ (**13**) was selectively formed (81 % isolated yield; 12 h) as the result of the formal olefination of the intermediate aldehyde $Ph_2C{=}CHCHO$ (see Scheme 3).[14]



Scheme 3. Formation of diene **13** from propargylic alcohol **2a** and 3-methyl-2-butanone.

Tandem Isomerization/Aldol Condensation of Propargylic Alcohols with β-Dicarbonyl Compounds: Synthesis of Conjugated Diene-Diones

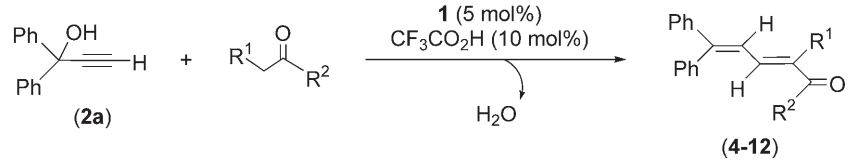
Aldol-type condensations between aldehydes (R^1CHO) and β-dicarbonyl compounds (1,3-diketones; $R^2C(=O)CH_2C(=O)R^3$) are well-known processes, the resulting ene-diones $R^1CH{=}C\{C(=O)R^3\}C(=O)R^4$ being important synthetic intermediates for the construction of five- and six-membered heterocyclic systems.[15] This fact prompted us to investigate the coupling processes between propargylic alcohols and β-dicarbonyl compounds catalyzed by $[Ru(\eta^3\text{-}2\text{-}C_3H_4Me)(CO)(dppf)][SbF_6]/CF_3CO_2H$. Representative results of this unprecedented synthetic approach for the preparation of conjugated diene-diones are shown in Table 3.[16] Thus, we have found that, following our standard protocol, alkynols **2a–d** smoothly react with 2,4-pentanedione (entries 1–4), 3,5-heptanedione (entries 5–7) or 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (entry 8) to afford diene-diones **14–16** in excellent yields (84–95 %; quantitative GC yields). The structures of all these compounds were confirmed by IR and NMR spectroscopy, mass spectra and elemental analyses (see the Supporting Information). Remarkably, with the exception of the propargylic alcohol **2d**, which requires 11 h due to the presence of the electron-releasing methoxy substituents (entry 4), all these reactions proceed with a very high rate (1–3 h) conferring to this coupling process genuine potential for practical application in synthetic organic chemistry.

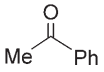
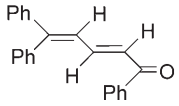
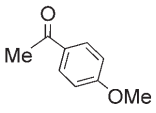
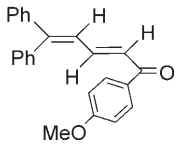
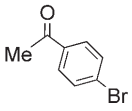
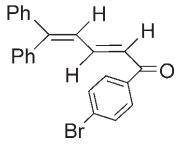
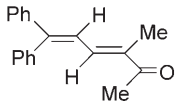
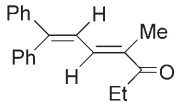
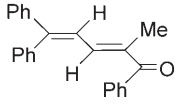
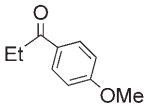
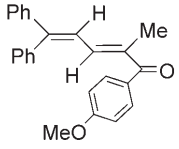
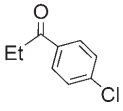
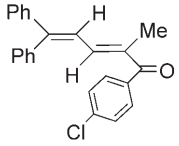
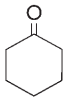
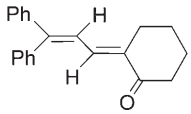
Related coupling reactions also occur starting from the highly activated methyl acetoacetate (Scheme 4). Nevertheless, the products **17** are in all cases obtained as a non-separable mixture of the corresponding *E*/*Z* stereoisomers. It should be also noted that no reaction was observed between **2a** and dimethyl malonate (the isomerization product 3,3-diphenyl-2-propenal is exclusively formed), pointing out that the presence of at least one keto function is indispensable to promote this coupling process.

Conclusions

In this work a new highly efficient catalytic synthetic approach to conjugated dienones and diene-diones starting from readily accessible propargylic alcohols

Table 2. Tandem isomerization/condensation of propargylic alcohol **2a** with different ketones catalyzed by [Ru]/CF_3CO_2H: Synthesis of conjugated dienones **4**–**12**.[a]

