Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron
Tetrahedron 63 (2007) 11803–11808

$ReBr(CO)_5$-catalyzed sequential addition–cyclization of 1,3-dicarbonyl compounds with electron-deficient internal alkynes affording trisubstituted 2*H*-pyran-2-ones

Wen-Guo Zhao and Ruimao Hua*

Department of Chemistry, Tsinghua University, Innovative Catalysis Program, Key Laboratory of Organic Optoelectronics and Molecular Engineering of Ministry of Education, Beijing 100084, China

Received 27 June 2007; revised 5 September 2007; accepted 21 September 2007
Available online 23 September 2007

Abstract—The reaction of 1,3-dicarbonyl compounds such as acetoacetate, acetylacetone, dibenzoylmethane, and benzoylacetate with electron-deficient internal alkynes in the presence of catalytic amount of $ReBr(CO)_5$ in toluene under neutral conditions resulted in the formation of 4,5,6-trisubstituted 2*H*-pyran-2-ones in moderate to high yield. The reaction took place via a two-step sequence including the rhenium(I)-catalyzed addition of the activated methylenes to alkynes to give enolic 2-alkenyl derivatives, and subsequently dealcoholic cyclization to form 2*H*-pyran-2-one derivatives.
© 2007 Elsevier Ltd. All rights reserved.

1. Introduction

Catalytic C–H bond activation and its addition to unsaturated hydrocarbons to construct C–C bond is one of the most attractive and valuable reactions in organic synthesis.[1] Among them, the catalytic addition of activated methylenes in 1,3-dicarbonyl compounds to alkynes in neutral conditions has attracted a great deal of focus. It has been reported that Au(I),[2] Ni(II)/Yb(III),[3] Pd(II),[4a] and Pd(II)/Yb(III)[4b] complexes may serve as efficient catalyst systems for the intramolecular cyclic addition of C–H bonds to alkynes. In contrast, the examples of the intermolecular addition reactions are rather limited. Only two catalyst systems, $In(OTf)_3$[5] and $[ReBr(CO)_3(THF)]_2$[6] have been recently reported to catalyze the intermolecular addition of 1,3-dicarbonyl compounds to terminal alkynes to give (enolic) 2-alkenyl derivatives. Moreover, further synthetic applications of such type of intermolecular addition reactions remain to be developed.

Development of the synthetic methods for substituted 2*H*-pyran-2-ones is one of the important and interesting research topics in organic chemistry, because 2*H*-pyran-2-one derivatives are not only valuable materials in diverse organic synthesis,[7] but also exhibit important pharmacological activities.[8] Therefore, many synthetic methods for the synthesis of the functionalized 2*H*-pyran-2-ones have been established.[9]

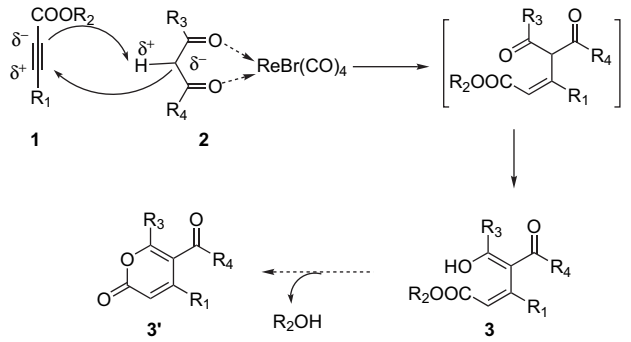
Recently we have been interested in the application of low-valent rhenium complexes in organic synthesis, and have demonstrated that $ReBr(CO)_5$ can catalyze the activation of E–H (E=O,[10] Si[11]) bond and for its addition to alkynes or alkenes. We have also found that $ReBr(CO)_5$ can effectively activate C–H bond of active methylene compounds toward the nucleophilic attack of carbonyl compounds.[12] As a continuation of this research, we have designed a new rhenium(I)-catalyzed synthetic route to trisubstituted 2*H*-pyran-2-ones utilizing the reaction of 1,3-dicarbonyl compounds with propiolates. This synthetic route includes the rhenium(I)-catalyzed addition of activated methylenes of 1,3-dicarbonyl compounds to propiolates to give the enolic adduct **3**,[13] which might serve as precursor to form the substituted 2*H*-pyran-2-one (**3′**) by dealcoholic reaction (Scheme 1).

2. Results and discussion

On the basis of the considerations above, we performed the reaction of phenyl propiolate **1a** and **1b** with 1,3-dicarbonyl compounds to determine the catalytic reaction conditions required for the formation of **3** in the presence of rhenium complexes. As shown in Table 1, when a mixture of **1a** (1.0 mmol), methyl acetoacetate (1.0 mmol) (**2a**), and $ReBr(CO)_5$ (0.005 mmol) in toluene (1.0 mL) under an air

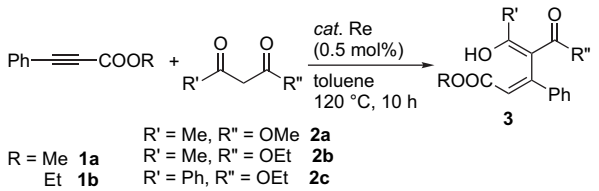
Keywords: 1,3-Dicarbonyl compounds; Internal electron-deficient alkynes; 2*H*-Pyran-2-ones; Rhenium complexes.
* Corresponding author. Tel./fax: +86 10 62792596; e-mail: ruimao@mail.tsinghua.edu.cn

0040–4020/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2007.09.038



Scheme 1.

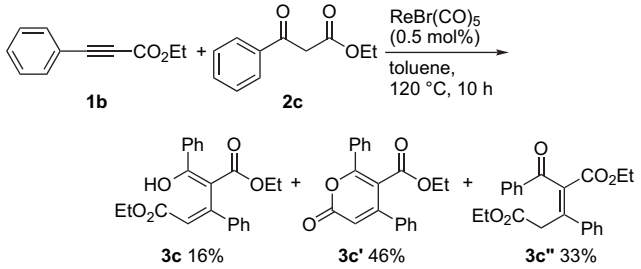
Table 1. Rhenium-catalyzed addition of phenyl propiolate with 1,3-dicarbonyl compound[a]



Entry	Catalyst	R	R′	R″		Yield[b] (%)
1	$ReBr(CO)_5$	Me	Me	OMe	**3a**	84
2	$ReBr(CO)_5$	Et	Me	OEt	**3b**	87
3	$ReBr(CO)_5$	Et	Ph	OEt	**3c**	16[c]
4	$ReCl(CO)_5$	Me	Me	OMe	**3a**	(61)
5	$Re_2(CO)_{10}$	Me	Me	OMe	**3a**	(21)
6	$CpRe(CO)_3$	Me	Me	OMe	**3a**	(<5)
7	$(NH_4)ReO_4$	Me	Me	OMe	**3a**	(<5)

[a] The reaction was carried out using 1.0 mmol of **1**, 1.0 mmol of **2**, and 0.005 mmol of catalyst in toluene (1.0 mL) at 120 °C for 10 h.
[b] Isolated yield. Number in the parenthesis was GC yield.
[c] NMR yield.

atmosphere was heated at 120 °C for 10 h, the enolic adduct **3a** was isolated in 84% yield (entry 1). The formation of the isomer of **3** and the corresponding cyclic product **3′** in trace amount (<5%) was also observed by GC and GC–MS analyses of the reaction mixture. The reaction of **1b** with **2b** resulted in the similar result (entry 2). However, under the same conditions, the reaction of **1b** with ethyl benzoylacetate (**2c**) afforded a mixture of products (Scheme 2). ^1H NMR of the reaction mixture disclosed that the corresponding enolic adduct **3c** was formed in only 16% yield (entry 3), and the predominant product was the heteroannulation product, 4,6-diphenyl-5-ethoxycarbonyl-2*H*-pyran-2-one (**3c′**) (46% NMR yield). Another considerable amount of product



Scheme 2.

was assigned as **3c″**. Unfortunately, attempts to isolate these products in analytical samples by column chromatography or preparative TLC (silica) failed.

The catalytic activities of other rhenium complexes in the reaction of **1a** with **2a** were also examined. $ReCl(CO)_5$ showed a moderate catalytic activity affording **3a** in 61% GC yield (entry 4). Compound **3a** was obtained in 21% GC yield when $Re_2(CO)_{10}$ was used as catalyst (entry 5). $CpRe(CO)_3$ and $(NH_4)ReO_4$ displayed very low catalytic activities for the same addition reaction. In these cases, the starting materials were recovered (entries 6 and 7).

It is of interest to note that, in contrast to the recent results of Taran and co-workers where the reaction of 1,3-dicarbonyl compounds with substituted propiolates in the presence of catalytic amount of phosphine as catalyst afforded α-(*gem*-dicarbonyl) acrylates,[14] our catalytic system gave only C–C bond formation at the carbon bonding to ester group in **1** to generally form the β-(*gem*-dicarbonyl) acrylates **3**.

Moreover, the trans-addition of C–H bond to **1** forming the *Z*-configuration in the acrylate moiety of **3** could be evidenced by its easy subsequent dealcoholic cyclization producing the six-membered cycle, 2*H*-pyran-2-one derivative (vide infra). In addition, the structure of **3a** (shown in Fig. 1) was finally ascertained by single-crystal X-ray diffraction analysis to confirm the regio- and stereoselectivity of the addition reaction.[15]

Table 2 summarizes the reaction results of the substituted propiolates with 1,3-dicarbonyl compounds in the presence of $ReBr(CO)_5$. The formation of enolic adduct **3** and/or 2*H*-pyran-2-one derivative **3′** depended on the structure of the reactants. The reaction of **1a** with acetylacetone (**2d**) at 120 °C for 24 h gave a mixture of the corresponding enolic adduct **3d** and trisubstituted 2*H*-pyran-2-one **3d′** in 47% and 32% isolated yields, respectively (Table 2, entry 1). A similar result was obtained in the reaction of **1b** with **2d** (Table 2, entry 2). A shorter reaction time lowered the