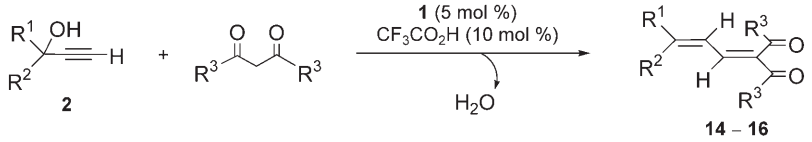


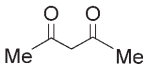
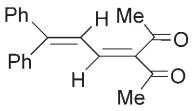
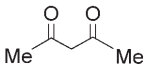
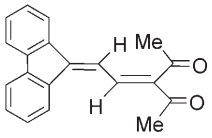
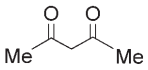
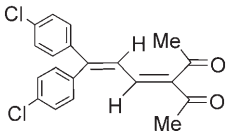
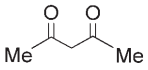
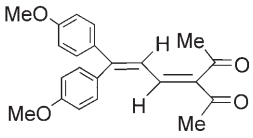
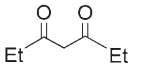
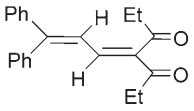
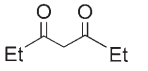
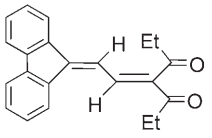
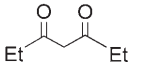
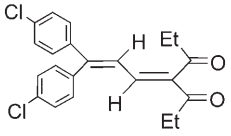
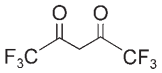
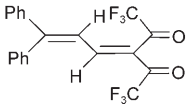
Entry	Ketone	Product		Time	Yield[b]
1			**4**	20 h	91 %
2			**5**	24 h	90 %
3			**6**	7 h	85 %
4			**7**	24 h	94 %
5			**8**	7 h	93 %
6			**9**	3 h	88 %
7			**10**	12 h	86 %
8			**11**	12 h	79 %
9			**12**	7 h	83 %

[a] Reactions performed under a N_2 atmosphere at 75 °C using 1 mmol of **2a** and 10 mmol of the corresponding ketone. [**2a**]:[ketone]:[Ru]:[CF_3CO_2H] ratio = 20:200:1:2.
[b] Isolated yield.

and commercially available enolizable ketones is described. This coupling reaction, which consists of a tandem isomerization/aldol condensation process, is catalyzed by the $16e^-$ complex [Ru(η^3-2-C_3H_4Me)(CO)(dppf)][SbF_6] (**1**) in the presence of CF_3CO_2H. The catalytic approach described herein is much more efficient than that using the dinuclear species [Cp*Ru(μ^2-XMe)$_2$RuCp*(OH_2)][OTf]$_2$ (X = S, Se, Te) recently reported.[9] In addition, we have also shown that this catalytic route is quite general, being applicable to a variety of aryl and alkyl ketones as well as β-dicarbonyl compounds, in contrast to that

Table 3. Tandem isomerization/condensation of propargylic alcohols **2** with β-dicarbonyl compounds catalyzed by [Ru]/CF_3CO_2H: synthesis of conjugated diene-diones **14–16**.[a]



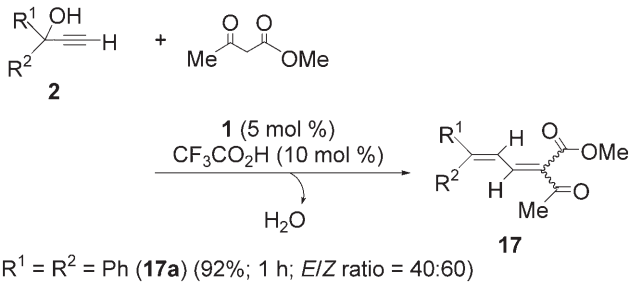
Entry	Substrate	Diketone	Product		Time	Yield[b]
1	**2a**			**14a**	2 h	87 %
2	**2b**			**14b**	3 h	90 %
3	**2c**			**14c**	1 h	95 %
4	**2d**			**14d**	11 h	93 %
5	**2a**			**15a**	1 h	92 %
6	**2b**			**15b**	2 h	86 %
7	**2c**			**15c**	1 h	84 %
8	**2a**			**16**	3 h	90 %

[a] Reactions performed under N_2 atmosphere at 75 °C using 1 mmol of the corresponding propargylic alcohol and 10 mmol of the appropriate diketone. [substrate]:[diketone]:[Ru]:[CF_3CO_2H] ratio = 20:200:1:2.
[b] Isolated yield.

reported previously which is limited to the use of acetone. In summary, selectivity, atom economy, time/cost saving and experimental simplicity, concepts to be assembled by modern academic and industrial synthetic chemist to reach the maximum of efficiency, are clearly represented in this *one-pot* and *solvent-free* catalytic transformation. In fact, we are confident that the high yields and remarkable stereoselectivity found using [Ru(η^3-2-C_3H_4Me)(CO)(dppf)][SbF_6]/CF_3CO_2H will be of interest to a wide range of synthetic organic chemists, may be including its use in their future research programmes.