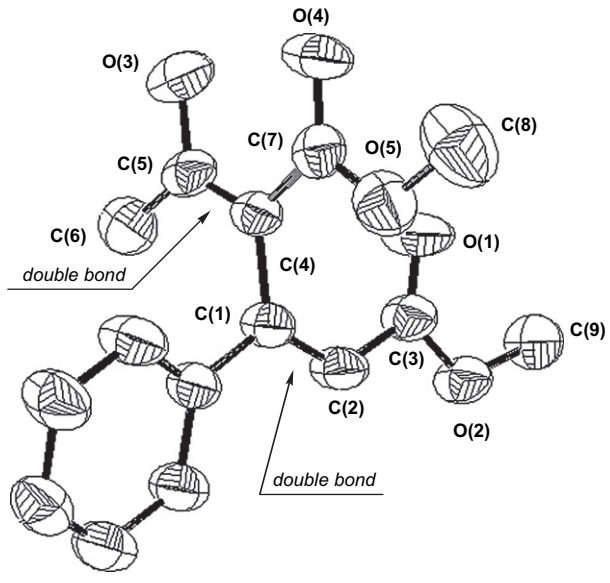
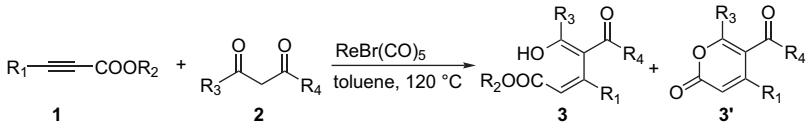
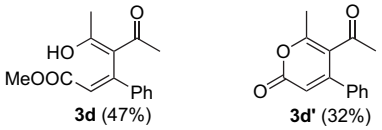
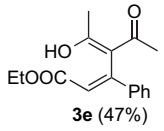
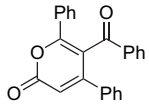
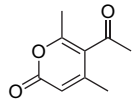
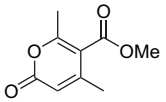
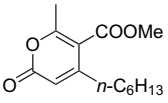
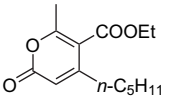
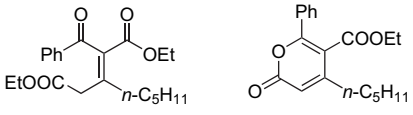


Figure 1. Molecular structure of **3a**. Hydrogen atoms are omitted for clarity.

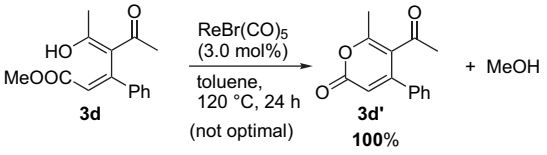
Table 2. Rhenium-catalyzed addition of propiolate derivative with 1,3-dicarbonyl compound[a]



Entry	$ReBr(CO)_5$ (equiv)	R_1	R_2	R_3	R_4	Time (h)	Product/yield[b] (%)
1	0.03	Ph	Me	Me	Me	24	 **3d** (47%) **3d'** (32%)
2	0.03	Ph	Et	Me	Me	24	 **3e** (47%) **3d′** (37%)
3	0.01	Ph	Me	Ph	Ph	15	 **3f'** (65%)
4	0.01	Me	Me	Me	Me	15	 **3g'** (58%)
5	0.005	Me	Me	Me	OMe	10	 **3h'** (94%)
6	0.005	n-C_6H_{13}	Me	Me	OMe	10	 **3i'** (74%)
7	0.005	n-C_5H_{11}	Et	Me	OEt	10	 **3j'** (52%)
8	0.005	n-C_5H_{11}	Et	Ph	OEt	10	 **3k"** (48%) **3k'** (33%)

[a] The reaction was carried out using 1.0 mmol of **1** and 1.0 mmol of **2** in toluene (1.0 mL) at 120 °C.
[b] Isolated yield.

formation of **3′**. For example, if the reaction of **1a** with **2d** was performed for 10 h, **3d** was isolated in 55% yield (59% GC yield) while **3d′** was obtained in only 3% yield (6% GC yield), indicating that increasing the reaction time from 10 h to 24 h resulted in the substantial increase in **3d′** formation. In addition, the formation of **3d′** resulting from the dealcoholic reaction of **3d** was confirmed by heating a solution of **3d** under similar reaction conditions to give quantitative **3d′** as shown in Scheme 3.

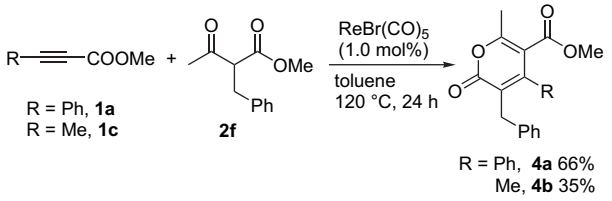


Scheme 3.

For the examined reactions, the reaction of **1a** with dibenzoylmethane (**2e**), methyl 2-butynoate (**1c**) with **2d**, **1c** with **2a**, methyl 2-nonynoate (**1d**) with **2a**, and methyl 2-octynoate (**1e**) with **2b** gave good to high selectivity for the formation of the corresponding 2*H*-pyran-2-one derivatives even in shorter reaction times (Table 2, entries 3–7). In the reaction between **1e** and **2c**, only a small amount of the enolic adduct was observed. For this reaction another addition–rearrangement product **3k″** and substituted

2*H*-pyran-2-one **3k′** were isolated in 48% and 33% yields, respectively (Table 2, entry 8).

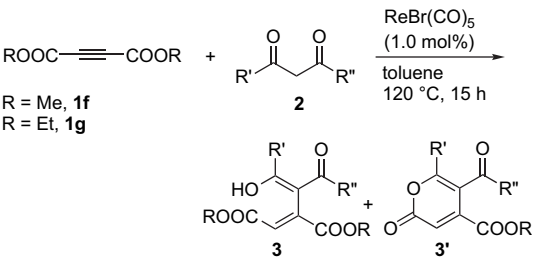
In an attempt to synthesize tetrasubstituted 2*H*-pyran-2-one derivatives by the present reaction, the reactions of **1a**, **1c** with methyl 2-benzylacetoacetate (**2f**) were examined. The addition–cyclization reactions also proceeded to furnish the corresponding tetrasubstituted 2*H*-pyran-2-one derivatives **4a** and **4b** in 66% and 35% isolated yields, respectively (Scheme 4).



Scheme 4.

Unlike the reactions of substituted propiolates with 1,3-dicarbonyl compounds, which gave **3** and/or **3′** as major products, the reactions of acetylenedicarboxylates with 1,3-dicarbonyl compounds were sluggish, resulting in the formation of complex mixtures. The corresponding products **3** and **3′** were formed in the moderate total yields only, and were isolated in low yields (Table 3). The major side-reaction was the cyclotrimerization of acetylenedicarboxylates disclosed by GC and GC–MS analyses of the reaction mixtures.

Table 3. Rhenium-catalyzed addition of acetyldicarboxylate with 1,3-dicarbonyl compound



Entry	R	R′	R″	Isolated yield (%)			
				3		**3′**	
1	Me	Me	Me	**3l**	23	**3l′**	26
2	Et	Me	Me	**3m**	23	**3m′**	—
3	Me	Me	OMe	**3n**	—	**3n′**	20
4	Me	Me	OEt	**3o**	—	**3o′**	18

3. Conclusions

We have developed the $ReBr(CO)_5$-catalyzed addition reaction of activated methylene compounds with electron-deficient internal alkynes to afford enolic adducts and/or substituted 2*H*-pyran-2-ones. The selectivity for the formation of enolic adducts or 2*H*-pyran-2-one derivatives depended on the structure of both the reactants. Enolic adducts can be easily converted into 2*H*-pyran-2-one derivatives by dealcoholic cyclization under our reaction conditions. Therefore, this study provides a new and practical one-pot synthesis of 4,5,6-trisubstituted 2*H*-pyran-2-ones from easily available 1,3-dicarbonyl compounds and electron-deficient internal alkynes via a sequential addition–cyclization reaction.

4. Experimental section

4.1. General methods

All the reactions were carried out under air atmosphere. Solvents and all reagents were used as received. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 300 and 75 MHz, respectively. The chemical shifts (δ) were referenced to TMS or solvent resonance. GC–MS was obtained using electron ionization (EI). High-resolution mass spectra and elemental analysis data were recorded in the Department of Chemistry of Peking University.

4.2. Typical procedure for the reaction of methyl phenyl propiolate (1a) with acetylacetone (2d) (Table 2, entry 1)

A mixture of **1a** (106.2 mg, 1.0 mmol), **2d** (103 μl, 1.0 mmol), and $ReBr(CO)_5$ (12.2 mg, 0.03 mmol) in toluene (1.0 mL) was heated with stirring in a thick-walled Pyrex sealed tube at 120 °C for 24 h. After cooling, the reaction was diluted with toluene to 1.5 mL and *n*-$C_{22}H_{46}$ (28.0 mg, as internal standard) was added. The resulting mixture was then analyzed by GC and GC–MS. Volatiles were removed in vacuum and the residue was subjected to isolation by preparative TLC (silica, eluted with a 3:1 petroleum ether–diethyl ether mixture). Compounds **3d** and **3d′** as pale yellow solids were isolated in 121.0 mg (0.47 mmol, 47%), and 74.0 mg (0.32 mmol, 32%), respectively, after removal of the solvent.

The selected spectroscopic data for new products are shown below. The characterization data for known products **3c′**, **3d′**, **3e**, **3g′**, **3h′**, **3l** and the copies of ^1H, ^{13}C NMR for all the products are provided in Supplementary data.

4.3. Characterization data for new products

4.3.1. (*Z*)-4-Acetyl-3-phenyl-2-pentene-1,5-dicarboxylic acid dimethyl 3a. Pale yellow solid, mp 73–75 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 13.0 (s, 1H), 7.52–7.36 (m, 5H), 6.43 (s, 1H), 3.72 (s, 3H), 3.65 (s, 3H), 1.77 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.1, 172.0, 166.0, 149.7, 139.7, 129.6, 128.7, 126.9, 119.6, 100.5, 51.8, 51.4, 19.6; GC–MS *m*/*z* (% rel inten.) 244 (M^+-32, 84), 229 (8), 216 (100), 201 (47), 184 (81), 171 (14), 156 (14), 145 (8), 128 (22), 115 (36), 102 (13), 77 (8). Anal. Calcd for $C_{15}H_{16}O_5$: C, 65.22; H, 5.80. Found: C, 65.01; H, 6.01.