Experimental Section

All reagents were obtained from commercial suppliers and used without further purification with the exception of complex [Ru(η^3-2-C_3H_4Me)(CO)(dppf)][SbF_6] (**1**)[5] and propargylic alcohols **2c**, **d** and **f**[17] which were prepared by follow-



$R^1 = R^2 =$ Ph (**17a**) (92%; 1 h; *E*/*Z* ratio = 40:60)

$R^1 = R^2 = 4\text{-}ClC_6H_4$ (**17c**) (95%; 1 h; *E*/*Z* ratio = 45:55)

$R^1 = R^2 = 4\text{-}MeOC_6H_4$ (**17d**) (88%; 9 h; *E*/*Z* ratio = 40:60)

Scheme 4. Coupling of propargylic alcohols **2** with methyl acetoacetate.

ing the methods reported in the literature. Gas chromatographic (GC) measurements were made on a Hewlett–Packard HP6890 instrument using a HP-INNOWAX cross-linked polyethylene glycol (30 m, 250 μm) or a Supelco Beta-Dex™ 120 (30 m, 250 μm) column. GC/MS measurements were performed on a Agilent 6890N instrument coupled to a 5973 mass detector (70 eV electron impact ionization) using an HP-1 MS column.

General Procedure for the Catalytic Tandem Isomerization/Aldol Condensation Reactions

The catalyst $[Ru(\eta^3\text{-}2\text{-}C_3H_4Me)(CO)(dppf)][SbF_6]$ (**1**) (0.049 g, 0.05 mmol), the corresponding propargylic alcohol **2a–f** (1 mmol), the appropriate enolizable ketone or diketone (10 mmol) and CF_3CO_2H (7.4 μL, 0.1 mmol) were introduced into a sealed tube under a nitrogen atmosphere. The reaction mixture was then heated at 75 °C for the indicated time (see Tables 1–3 and Scheme 3-4; the course of the reaction was monitored by regular sampling and analysis by GC or GC/MS). After removal of volatiles under vacuum, the residue was purified by column chromatography (silica gel) using a mixture EtOAc/hexane (1:10) as eluent (with the exception of compound **13** which was eluted with pure hexane).

Supporting Information

Characterization data for compounds **3**–**17**. Copy of the $^{13}C\{^1H\}$ NMR spectra of dienones **7** and **8**. Details of the X-ray diffraction analysis of compounds **5** and **9**.

Acknowledgements

We are indebted to the Ministerio de Ciencia y Tecnología (MCyT) of Spain (Project BQU2003–00255) and the Gobierno del Principado de Asturias (FICYT Project IB05–035) for financial support. S.E.G.G and V.C. thank the MCyT and the European Social Fund for the award of a Ph.D. grant and a "Ramón y Cajal" contract, respectively.

References

[1] For reviews covering this field see: a) C. Bruneau, P. H. Dixneuf, *Chem. Commun.* **1997**, 507–512; b) T. Naota, H. Takaya, S.-I. Murahashi, *Chem. Rev.* **1998**, *98*, 2599–2660; c) B. M. Trost, F. D. Toste, A. B. Pinkerton, *Chem. Rev.* **2001**, *101*, 2067–2096; d) T. M. Trnka, R. H. Grubbs, *Acc. Chem. Res.* **2001**, *34*, 18–29; e) V. Ritleng, C. Sirlin, M. Pfeffer, *Chem. Rev.* **2002**, *102*, 1731–1769; f) B. M. Trost, M. U. Frederickson, M. T. Rudd, *Angew. Chem. Int. Ed.* **2005**, *44*, 6630–6666; g) C. Bruneau, P. H. Dixneuf, *Angew. Chem. Int. Ed.* **2006**, *45*, 2176–2203.

[2] For books covering this field see: a) *Ruthenium in Organic Synthesis*, (Ed.: S.-I. Murahashi), Wiley-VCH, Weinheim, **2004**; b) *Ruthenium Catalysts and Fine Chemistry*, (Eds.: C. Bruneau, P. H. Dixneuf), Springer, Berlin, **2004**.

[3] *Ruthenium Catalyzed Processes*, (Guest Ed.: J. Gimeno), in: *Curr. Org. Chem.* **2006**, 10, 113–225 (a thematic issue devoted to this topic).

[4] For reviews on atom-economical processes see: a) B. M. Trost, *Science* **1991**, *254*, 1471–1477; b) B. M. Trost, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 259–281; c) B. M. Trost, *Acc. Chem. Res.* **2002**, *35*, 695–705.

[5] The synthesis of complex **1**, as well as its application in catalytic propargylic substitution processes, has been reported in: V. Cadierno, J. Díez, S. E. García-Garrido, J. Gimeno, *Chem. Commun.* **2004**, 2716–2717.

[6] V. Cadierno, S. E. García-Garrido, J. Gimeno, *Adv. Synth. Catal.* **2006**, *348*, 101–110.

[7] Complex **1** represents the first example of a ruthenium catalyst for the Rupe-type rearrangement of propargylic alcohols. In contrast, other ruthenium complexes, such as $[Ru(\eta^3\text{-}2\text{-}C_3H_4Me)_2(dppe)]/PhCO_2H$ and $[RuCl(\eta^5\text{-}C_5H_5)(PMe_3)_2]$, are known to promote efficiently the Meyer–Schuster rearrangement: a) M. Picquet, C. Bruneau, P. H. Dixneuf, *Chem. Commun.* **1997**, 1201–1202; b) M. Picquet, A. Fernández, C. Bruneau, P. H. Dixneuf, *Eur. J. Org. Chem.* **2000**, 2361–2366; c) T. Suzuki, M. Tokunaga, Y. Wakatsuki, *Tetrahedron Lett.* **2002**, *43*, 7531–7533.

[8] Y. Nishibayashi, S. Uemura, *Curr. Org. Chem.* **2006**, *10*, 135–150, and references cited therein.

[9] G. Onodera, H. Matsumoto, Y. Nishibayashi, S. Uemura, *Organometallics* **2005**, *24*, 5799–5801.

[10] For a recent review see: D. E. Fogg, E. N. dos Santos, *Coord. Chem. Rev.* **2004**, *248*, 2365–2379.

[11] We also note that, while 1,1-diphenyl-2-propyn-1-ol (**2a**) remains unreacted in the absence of **1**, only the isomerization of **2a** into 3,3-diphenyl-2-propenal ($Ph_2C{=}CHCHO$) exclusively occurs when CF_3CO_2H is not present in the reaction media.

[12] The stereochemistry of the C=C double bond in compounds **1–6** was clearly assessed by ^1H NMR spectroscopy (see the Supporting Information). In the case of dienones **7–12** it was elucidated by measuring the $^3J_{CH}$ coupling constants ($^1H\text{-}C{=}C\text{-}^{13}C$) of the carbonyl and methyl (or methylenic) groups [$^3J_{CH} = 6–8$ (*trans*) *vs.* 2–4 Hz (*cis*)]; see: U. Vögeli, W. V. Philipsborn, *Org. Magn. Reson.* **1975**, *7*, 617–627). Moreover, the structures of dienones **5** and **9** were unambiguously con-

firmed by single-crystal X-ray diffraction methods (details are given in the Supporting Information).
[13] Although complex **1** is known to be an active catalyst in propargylic substitution processes of alkynols with alcohols (see ref.[5]), formation of 5-hexyn-2-ones HC≡CCR^{1}R^2(CH$_2$COMe) was not observed (see ref.[8]). In fact, we have found that, even in the absence of CF_3CO_2H, complex **1** is not able to catalyze the propargylic substitution of propargylic alcohols **2** with acetone or related carbonyl compounds, the only products formed in these reactions being the corresponding enals derived from the Meyer–Schuster rearrangement of the alkynols.
[14] The mechanism, as well as the scope, of such an unusual olefination reaction is still unknown, being actually under active investigation.
[15] See, for example: a) M. Iwata, S. Emoto, *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1369–1374; b) K. Fuschs, L. A. Paquette, *J. Org. Chem.* **1994**, *59*, 528–532; c) M. Bao, Y. Zhang, J. Wang, *Synth. Commun.* **1996**, *26*, 3025–3028; d) V. Henryon, L. W. Liu, R. Lopez, J. Prunet, J. P. Férézou, *Synthesis* **2001**, 2401–2414; e) S. Onitsuka, H. Nishino, K. Kurosawa, *Tetrahedron Lett.* **2000**, *41*, 3149–3152; f) R. Antonioletti, P. Bovicelli, S. Malancona, *Tetrahedron* **2002**, *58*, 589–596; g) C. Simon, T. Constantieux, J. Rodriguez, *Eur. J. Org. Chem.* **2004**, 4957–4980, and references cited therein.
[16] The catalytic coupling of propargylic alcohols with cyclic 1,3-diketones to yield chromen-5-ones and pyran-5-ones has been recently reported. The first step of this coupling, which is catalyzed by the dinuclear ruthenium species [Cp*RuCl(μ^2-SR)$_2$RuCp*Cl] (R = Me, *n*-Pr, *i*-Pr), involves a propargylic substitution process: Y. Nishibayashi, M. Yoshikawa, Y. Inada, M. Hidai, S. Uemura, *J. Org. Chem.* **2004**, *69*, 3408–3412.
[17] M. M. Midland, *J. Org. Chem.* **1975**, *40*, 2250–2252.