4.3.2. (*Z*)-4-Acetyl-3-phenyl-2-pentene-1,5-dicarboxylic acid diethyl 3b. Pale yellow viscous oil; ^1H NMR (300 MHz, $CDCl_3$) δ 13.1 (s, 1H), 7.50–7.35 (m, 5H), 6.39 (s, 1H), 4.22–4.10 (2×q, 4H), 1.78 (s, 3H), 1.30 (t, 3H, J=7.0 Hz), 1.08 (t, 3H, J=7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.9, 171.6, 165.8, 149.4, 140.1, 129.4, 128.7, 126.9, 126.6, 120.2, 101.0, 60.5, 60.1, 19.6, 14.3, 14.0;

GC–MS *m/z* (% rel inten.) 258 (M^+-46, 99), 243 (3), 230 (100), 213 (43), 201 (63), 184 (79), 171 (26), 160 (18), 145 (4), 128 (23), 115 (50), 103 (10), 89 (8), 77 (9). Anal. Calcd for $C_{17}H_{20}O_5$: C, 67.09; H, 6.62. Found: C, 67.27; H, 6.57.

4.3.3. (*Z*)-4-Benzoyl-3-phenyl-2-pentene-1,5-dicarboxylic acid diethyl 3c. ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.6 (s, 1H), 6.26 (s, 1H); GC–MS *m/z* (% rel inten.) 366 (M^+, 5), 320 (75), 292 (75), 263 (74), 247 (44), 220 (35), 191 (25), 147 (7), 105 (100), 77 (31).

4.3.4. (*Z*)-2-Benzoyl-3-phenyl-2-pentene-1,5-dicarboxylic acid diethyl 3c″. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.25 (q, 2H, J=7.0 Hz), 4.06 (s, 2H), 3.93 (q, 2H, J=7.0 Hz); GC–MS *m/z* (% rel inten.) 366 (M^+, 4), 320 (82), 292 (100), 274 (24), 264 (52), 247 (66), 220 (30), 191 (40), 105 (64), 77 (35).

4.3.5. Methyl (*Z*)-4-acetyl-5-oxo-3-phenyl-2-hexenoate 3d. Pale yellow solid, mp 56–57 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 16.7 (s, 1H), 7.54–7.42 (m, 5H), 6.58 (s, 1H), 3.74 (s, 3H), 1.91(s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.9 (2C), 166.0, 151.0, 139.0, 130.2, 129.1, 127.0, 119.9, 110.6, 51.6, 23.4 (2C); GC–MS *m/z* (% rel inten.) 260 (M^+, 32), 245 (1), 229 (13), 217 (51), 201 (100), 185 (42), 171 (16), 158 (19), 129 (18), 115 (45), 105 (7), 91 (7), 77 (10), 43 (89). Anal. Calcd for $C_{15}H_{16}O_4$: C, 69.22; H, 6.20. Found: C, 69.41; H, 6.23.

4.3.6. 5-Benzoyl-4-methyl-6-phenyl-2*H*-pyran-2-one 3f′. Pale yellow solid, mp 110–112 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78–7.21 (m, 10H), 6.25 (s, 1H), 2.09 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.4, 160.9, 159.0, 154.6, 136.5, 134.1, 131.4, 130.9, 129.4, 128.8, 128.5, 128.5, 118.0, 113.0, 20.3; GC–MS *m/z* (% rel inten.) 290 (M^+, 89), 261 (100), 245 (14), 233 (7), 185 (19), 169 (3), 157 (2), 128 (5), 105 (58), 77 (57), 51 (10). Anal. Calcd for $C_{19}H_{14}O_3$: C, 78.61; H, 4.86. Found: C, 78.32; H, 4.83.

4.3.7. 4-(*n*-Hexyl)-5-methoxycarbonyl-6-methyl-2*H*-pyran-2-one 3i′. Pale yellow viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.02 (s, 1H), 3.88 (s, 3H), 2.52 (t, 2H, J=7.6 Hz), 2.36 (s, 3H), 1.52–1.42 (m, 2H), 1.38–1.22 (m, 6H), 0.87 (t, 3H, J=6.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 164.1, 161.0, 158.3, 112.8, 110.8, 52.5, 33.8, 31.4, 28.9, 28.4, 22.5, 19.5, 14.0; GC–MS *m/z* (% rel inten.) 252 (M^+, 20), 237 (3), 221 (15), 182 (46), 167 (32), 154 (100), 140 (16), 122 (14), 95 (11), 79 (8), 65 (6), 55 (4). Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: C, 66.43; H, 8.03.

4.3.8. 5-Ethoxycarbonyl-6-methyl-4-(*n*-pentyl)-2*H*-pyran-2-one 3j′. Pale yellow viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.01 (s, 1H), 4.35 (q, 2H, J=7.1 Hz), 2.52 (t, 2H, J=7.8 Hz), 2.37 (s, 3H), 1.55–1.42 (m, 2H), 1.37 (t, 3H, J=7.1 Hz), 1.32–1.25 (m, 4H), 0.89 (t, 3H, J=6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8, 163.8, 161.1, 158.3, 113.1, 110.8, 61.7, 33.7, 31.4, 28.2, 22.3, 19.3, 14.1, 13.9; GC–MS *m/z* (% rel inten.) 252 (M^+, 26), 237 (4), 224 (6), 207 (31), 196 (44), 181 (29), 168 (100), 140 (31), 122 (17), 108 (9), 95 (14), 77 (6). Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: C, 66.38; H, 8.05.

4.3.9. 5-Ethoxycarbonyl-4-(*n*-pentyl)-6-phenyl-2*H*-pyran-2-one 3k′. Pale yellow viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59–7.40 (m, 5H), 6.15 (s, 1H), 4.10 (q, 2H, J=7.1 Hz), 2.55 (t, 2H, J=7.6 Hz), 1.61–1.53 (m, 2H), 1.40–1.25 (m, 4H), 1.03 (t, 3H, J=7.1 Hz), 0.91 (t, 3H, J=6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 161.0, 160.9, 158.1, 132.1, 130.9, 128.5, 128.0, 113.6, 111.5, 61.9, 33.1, 31.4, 28.1, 22.3, 13.9, 13.5; GC–MS *m/z* (% rel inten.) 314 (M^+, 18), 285 (3), 269 (10), 257 (39), 243 (6), 230 (34), 158 (9), 128 (7), 105 (100), 77 (35). HRMS calcd for $C_{19}H_{22}O_4$ 314.1518, found 314.1518.

4.3.10. (*E*)-2-Benzoyl-3-(*n*-pentyl)-2-pentene-1,5-dicarboxylic acid diethyl 3k″. Pale yellow viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05–8.02 (m, 2H), 7.58–7.45 (m, 3H), 4.24 (q, 2H, J=7.1 Hz), 4.08 (q, 2H, J=7.1 Hz), 3.76 (s, 2H), 2.06 (t, 2H, J=7.9 Hz), 1.45–1.38 (m, 2H), 1.33 (t, 3H, J=7.1 Hz), 1.25–1.10 (m, 4H), 1.02 (t, 3H, J=7.1 Hz), 0.79 (t, 3H, J=6.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.9, 170.2, 164.2, 152.7, 137.0, 133.5, 131.8, 129.3, 128.7, 61.0, 60.7, 38.2, 36.9, 31.7, 27.0, 22.2, 14.2, 13.8, 13.8; GC–MS *m/z* (% rel inten.) 360 (M^+, 0.1), 315 (8), 286 (12), 273 (6), 257 (8), 243 (9), 230 (12), 211 (4), 171 (5), 158 (7), 105 (100), 77 (23). HRMS calcd for $C_{19}H_{23}O_4$ (M−OEt) 315.1596, found 315.1591.

4.3.11. 5-Acetyl-4-methoxycarbonyl-6-methyl-2*H*-pyran-2-one 3l′. Pale yellow solid, mp 67–68 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.70 (s, 1H), 3.91 (s, 3H), 2.43 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.7, 163.9, 161.3, 160.2, 143.6, 118.3, 115.8, 53.5, 31.7, 18.5; GC–MS *m/z* (% rel inten.) 210 (M^+, 39), 195 (61), 178 (40), 167 (21), 151 (100), 139 (14), 125 (51), 109 (24), 93 (20), 65 (7), 43 (75). Anal. Calcd for $C_{10}H_{10}O_5$: C, 57.14; H, 4.80. Found: C, 57.11; H, 4.74.

4.3.12. Ethyl (*E*)-4-acetyl-3-ethoxycarbonyl-5-oxo-2-hexenoate 3m. Pale yellow viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 16.5 (s, 1H), 7.08 (s, 1H), 4.30 (q, 2H, J=7.1 Hz), 4.19 (q, 2H, J=7.1 Hz), 1.96 (s, 6H), 1.33 (t, 3H, J=7.1 Hz), 1.26 (t, 3H, J=7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.9, 166.2, 164.8, 139.5, 132.4, 107.2, 62.2, 61.2, 23.5, 14.2, 14.1; GC–MS *m/z* (% rel inten.) 270 (M^+, 1), 227 (4), 197 (47), 181 (18), 151 (100), 109 (15), 93 (3), 82 (2), 67 (2), 53 (3), 43 (26). Anal. Calcd for $C_{13}H_{18}O_6$: C, 57.77; H, 6.71. Found: C, 57.94; H, 6.83.

4.3.13. 4,5-Bis(methoxycarbonyl)-6-methyl-2*H*-pyran-2-one 3n′. Pale yellow solid, mp 50–52 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.48 (s, 1H), 3.89 (s, 3H), 3.84 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.0, 164.7, 164.6, 159.7, 145.8, 113.8, 109.1, 53.3, 52.8, 19.4; GC–MS *m/z* (% rel inten.) 226 (M^+, 26), 211 (3), 195 (43), 183 (14), 167 (100), 151 (13), 137 (10), 125 (25), 108 (7), 93 (19), 59 (7), 43 (29). Anal. Calcd for $C_{10}H_{10}O_6$: C, 53.10; H, 4.46. Found: C, 53.43; H, 4.85.

4.3.14. 4,5-Bis(ethoxycarbonyl)-6-methyl-2*H*-pyran-2-one 3o′. Pale yellow viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.48 (s, 1H), 4.34 (q, 2H, J=7.0 Hz), 4.30 (q, 2H, J=7.0 Hz), 2.48 (s, 3H), 1.36 (t, 3H, J=7.0 Hz), 1.33 (t, 3H, J=7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 164.3, 164.2, 159.8, 146.2, 113.6, 109.5, 62.6,

62.1, 19.3, 14.0 (2C); GC–MS *m/z* (% rel inten.) 254 (M^+, 23), 208 (29), 187 (100), 165 (12), 153 (65), 139 (9), 111 (10), 93 (18), 65 (5), 43 (29).

4.3.15. 3-Benzyl-4-phenyl-5-methoxycarbonyl-6-methyl-2*H*-pyran-2-one 4a. Pale yellow viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38–6.96 (m, 10H), 3.70 (s, 2H), 3.35 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 162.1, 160.6, 151.6, 138.9, 135.9, 128.6, 128.4, 128.3, 128.2, 127.3, 126.2, 122.7, 114.3, 52.1, 33.1, 18.8; GC–MS *m/z* (% rel inten.) 334 (M^+, 100), 319 (18), 306 (13), 291 (13), 275 (12), 260 (8), 247 (14), 231 (35), 202 (37), 91 (14), 77 (7), 43 (19). Anal. Calcd for $C_{21}H_{18}O_4$: C, 75.45; H, 5.39. Found: C, 75.51; H, 5.12.

4.3.16. 3-Benzyl-4,6-dimethyl-5-methoxycarbonyl-2*H*-pyran-2-one 4b. Pale yellow viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28–7.16 (m, 5H), 3.90 (s, 2H), 3.87 (s, 3H), 2.33 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 162.2, 160.4, 148.7, 138.4, 128.5, 128.2, 126.4, 122.3, 114.2, 52.4, 32.3, 19.1, 17.6; GC–MS *m/z* (% rel inten.) 272 (M^+, 100), 244 (41), 229 (93), 213 (17), 185 (23), 167 (17), 141 (34), 128 (21), 115 (23), 91 (37), 77 (12), 43 (39). Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.59; H, 5.88. Found: C, 70.11; H, 5.49.

Acknowledgements

This project (20573061) was supported by National Natural Science Foundation of China and Specialized Research Fund for the Doctoral Program of Higher Education (20060003079).

Supplementary data

Characterization data for the known products, copies of ^{1}H, ^{13}C NMR charts of **3** and **4**, and the full X-ray structural details for **3a**. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.09.038.

References and notes

1. Recent reviews, see: (a) Jia, C.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633–639; (b) Miura, M.; Nomura, M. *Top. Curr. Chem.* **2002**, *219*, 211–241; (c) Ritleng, V.; Sirlin, C.; Pfeffer, M. *Chem. Rev.* **2002**, *102*, 1731–1769; (d) Kakiuchi, F.; Murai, S. *Acc. Chem. Res.* **2002**, *35*, 826–834; (e) Davies, H. M. L.; Beckwith, R. E. J. *Chem. Rev.* **2003**, *103*, 2861–2903.
2. (a) Kennedy-Smith, J. J.; Staben, S. T.; Toste, F. D. *J. Am. Chem. Soc.* **2004**, *126*, 4526–4527; (b) Staben, S. T.; Kennedy-Smith, J. J.; Toste, F. D. *Angew. Chem., Int. Ed.* **2004**, *43*, 5350–5352.
3. Gao, Q.; Zheng, B.-F.; Li, J.-H.; Yang, D. *Org. Lett.* **2005**, *7*, 2185–2188.
4. (a) Balme, G.; Bouyssi, D.; Faure, R.; Gore, J.; Van Hemelryck, B. *Tetrahedron* **1992**, *48*, 3891–3902; (b) Corkey, B. K.; Toste, F. D. *J. Am. Chem. Soc.* **2005**, *127*, 17168–17169.
5. Nakamura, M.; Endo, K.; Nakamura, E. *J. Am. Chem. Soc.* **2003**, *125*, 13002–13003.
6. Kuninobu, Y.; Kawata, A.; Takai, K. *Org. Lett.* **2005**, *7*, 4823–4825.
7. Examples of recent reports, see: (a) Ram, V. J.; Srivastava, P.; Saxena, A. S. *J. Org. Chem.* **2001**, *66*, 5333–5337; (b) Farhanullah; Agarwal, N.; Goel, A.; Ram, V. J. *J. Org. Chem.* **2003**, *68*, 2983–2985; (c) Sil, D.; Farhanullah; Ram, V. J. *Tetrahedron Lett.* **2004**, *45*, 9025–9027; (d) Kranjc, K.; Kocevar, M. *New J. Chem.* **2005**, *29*, 1027; (e) Goel, A.; Dixit, M.; Verma, D. *Tetrahedron Lett.* **2005**, *46*, 491–493; (f) Sil, D.; Kumar, R.; Sharon, A.; Maulik, P. R.; Ram, V. J. *Tetrahedron Lett.* **2005**, *46*, 3807–3809; (g) Sil, D.; Ram, V. J. *Tetrahedron Lett.* **2005**, *46*, 5013–5015; (h) Pratap, R.; Sil, D.; Ram, V. J. *Tetrahedron Lett.* **2005**, *46*, 5025–5027; (i) Goel, A.; Singh, F. V. *Tetrahedron Lett.* **2005**, *46*, 5585–5587; (j) Goel, A.; Verma, D.; Singh, F. V. *Tetrahedron Lett.* **2005**, *46*, 8487–8491; (k) Goel, A.; Verma, D.; Dixit, M.; Raghunandan, R.; Maulik, P. R. *J. Org. Chem.* **2006**, *71*, 804–807; (l) Pratap, R.; Kumar, R.; Maulik, P. R.; Ram, V. J. *Tetrahedron Lett.* **2006**, *47*, 2949–2952; (m) Dixit, M.; Goel, A. *Tetrahedron Lett.* **2006**, *47*, 3557–3560; (n) Sil, D.; Pratap, R.; Kumar, R.; Maulik, P. R.; Ram, V. J. *Tetrahedron Lett.* **2006**, *47*, 3759–3762; (o) Singh, F. V.; Kumar, A.; Goel, A. *Tetrahedron Lett.* **2006**, *47*, 7767–7770; (p) Pratap, R.; Kumar, B.; Ram, V. J. *Tetrahedron* **2006**, *62*, 8158–8163.
8. (a) Charlton, R. E.; Webster, F. X.; Zhang, A.; Schal, C.; Liang, D.; Sreng, I.; Roelofs, W. L. *Proc. Natl. Acad. Sci. U.S.A.* **1993**, *90*, 10202–10205; (b) Ram, V. J.; Haque, N.; Nath, M.; Singh, S. K.; Hussaini, F. A.; Tripathi, S. C.; Shoeb, A. *Bioorg. Med. Chem. Lett.* **1997**, *7*, 3149–3152; (c) Ellsworth, E. L.; Domagala, J.; Vara Prasad, J. V. V.; Hagen, S.; Ferguson, D.; Holler, T.; Hupe, D.; Graham, N.; Nouhan, C.; Tummino, P. J.; Zeikus, G.; Lunney, E. A. *Bioorg. Med. Chem. Lett.* **1999**, *9*, 2019–2024; (d) Bellina, F.; Carpita, A.; Mannocci, L.; Rossi, R. *Eur. J. Org. Chem.* **2004**, 2610–2619; (e) Chattapadhyay, T. K.; Dureja, P. *J. Agric. Food Chem.* **2006**, *54*, 2129–2133; (f) Leutbecher, H.; Williams, L. A. D.; Rosner, H.; Beifuss, U. *Bioorg. Med. Chem. Lett.* **2007**, *17*, 978–982.
9. (a) Hua, R.; Tanaka, M. *New J. Chem.* **2001**, *25*, 179–184 and references therein; (b) Rousset, S.; Abarbri, M.; Thibonnet, J.; Parrain, J. L.; Duchene, A. *Tetrahedron Lett.* **2003**, *44*, 7633–7636; (c) Downs, J. R.; Grant, S. P.; Townsend, J. D.; Schady, D. A.; Pastine, S. J.; Embree, M. C.; Metz, C. R.; Pennington, W. T.; Bailey Walsch, R. D.; Beam, C. F. *Can. J. Chem.* **2004**, *82*, 659–664; (d) Gerus, I. I.; Tolmachova, N. A.; Vdovenko, S. I.; Froehlich, R.; Haufe, G. *Synthesis* **2005**, *8*, 1269–1278.
10. Hua, R.; Tian, X. *J. Org. Chem.* **2004**, *69*, 5782–5784.
11. Zhao, W.-G.; Hua, R. *Eur. J. Org. Chem.* **2006**, 5495–5498.
12. Zuo, W.-X.; Hua, R.; Qiu, X. *Synth. Commun.* **2004**, *34*, 3219–3225.
13. $ReBr(CO)_4$, which was formed by the decarbonylation of $ReBr(CO)_5$ was proposed as the active species for catalytic activation of C–H bond of 1,3-dicarbonyl compounds, see Ref. 12.
14. There are two papers reported on the catalytic addition reaction of 1,3-dicarbonyl compounds with internal electron-deficient alkynes to give α-(*gem*-dicarbonyl) acrylates, see: (a) Hanedanian, M.; Loreau, O.; Taran, F.; Mioskowski, C. *Tetrahedron Lett.* **2004**, *45*, 7035–7038; (b) Hanedanian, M.; Loreau, O.; sawicki, M.; Taran, F. *Tetrahedron* **2005**, *61*, 2287–2294.
15. Crystals for X-ray diffraction analysis were obtained by recrystallization from cyclohexane. CCDC645448 contains supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk.