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Ruthenium complex-catalyzed allylic alkylation of carbonucleophiles with allylic carbonates

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Abstract

Allylic carbonates except for allyl methyl carbonate reacted with carbonucleophiles such as ethyl acetoacetate in the presence of a catalytic amount of Ru(cod)(cot) [cod = cycloocta-1,5-diene, cot = cycloocta-1,3,5-triene] in *N*-methylpiperidine at 80°C to give the corresponding monoallylated carbonucleophiles in high yields with high regioselectivity. The regioselectivity was quite different from that in the palladium-catalyzed reactions. The allylation of carbonucleophiles using allyl methyl carbonate selectively gave the diallylated carbonucleophiles in high yields.

1. Introduction

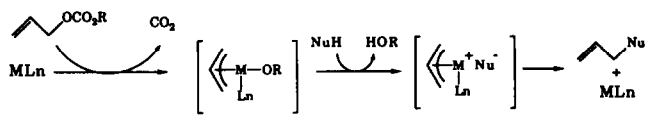
Among the carbon–carbon bond forming reactions promoted by transition-metal complexes, allylic alkylations of carbonucleophiles, especially those catalyzed by palladium complexes, have been extensively studied [1]. For example, it has been reported that allylic carbonates reacted smoothly, in the presence of Pd catalysts, with active methylene compounds such as β-keto esters or malonates under neutral conditions [2], silyl enol ether [3], ketene silyl acetals [4] and enol acetates [5] via a π-allylpalladium intermediate (Scheme 1). In addition to palladium, Rh, Ni, Ru [6] and Mo complexes [6,7] were also found to be good catalysts for the reaction. However, the details of the reactivity and regioselectivity of the allylation of carbonucleophile when catalyzed by ruthenium complexes have not been investigated.

We have found many carbon–carbon bond forming reactions catalyzed in a characteristic way by ruthenium complexes. [8] Here, the matching or tuning of the substrates and ligands is the most important factor for high yields and selectivity of the products. In particular, we found that a π-allylruthenium intermediate acts not only as an electrophile, in the same way as a π-allylpalladium generally, but also it acts as a nucleophile [9]. Ruthenium complexes, especially a zero-valent (η^4-1,5-cyclooctadiene)(η^6-1,3,5-cyclooctatriene) ruthenium, Ru(cod)(cot), often showed catalytic activity and product selectivity quite different from those with palladium complexes or other complexes [10]. These facts led us to a precise investigation of the ruthenium catalyzed allylic alkylation of carbonucleophiles. In this paper, ruthenium-catalyzed allylic alkylation of carbonucleophiles with allylic carbonates was systematically examined. The results showed that reactivity of the substrates and regioselectivity of products in ruthenium-catalyzed reactions were strongly affected by the combinations of substrates and ligands and that the diallylation reaction was smoothly performed, which is rather difficult in the case of Pd complexes.

2. Results and discussion

2.1. Allylation of β-keto esters and malonates using allylic carbonates

The reaction of ethyl acetoacetate with cinnamyl methyl carbonate in the presence of a catalytic amount



Scheme 1.

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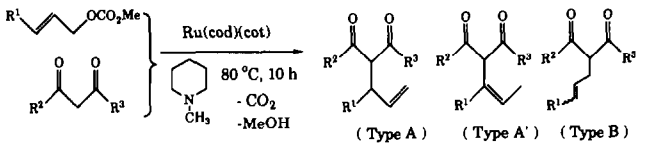
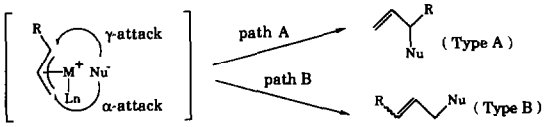


Scheme 2.

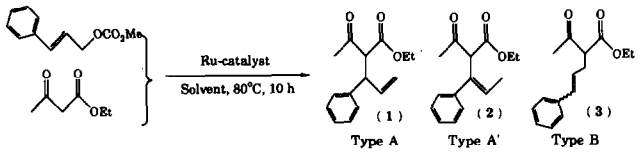


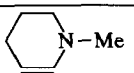
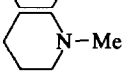
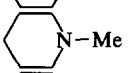
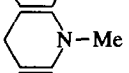
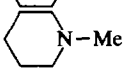
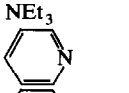
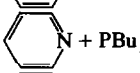
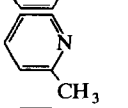
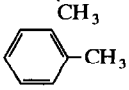
Scheme 3.

of Ru(cod)(cot) gave allylated carboxylic esters in high yield with high regioselectivity accompanied by the liberation of CO_2 and MeOH (Scheme 2). The reaction proceeded smoothly in *N*-methylpiperidine under mild reaction conditions (at 80°C for 10 h).

The reaction was performed in the presence of various ruthenium complexes, and the results are summarized in Table 1. The zero-valent ruthenium complex, Ru(cod)(cot), was the best catalyst in this reaction (Run 1). $Ru_3(CO)_{12}$ catalyzed only the decomposition of cinnamyl methyl carbonate to give 1-phenyl-1-propene (Run 2). $RuH_2(PPh_3)_4$, which was investigated by Tsuji *et al.* [2,6], showed lower catalytic activity under the present reaction conditions (Run 3). $RuCl_2(PPh_3)_3$ showed no catalytic activity even for decomposition of cinnamyl methyl carbonate (Run 4). In these results, it was noteworthy that Ru(cod)(cot) and $RuH_2(PPh_3)_4$ showed quite different regioselectivities for the products. As proposed previously, the allylation of carbonucleophiles proceeds via a π-allylmetal intermediate (M = Mo [2,7] and Pd [2,6]) (Scheme 1). In the reaction of cinnamyl methyl carbonate with methyl acetoacetate catalyzed by $Pd_2(dba)_3 \cdot CHCl_3$–PPh_3 [2], methyl 2-acetyl-5-phenyl-4-pentenoate, the product of type B, was obtained as sole product owing to α-attack of the nucleophile (Scheme 3, path B) in similar manner to that catalyzed by $RuH_2(PPh_3)_4$ in the present reaction.

TABLE 1. Activities of ruthenium catalysts and effect of solvents in the reaction of cinnamyl methyl carbonate with ethyl acetoacetate [a]

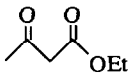
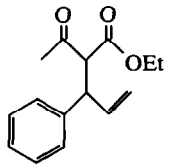
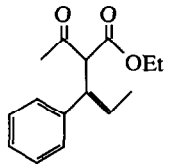
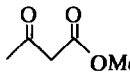
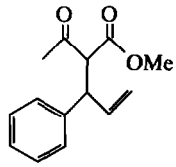
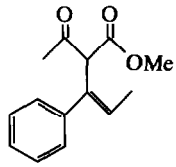
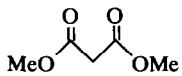
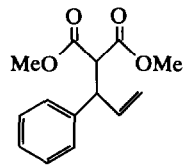
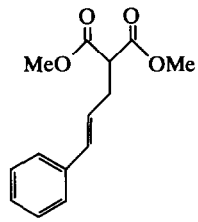
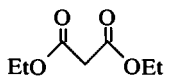
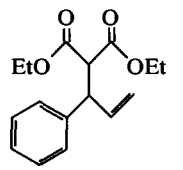
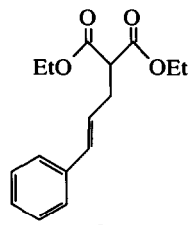
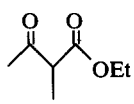
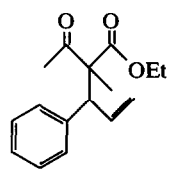
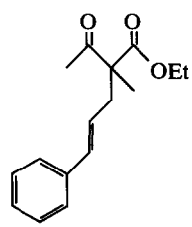
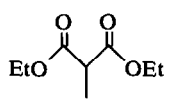
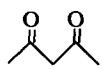


Run	Catalyst	Solvent	Conversion (%) [b]	Product	Yield (%) [c] (selectivity)
1	Ru(cod)(cot)		100	**1** + **2**	69 (**1**:**2** = 93:7)
2	$Ru_3(CO)_{12}$		trace	1-phenyl-1-propene	trace
3	$RuH_2(PPh_3)_4$		100	**3** [d]	50
4	$RuCl_2(PPh_3)_3$		trace	–	–
5	$RuCl_3 \cdot nH_2O$		trace	(A)	trace
6	Ru(cod)(cot)	none	trace	**1**	trace
7	Ru(cod)(cot)	NEt_3	100	**1** + **2**	52 (**1**:**2** = 92:8)
8	Ru(cod)(cot)		100	**1** + **2**	54 (**1**:**2** = 92:8)
9	Ru(cod)(cot)		–	–	–
10	Ru(cod)(cot)		trace	**1**	trace
11	Ru(cod)(cot)		trace	**1**	trace
12	Ru(cod)(cot)	THF	trace	**1**	trace

[a] A mixture of cinnamyl methyl carbonate (2.5 mmol), ethyl acetoacetate (2.5 mmol), solvent (2.5 mmol) and Ru(cod)(cot) (0.10 mmol) was stirred at 80°C for 10 h. [b] Based on the amount of cinnamyl methyl carbonate. [c] Yield of the mixture of the isomers obtained by Kugelrohr distillation. [d] A mixture of (*E*) and (*Z*) isomers (*ca* 1:1).

Using Ru(cod)(cot) catalyst, only the product derived by selective γ-attack, ethyl 2-acetyl-3-phenyl-4-pentenoate, the product of type A, was obtained (Scheme 3, path A). Thus the regioselectivity of the product was remarkably influenced by the ligands coordinated to the ruthenium.

TABLE 2. Ru(cod)(cot)-catalyzed reactions of β-keto esters, malonates or β-diketones with cinnamyl methyl carbonate [a]

Run	Carbonucleophile	Conversion (%) [b]	Product		Yield (%) [c] (Selectivity)
2		100	 **1** [e]	 **2**	69 (**1**:**2** = 93:7)
13		100	 **4** [e]	 **5**	65 (**4**:**5** = 50:50)
14		100	 **6**	 **7**	52 (**6**:**7** = 50:50)
15		100	 **8**	 **9**	52 (**8**:**9** = 50:50)
16			 **10**	 **11**	72 (**10**:**11** = 20:80)
17 [d]		100	–	–	trace
18		trace	–	–	–

[a] A mixture of cinnamyl methyl carbonate (2.5 mmol), ethyl acetoacetate (2.5 mmol), *N*-methylpiperidine (2.5 mmol) and Ru(cod)(cot) (0.10 mmol) was stirred at 80°C for 10 h. [b] Conversion of cinnamyl methyl carbonate determined by GLC. [c] Yield of the mixture of the isomers obtained by Kugelrohr distillation. [d] For 20 h. [e] 1:1 Mixture of erythro and threo isomers.

Effects of solvent on the reaction of cinnamyl methyl carbonate with ethyl acetoacetate were examined, and the results are also shown in Table 1. The reaction did not proceed without amines as solvents (Run 6). *N*-Methylpiperidine was a good solvent, and triethylamine and pyridine were also appropriate in these reactions (Runs 1, 7 and 8). These solvents would co-ordinate to the metal centre as ligands which control the catalytic activity. In 2-methylpyridine, no reaction occurred (Run 10). When tertiary phosphine such as PBu_3 was added (Run 9), the ruthenium catalyst showed no catalytic activity. Tetrahydrofuran (THF) and toluene, which were effective solvents in palladium-catalyzed allylation reactions [6], were not effec-

TABLE 3. Ru(cod)(cot)-catalyzed reactions of allylic carbonates with carbonucleophiles [a]

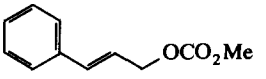
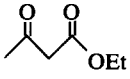
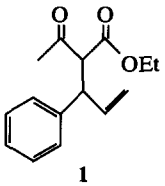
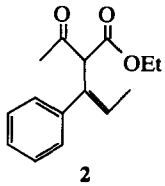
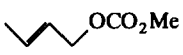
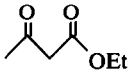
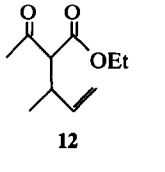
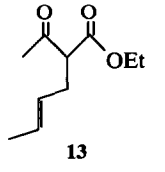
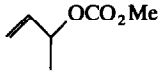
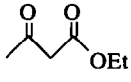
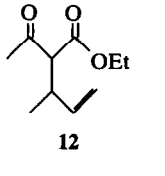
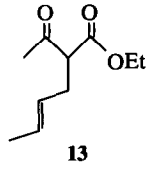
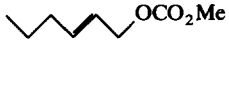
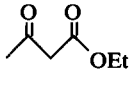
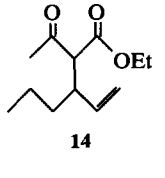
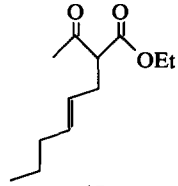
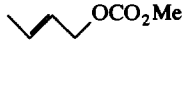
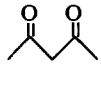
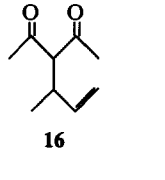
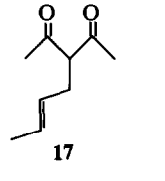
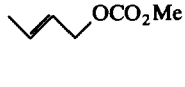
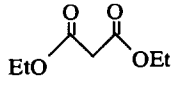
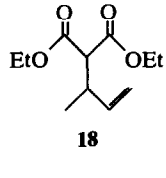
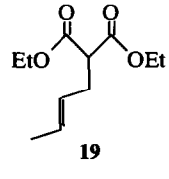
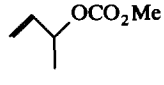
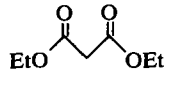
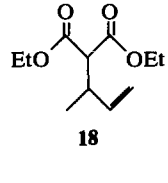
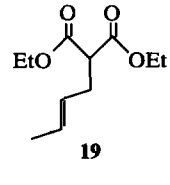
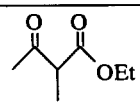
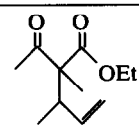
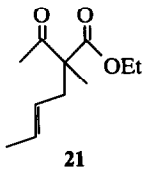
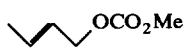
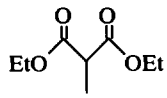
Run	Carbonate	Nucleophile	Product		Yield (%) [b] (selectivity) [c]
2			 **1**	 **2**	69 (**1**:**2** = 93:7)
19			 **12**	 **13**	73 (**12**:**13** = 90:10)
20			 **12**	 **13**	69 (**12**:**13** = 80:20)
21 [d]			 **14**	 **15**	57 (**14**:**15** = 75:25)
22			 **16**	 **17**	85 (**16**:**17** = 70:30) [e]
23			 **18**	 **19**	46 (**18**:**19** = 50:50)
24			 **18**	 **19**	62 (**18**:**19** = 80:20)

TABLE 3 (continued)

Run	Carbonate	Nucleophile	Product		Yield (%) [b] (selectivity) [c]
25			 **20**	 **21**	86 (**20**:**21** = 10:90)
26			–	–	0

[a] A mixture of allylic carbonate (2.5 mmol), carbonucleophile (2.5 mmol),1 *N*-methylpiperidine (2.5 mmol) and Ru(cod)(cot) (0.10 mmol) was stirred at 80°C for 10 h. [b] Yield of the mixture of the isomers obtained by Kugelrohr distillation. [c] No other products were detected. [d] At 70°C for 20 h. [e] Small amounts of tautomers of **15** and **16** were detected.

tive in the present reaction (Runs 11 and 12). The products obtained in the reaction of cinnamyl methyl carbonate with ethyl acetoacetate catalyzed by Ru(cod)(cot) were type A and its isomer type A′ derived from γ-attack and no product of type B by α-attack was detected.

Results of the Ru(cod)(cot)-catalyzed reactions of cinnamyl methyl carbonate with the various carbonucleophiles are summarized in Table 2. The reactions were performed at 80°C in *N*-methylpiperidine. Upon changing the carbonucleophiles, regioselectivity in these reactions greatly changed. For example, the reaction of cinnamyl methyl carbonate with ethyl acetoacetate gave a major product ethyl 2-acetyl-3-phenyl-4-pentenoate (**1**) (69% yield, 93% selectivity), with its isomer ethyl 2-acetyl-3-phenyl-3-pentenoate (**2**) (7% selectivity) (Run 14). The reaction with methyl acetoacetate also gave the corresponding products **4** and **5**, methyl 2-acetyl-3-phenyl-4-pentenoate and 2-acetyl-3-phenyl-3-pentenoate in 65% yield with the ratio of 50:50. The products **1** and **4** consisted of a 1:1 mixture of the diastereomers (see NMR data in the Experimental section). The reactions of cinnamyl methyl carbonate with dimethyl malonate gave a mixture of the isomers **6** and **7** in the ratio of 50:50 in 52% yield (Run 14). The reaction with ethyl 2-methylacetoacetate gave isomers **10** and **11** in 72% yield in the ratio of 20:80 (Run 16). The ratio of the isomers obtained would depend on the different attacks, α-attack or γ-attack, of the carbonucleophile to a (π-allyl)ruthenium intermediate (see Scheme 3). The steric hindrance of the methyl group may enhance the α-attack. In the reaction with diethyl methylmalonate, only a trace amount of product was obtained (Run 17). There was no reaction with 2,4-pentandione (Run 18).

Reactions of various allylic carbonates with several carbonucleophiles were successful and the results are summarized in Table 3. Under the reaction conditions, no allylic acetates reacted. Most allylic carbonates reacted with β-keto esters and β-diketones. The reactions of ethyl acetoacetate with crotyl methyl carbonate gave two isomers **12** and **13** in 73% yield in the ratio of 90:10 (Run 21). The reaction of ethyl acetoacetate with the isomer of crotyl methyl carbonate, 1-methyl-2-propenyl carbonate, gave the similar mixture of two isomeric products **12** and **13** in the ratio of 80:20 (Run 20). These results strongly suggest that the allylation reaction must proceed via a common π-allylruthenium intermediate. In the allylation reaction of ethyl acetoacetate with methyl 2-hexenyl carbonate, allylated products, ethyl (*E*)-2-acetyl-3-propyl-4-pentenoate and ethyl 2-acetyl-4-octenoate, were obtained in 57% yield in the ratio of 75:25 (Run 21). The reaction of crotyl methyl carbonate with 2,4-pentandione gave two isomers **16** and **17** in high yield (85%) in the ratio of 70:30 (Run 22), accompanied by small amounts of their tautomers. Diethyl malonate gave the corresponding products in 46% yield and the ratio of **18** and **19** was 50:50 (Run 25). 1-Methyl-2-propenyl carbonate, the isomer of crotyl methyl carbonate, reacted with diethyl malonate go give the corresponding products **18** and **19** (62% yield, **18**:**19** = 80:20) (Run 24). The reaction of crotyl methyl carbonate with ethyl 2-methylacetoacetate gave isomers **20** and **21** in 86% yield in the ratio of 10:90 (Run 25). The similar reaction catalyzed by $RuH_2(PPh_3)_4$ was found by Tsuji and his co-workers to give a mixture of the products in very poor yield (9%) [6]. In the reaction of crotyl methyl carbonate with diethyl methylmalonate, only the starting materials were recovered under the reaction conditions (Run 26).

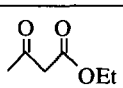
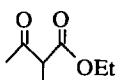
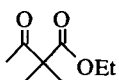
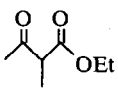
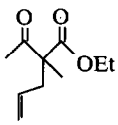
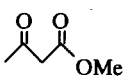
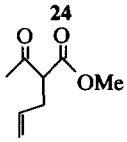
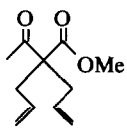
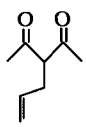
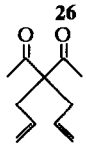
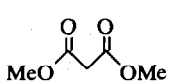
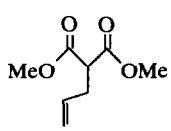
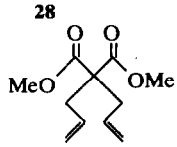
It should be noted that the allylic alkylation of

diethyl malonate with crotyl methyl carbonate and its isomer, 1-methyl-2-propenyl carbonate, showed different reactivity and regioselectivity, but that the reaction of ethyl acetoacetate with the two carbonates showed almost the same reactivity and regioselectivity. These facts show that the reactivity and regioselectivity in the present reaction were strongly influenced by the substituents on the substrates. In the cases of rhodium complex-catalyzed allylation reactions [6], there was not so large a difference in regioselectivity. The palladium complex-catalyzed reaction of cinnamyl methyl carbonate with methyl acetoacetate gave a sole product of type B, methyl 2-acetyl-4-pentenoate [2]. But when this reaction was carried out using Ru(cod)(cot) under the present reaction conditions, a highly regioselective product of type A, methyl 2-acetyl-3-phenyl-4-pentenoate, was obtained accompanied by its olefinic isomer, methyl 2-acetyl-3-phenyl-3-pentenoate. No product of type B, methyl 2-acetyl-3-phenyl-4-pentenoate, was detected. These results showed that quite different regioselectivities of the products can be realized by using ruthenium or palladium catalysts.

2.2. *Diallylation of β-keto esters using allyl methyl carbonate*

The reaction of allyl methyl carbonate with ethyl acetoacetate at 80°C for 10 h gave a complicated mixture of products. This may be due to the high reactivity of allyl methyl carbonate. The reaction at room temperature (20°C) gave two products (Scheme 4) which involved a monoallylated product, ethyl 2-acetyl-4-pentenoate, and a diallylated product, ethyl 2-acetyl-2-allyl-4-pentenoate, in 61% yield in the ratio of 50:50 (Table 4, Run 27). When the molar ratio of allyl methyl carbonate and ethyl acetoacetate was changed to 2:1, the reaction yielded almost monoallylated product in 20% (Run 28). Furthermore, when the reaction was performed at 42°C in the same molar ratio (2:1), the resulting products were obtained in 96% yield in the ratio of 20:80 of monoallylated and

TABLE 4. Ru(cod)(cot) catalyzed reactions of allyl methyl carbonate with carbonucleophiles [a]

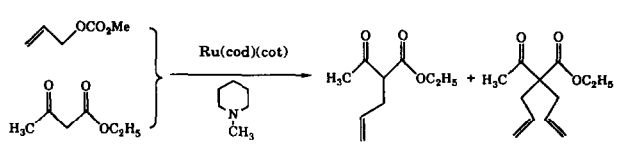
Run	Nuclophile	Carbonate/Nu (ratio of mole)	Temperature (°C)	Time (h)	Product		Yield (%) (selectivity) [b]
27		1:1	20	20			61 (**22**:**23** = 50:50)
28		2:1	20	20			20 (**22**:**23** = 98:2) [c]
29		2:1	42	20			96 (**22**:**23** = 20:80)
30		2:1	50	20			79 (**22**:**23** = 2:98)
31		3:1	50	20			91 (**22**:**23** = 3:97)
					22	**23**	
32		1:1	50	20			87
					24		
33		3:1	50	20			79 (**25**:**26** = 10:90)
					25	**26**	
34		3:1	50	15			87 (**27**:**28** = 7:93)
					27	**28**	
35		3:1	55	25			90 (**29**:**30** = 40:60)
					29	**30**	

[a] Carbonucleophile (2.5 mmol), allyl methyl carbonate (2.5–7.5 mmol), *N*-methylpiperidine (2.5 mmol), Ru(cod)(cot) (0.10 mmol). [b] Isolated yield obtained by Kugelrohr distillation. [c] GLC yield.

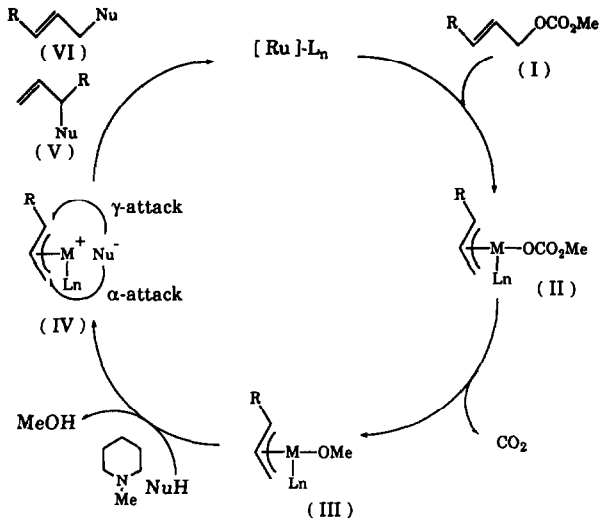
diallylated product (Run 29). The reaction at 50°C for 20 h gave the corresponding diallylated product in 79% yield with high selectivity (98%) (Run 30). When the reaction was carried out in the mole ratio of 3:1 at 50°C, the allylated products were obtained in 91% yield and the selectivity of **23** was 97% (Run 31). The reaction with ethyl 2-methylacetoacetate gave selectively **24** in 87% yield (Run 32), which is the same as reported by Tsuji *et al.* for catalysis by $RuH_2(PPh_3)_4$ [6]. The reaction of methyl acetoacetate gave monoallylated product **25** and diallylated product **26** in 79% yield and their ratio was 10:90 (Run 33). The reaction of 2,4-pentandione with allyl methyl carbonate also gave diallylated product **28** in high yield (87%) with high selectivity (93%) (Run 34). The reaction of dimethyl malonate showed lower selectivity under the reaction conditions.

Diallylation of carbonucleophile is not easy even when palladium catalyst is used. It was reported that $Pd(acac)_2$-PPh_3-catalyzed reaction of 2,4-pentandione with allyldiethylamine at 85°C gives a monoallylated product, 3-acetyl-5-hexen-2-one, in 70% yield and diallylated product, 3-acetyl-3-allyl-5-hexen-2-one, in only 20% yield [11]. The reaction of methyl acetoacetate with phenyl allyl ether in the presence of $PdCl_2$-$(PPh_3)_2NaOPh$ also gave monoallylated product in 18% yield and diallylated product in 47% yield [12]. Recently, Lu *et al.* reported that the $Pd(PPh_3)_4$-catalyzed allylic alkylation of carbonucleophiles with allylic borates selectively gives the diallylated products in high yields [13]. To our knowledge, the present reaction is the first example of selective diallylation reaction using allyl carbonate.

A possible catalytic cycle is shown in Scheme 5, which is similar to that proposed for palladium catalyst [2]. Firstly, allylic carbonate adds oxidatively to a low valent ruthenium complex to give a π-allyl-[Ru] complex (**II**), which undergoes decarboxylation to give a π-allyl-[Ru] alkoxide (**III**). The active methylene or methine proton of the nucleophile was abstracted by alkoxide ligand to produce an intermediate (**IV**), accompanied with liberation of MeOH. Nucleophilic attack of the α- or γ-position on the [π-allyl]-ruthenium complex gives the allylated compound (**V**) or (**VI**), and the low-valent Ru complex would be regenerated.



Scheme 4.



Scheme 5.

In conclusion, under neutral conditions, ruthenium-catalyzed allylation of carbonucleophiles using allylic carbonates proceeded smoothly; the regioselectivity was controlled by the catalyst precursors such as Ru(cod)(cot) and $RuH_2(PPh_3)_4$. The reactivity and regioselectivity of products in these reactions depended strongly on the substrates and ligands coordinated to the ruthenium, and differed from those catalyzed by palladium complexes. Further, selective diallylation of carbonucleophiles using allyl methyl carbonate was performed by the ruthenium complexes in high yield, while this reaction was not easily catalyzed by other metal catalysts.

3. Experimental details

β-Keto esters and malonates were commercial products. Solvents were distilled before use. Allylic compounds were prepared by published methods [14]. Ru(cod)(cot) [15], $RuH_2(PPh_3)_4$ [16] and $RuCl_2(PPh_3)_3$ [17] were prepared according to literature methods. $RuCl_3 \cdot nH_2O$ and $Ru_3(CO)_{12}$ were purchased from Wako Pure Chemical Industries, and from Strem Chemicals respectively, and used without further purification.

All products were identified by means of ^1H NMR, ^{13}C NMR, FT-IR and GC-MS and elemental analysis. ^1H NMR (270 MHz) and ^{13}C NMR (67.8 MHz) spectra were recorded on a Jeol GSX-270 spectrometer using $CDCl_3$ as a solvent and tetramethylsilane as an internal standard. Methyl, methylene and methyne group were confirmed by DEPT mode measurement. IR spectra were measured on Shimadzu FTIR-8100. GLC analyses were performed with a Shimadzu GC-8A

chromatograph with a FID detector (column, SE-30, 3 mm i.d.× 3 m). Mass spectra were obtained with a Shimadzu GCMS-QP2000. Microanalyses were performed by the Laboratory for Organic Elemental Microanalysis of Kyoto University.

3.1. General reaction procedure

The reaction of cinnamyl methyl carbonate with ethyl acetoacetate is representative. To a heavy-walled glass tube was added Ru(cod)(cot) (0.1 mmol, 0.031 g), *N*-methylpiperidine (2.5 mmol, 0.30 ml), cinnamyl methyl carbonate (2.5 mmol, 0.46 ml), ethyl acetoacetate (2.5 mmol, 0.32 ml), and a stirring magnetic bar under an argon atmosphere. The glass tube was sealed and the mixture was stirred magnetically at 80°C for 10 h. A mixture of products, ethyl 2-acetyl-3-phenyl-4-pentenoate, and ethyl 2-acetyl-3-phenyl-3-pentenoate, was separated from the reaction mixtures by Kugelrohr distillation (85°C/0.25 mmHg, 0.43 g 69% yield). The ratio of the isomers was determined by GLC. Spectral and analytical data for representative products are described below.

3.1.1. Ethyl 2-acetyl-3-phenyl-4-pentenoate (1)

Kugelrohr distillation (85°C/0.25 mmHg). Compound **1** was obtained as a 1 : 1 mixture of the diastereomers, IR (neat): 1743, 1716, 1641 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): δ 0.96 (t, 3H, *J* 7.3 Hz, $-OCH_2CH_3$) and 1.27 (t, 3H, *J* 7.3 Hz, $-OCH_2CH_3$), 1.98 (s, 3H, $-COCH_3$) and 2.29 (s, 3H, $-COCH_3$), 3.90 (q, 2H, *J* 7.3 Hz, $-OCH_2CH_3$) and 4.19 (q, 2H, *J* 7.3 Hz, $-OCH_2CH_3$), 4.00 (d, 1H, *J* 11.4 Hz, $-COCHCO-$) and 4.02 (d, 1H, *J* 11.4 Hz, $-COCHCO-$), 4.11 (dd, 1H × 2, *J* 11.4 and 7.7 Hz, $-CH-C_6H_5$), 5.06 (d, 1H × 2, *J* 10.3 Hz, $-CH=CH_2$ (*cis*)), 5.07 (d, 1H, *J* 17.2 Hz, $-CH=CH_2$ (*trans*-)) and 5.09 (d, 1H, *J* 17.2 Hz, $-CH=CH_2$ (*trans*)), 5.90 (ddd, 1H, *J* 7.7, 10.3 and 17.2 Hz, $-CH=CH_2$) and 5.98 (ddd, 1H, *J* 7.7, 10.3 and 17.2 Hz, $-CH=CH_2$), 7.19 ~ 7.27 (m, 5H × 2, phenyl). ^{13}C NMR ($CDCl_3$, ppm): δ 13.6 and 14.0 ($-OCH_2CH_3$), 29.6 and 29.9 (CH_3CO-), 49.3 and 49.4 ($-CH-CH=CH_2$), 61.2 and 61.5 ($-OCH_2CH_3$), 64.8 and 65.3 ($-COCHCO-$), 116.2 and 116.5 ($-CH=CH_2$), 125.2 ~ 128.2 (phenyl), 138.1 and 139.9 ($-CH=CH_2$), 167.5 and 167.8 ($-COOC_2H_5$), 201.5 and 201.6 ($-COCH_3$). MS (*m/z*): 246 (M^+). Anal. Found: C, 72.98; H, 7.40. Calc. for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37%.

3.1.2. Ethyl 2-acetyl-3-phenyl-3-pentenoate (2)

Kugelrohr distillation (85°C/0.25 mmHg). ^1H NMR ($CDCl_3$, ppm): δ 1.06 (t, 3H, *J* 7.0 Hz, $-OCH_2CH_3$), 1.72 (d, 3H, *J* 7.0 Hz, $-C=CH-CH_3$), 1.88 (s, 3H, CH_3CO-), 4.05 (s, 1H, $-COCHCO-$), 4.10 (q, 2H, *J* 7.0 Hz, $-OCH_2CH_3$), 6.18 (q, 1H, *J* 7.0 Hz, $-C=CH-CH_3$), 7.26 ~ 7.32 (m, 5H, phenyl). ^{13}C NMR ($CDCl_3$, ppm): δ 15.4 ($-OCH_2CH_3$), 19.1 ($-C=CH-CH_3$), 31.4 (CH_3CO-), 60.2 ($-COCHCO-$), 132.5 ($-C=CH-CH_3$), 126.1 ~ 128.7 (phenyl), 173.9 ($-COOC_2H_5$), 201.5 ($-COCH_3$). MS (*m/z*): 246 (M^+).

3.1.3. Methyl 2-acetyl-3-phenyl-4-pentenoate (4)

Kugelrohr distillation (85°C/0.3 mmHg). Compound **4** was obtained as a 1 : 1 mixture of the diastereomers. ^1H NMR ($CDCl_3$, ppm): δ 2.00 (s, 3H, $-COCH_3$) and 2.32 (s, 3H, $-COCH_3$), 3.66 (s, 3H $-OCH_3$) and 3.76 (s, 3H, $-OCH_3$), 4.04 (d, 1 H, *J* 11.4 Hz, $-COCHCO-$) and 4.07 (d, 1H, *J* 11.4 Hz, $-COCHCO-$), 4.16 (dd, 1H × 2, *J* 11.4 and 7.7 Hz, $-CH-C_6H_5$), 5.10 (d, 1H × 2, *J* 9.9 Hz, $-CH=CH_2$ (*cis*)), 5.11 (d, 1H, *J* 17.2 Hz, $-CH=CH_2$ (*trans*)) and 5.13 (d, 1H, *J* 17.2 Hz, $-CH=CH_2$ (*trans*)), 5.92 (ddd, 1H, *J* 7.7, 9.9 and 17.2 Hz, $-CH=CH_2$) and 6.00 (ddd, 1H, *J* 7.7, 10.3 and 17.2 Hz, $-CH=CH_2$), 7.22 ~ 7.32 (m, 5H, phenyl). MS (*m/z*): 232 (M^+). Anal. Found: C, 72.35; H, 7.11. Calc. for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94%.

3.1.4. Methyl 2-acetyl-3-phenyl-3-pentenoate (5)

Kugelrohr distillation (85°C/0.3 mmHg). ^1H NMR ($CDCl_3$, ppm): δ1.75 (d, 3H, *J* 7.0 Hz, $-C=CH-CH_3$), 1.91 (s, 3H, CH_3CO-), 3.49 (s, 3H, $-OCH_3$), 4.06 (s, 1H, $-COCHCO-$), 6.27 (q, 1H, *J* 7.0 Hz, $C=CH-CH_3$), 7.29 ~ 7.37 (m, 5H, phenyl). MS (*m/z*: 232 (M^+).

3.1.5. Methyl 2-methoxycarbonyl-3-phenyl-4-pentenoate (6)

Kugelrohr distillation (160°C/0.35 mmHg). ^1H NMR ($CDCl_3$, ppm): δ 3.74 (s, 6H, $-CO_2CH_3$), 3.86 (d, *J* 11.0 Hz, 1H, $-CH(CO_2CH_3)_2$, 4.11 (dd, *J* 8.1 and 11.0 Hz, 1H, $-CH(C_6H_5)CH=CH_2$), 5.08 (d, *J* 10.3 Hz, 1H, $-CH=CH_2$ (*cis*)), 5.12 (d, *J* 16.9 Hz, 1H, $-CH=CH_2$(*trans*)), 5.99 (ddd, *J* 8.1, 10.3 and 16.9 Hz, 1H, $-CH=CH_2$), 7.21 ~ 7.31 (m, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$, ppm): δ 49.7 ($-CH(CO_2CH_3)_2$), 52.5 ($-CO_2CH_3$), 57.3 ($-CH(C_6H_5)CH=CH_2$), 116.6 ($-CH=CH_2$), 125.4 ~ 132.9 (phenyl), 137.8 ($-CH=CH_2$), 167.5 ($C=O$). MS (*m/z*): 248 (M^+).

3.1.6. Methyl (E)-2-methoxycarbonyl-5-phenyl-4-pentenoate (7)

Kugelrohr distillation (160°C/0.35 mmHg). ^1H NMR ($CDCl_3$, ppm): δ2.80 (dd, 2H, *J* 6.2 and 7.3 Hz, $-CH_2-$), 3.48 (s, 6H, $-CO_2CH_3$), 3.53 (t, 1H, *J* 7.3 Hz, $-CH(CO_2(CO_2CH_3)$, 6.13 (dt, 1H, *J* 15.8 and 6.2 Hz, $-CH=CH-C_6H_5$), 6.46 (d, 1H, *J* 15.8 Hz, $-CH=CH-C_6H_5$), 7.21 ~ 7.31 (m, 5H, C_6H_5-). ^{13}C NMR ($CDCl_3$, ppm): δ 32.2 ($-CH_2-$), 51.7 ($-CH(CO_2CH_3)$, 52.4 ($-CO_2CH_3$), 125.4 ~ 132.9

(phenyl), 132.9 (-*C*H=CH-C_6H_5), 140.5 (-CH=*C*H-C_6H_5), 169.5 (*C*=O). MS (*m/z*: 248 (M^+).

3.1.7. Ethyl 2-ethoxycarbonyl-3-phenyl-4-pentenoate (8)

Kugelrohr distillation (150°C/0.2 mmHg). ^{1}H NMR ($CDCl_3$, ppm): δ 0.98 (t, 6H, *J* 7.3 Hz, $-CO_2CH_2(CH_3)$, 3.35 (dd, 1H, *J* 7.3 and 11.0 Hz, -C*H* (C_6H_5)CH=CH_2), 3.82 (d, 1H, *J* 11.0 Hz, $-CH(CO_2C_2H_5)_2$), 3.93 (q, 2H, *J* 7.3 Hz, $-OCH_2CH_3$), 5.07 (d, 1H, *J* 10.1 Hz, -CH=CH_2 (*cis*)), 5.11 (d, 1H, *J* 14.7 Hz, -CH=CH_2 (*trans*)), 6.03 (ddd, 1 H, *J* 10.1, 11.0 and 14.7 Hz, -C*H*=CH_2), 7.17 ~ 7.30 (m, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$, ppm): δ 13.7 ($-CO_2CH_2CH_3$), 49.6 (-*C*H(C_6H_5)CH=CH_2), 57.3 (~*C*H($CO_2C_2H_5$)$_2$), 61.2 ($-OCH_2CH_3$), 125.4 ~ 128.8 (phenyl), 116.4 (-CH=*C*H_2), 137.9 (-*C*H=CH_2), 167.8 (*C*=O). MS (*m/z*) 276 (M^+).

3.1.8. Ethyl (E)-2-ethoxycarbonyl-5-phenyl-4-pentenoate (9)

Kugelrohr distillation (150–170°C/0.2 mmHg). ^{1}H NMR ($CDCl_3$, ppm): δ 1.25 (t, *J* 7.0 Hz, 6H, $-CO_2CH_2(CH_3)$, 2.80 (dd, *J* 7.3 and 7.7 Hz, 2H, $-CH_2$-CH=CH_2), 3.49 (t, *J* 7.7 Hz, $-CH(CO_2C_2H_5)_2$), 4.21 (q, 4H, *J* 7.0 Hz, $-OCH_2CH_3$), 6.16 (dt, *J* 15.8 and 7.3 Hz, -C*H*=CH-C_6H_5), 6.48 (d, *J* 15.8 Hz, -CH=C*H*-C_6H_5), 7.19 ~ 7.33 (m, C_6H_5). ^{13}C NMR ($CDCl_3$, ppm): δ 14.0 ($-OCH_2CH_3$), 32.2 ($-CH_2$-), 51.9 (-*C*H-), 61.4 ($-OCH_2CH_3$), 125.5 (-*C*H=CH-C_6H_5), 126.1 ~ 137.0 (phenyl), 132.7 (-CH=*C*H-C_6H_5), 168.8 (*C*=O). MS (*m/z*): 276 (M^+).

3.1.9. Ethyl (E)-2-acetyl-2-methyl-5-phenyl-4-pentenoate (11)

Kugelrohr distillation (140°C/0.3 mmHg). ^{1}H NMR ($CDCl_3$, ppm): δ1.26 (t, 3H, *J* 7.3 Hz, $-OCH_2CH_3$), 1.38 (s, 3H, CH_3CO-), 2.18 (s, 3H, CH_3-), 2.46 (dd, 1H, *J* 14.3 and 7.7 Hz, $-CH_2$-) and 2.78 (dd, 1H, *J* 14.3 and 7.0 Hz, $-CH_2$-), 4.20 (q, 2H, *J* 7.3 Hz, $-OCH_2(CH_3)$, 6.05 (dt, 1H, *J* 15.8 and 7.3 Hz, -CH=C*H*-CH_2), 6.43 (d, 1H, *J* 15.8 Hz, -C*H*=CH-CH_2), 7.20 ~ 7.33 (m, 5H, phenyl). ^{13}C NMR)$CDCl_3$, ppm): δ 14.1 ($-OCH_2CH_3$), 19.1 ($-CH_3$), 26.3 (CH_3CO-), 38.6 ($-CH_2$-), 59.8 (*C*), 61.4 ($-OCH_2CH_3$) 124.2 (-CH=CH-CH_2), 126.1 ~ 128.7 and 137.0 (phenyl), 133.2 (-CH=*C*H-C_6H_5), 172.5 (-*C*OO-C_2H_5), 205.1 (-*C*OCH_3).

3.1.10. Ethyl 2-acetyl-3-methyl-4-pentenoate (12)

Kugelrohr distillation (60°C/0.7 mmHg). Compound **12** was obtained as a 1 : 1 mixture of the diastereomers. IR (neat): 1741, 1714, 1641 cm^{-1}. ^{1}H NMR ($CDCl_3$, ppm): δ 1.03 (d, 3H, *J* 6.9 Hz, $-CH_3$) and 1.07 (d, 3H, *J* 6.9 Hz, $-CH_3$), 1.25 (t, 3H, *J* 7.0 Hz, $-OCH_2CH_3$) and 1.28 (t, 3H, *J* 7.0 Hz, $-OCH_2H_3$), 2.19 (s, 3H, CH_3CO-) and 2.24 (s, 3H, CH_3CO-), 2.98 (ddq, 1H × 2, *J* 8.0, 9.5 and 6.9 Hz, -C*H*-), 3.36 (d, 1H × 2, *J* 9.5 Hz, -COC*H*CO-), 4.15 (q, 2H, *J* 7.0 Hz, $-OCH_2CH_3$) and 4.19 (q, 2H, *J* 7.0 Hz, $-OCH_2CH_3$), 5.01 (d, 1H, *J* 10.3 Hz, -CH=CH_2 (*cis*)) and 5.08 (d, 1H, *J* 10.3 Hz, -CH=CH_2 (*cis*)), 5.07 (d, 1H × 2, *J* 17.2 Hz, -CH=CH_2 (*trans*)), 5.71 (ddd, 1H, *J* 8.0, 10.3 and 17.2 Hz, -C*H*=CH_2) and 5.74 (ddd, 1H, *J* 8.0, 10.3 and 17.2 Hz, -C*H*=CH_2). ^{13}C NMR ($CDCl_3$, ppm): δ 14.1 ($-CH_3$ × 2), 18.0 and 18.1 ($-OCH_2CH_3$), 29.3 and 29.4 ($-COCH_3$), 37.7 and 37.9 (-*C*HCH_3), 61.2 and 61.3 ($-OCH_2CH_3$), 65.9 (-COCHCO- × 2), 115.3 and 115.5 (-CH=*C*H_2), 139.8 (-*C*H=CH_2 × 2), 168.6 ($-COOC_2H_5$ × 2), 202.0 ($-COCH_3$ × 2). MS (*m/z*): 184 (M^+). Anal. Found: C, 65.22; H, 8.53. Calc. for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75%.

3.1.11. Ethyl 2-acetyl-4-hexenoate (13)

^{1}H NMR ($CDCl_3$, ppm): δ 1.26 (t, 3H, *J* 6.3 Hz, $-OCH_2CH_3$), 1.63 (d, 3H, *J* 6.2 Hz, $-CH_3$), 2.22 (s, 3H, CH_3CO-), 2.52 (dd, 2H, *J* 6.2 and 7.0 Hz, $-CH_2$-), 3.46 (t, 1H, *J* 7.0 Hz, -COC*H*CO-), 4.17 (q, 2H, *J* 6.3 Hz, $-OCH_2CH_3$), 5.35 (dt, 1H, *J* 15.2 and 6.3 Hz, $-CH_2$-C*H*=CH-), 5.52 (dq, 1H, *J* 15.2 and 6.2 Hz, -CH=C*H*-CH_3). MS (*m/z*): 184 (M^+).

3.1.12. Ethyl 2-acetyl-3-propyl-4-pentenoate (14)

Kugelrohr distillation (85°C/0.8 mmHg). Compound **14** was obtained as a 1 : 1 mixture of the diastereomers. ^{1}H NMR ($CDCl_3$, ppm): δ 0.86 (t, 3H, *J* 6.6 Hz, CH_3CH_2-) and 0.88 (t, 3H, *J* 6.6 Hz, CH_3CH_2-), 1.23 (t, 3H, *J* 7.0 Hz, $-OCH_2CH_3$) and 1.28 (t, 3H, *J* 7.0 Hz, $-OCH_2(CH_3)$, 1.30 (m, 2H × 2, $CH_3CH_2CH_2$-) and 1.32 (m, 2H × 2, $CH_3CH_2CH_2$-), 2.17 (s, 3H, CH_3CO-) and 2.23 (s, 3H, CH_3CO-), 2.80 (ddt, 1H × 2, *J* 7.3, 9.4 and 6.6 Hz, -C*H*-CH=CH_2), 3.41 (d, 1H, *J* 9.4 Hz, -COC*H*CO-) and 3.42 (d, 1H, *J* 9.4 Hz, -COC*H*CO-), 4.14 (q, 2H, *J* 7.0 Hz, $-OCH_2CH_3$) and 4.20 (q, 2H, *J* 7.0 Hz, $-OCH_2CH_3$), 5.05 (d, 1H, *J* 10.6 Hz, -CH=CH_2 (*cis*)) and 5.07 (d, 1H, *J* 10.6 Hz, -CH=CH_2 (*cis*)), 5.06 (d, 1H × 2, *J* 16.5 Hz, -CH=CH_2 (*trans*)), 5.54 (ddd, 1H, *J* 7.3, 10.6 and 16.5 Hz, -C*H* = CH_2) and 5.60 (ddd, 1H, *J* 7.3, 10.6 and 16.5 Hz, -C*H*=CH_2). MS (*m/z*): 212 (M^+). Anal. Found: C, 67.73; H, 9.68. Calc. for $C_{12}H_{20}O_3$: C, 67.88; H, 9.50%.

3.1.13. Ethyl (E)-2-acetyl-3-octenoate (15)

^{1}H NMR ($CDCl_3$, ppm): δ 0.88 (t, 3H, *J* 6.9 Hz, CH_3CH_2-), 1.26 (t, 3H, *J* 6.9 Hz, $-OCH_2CH_3$), 1.32 (m, 2H, $CH_3CH_2CH_2$-), 1.93 (dt, 2H, *J* 6.9 and 9.5 Hz, $CH_3CH_2CH_2CH$=), 2.22 (s, 3H, CH_3CO), 3.48 (t,

1H, *J* 7.3 Hz, $-COCHCO$), 4.23 (q, 2H, *J* 6.9 Hz, $-OCH_2CH_3$), 5.35 (dt, 1H, *J* 15.2 and 6.9 Hz, $=CH-CH_2-$), 5.53 (dt, 1H, *J* 15.2 and 9.5 Hz, $CH_3CH_2CH_2CH=$).

3.1.14. 3-Acetyl-4-methyl-5-hexen-2-one (16) [6]

Kugelrohr distillation (80°C/0.4 mmHg), ^{1}H NMR ($CDCl_3$, ppm): δ 1.0 (d, 3H, *J* 7.0 Hz, CH_3-), 2.20 (s, 3H, $-COCH_3$), 3.03 (ddq, 1H, *J* 8.1, 10.6 and 7.0 Hz, $-CH-CH(COCH_3)_2$), 3.61 (d, 1H, *J* 10.6 Hz, $-CH(COCH_3)_2$), 5.01 (d, 1H, *J* 10.3 Hz, $-CH=CH_2$ (*cis*)), 5.08 (d, 1H, *J* 17.2 Hz, $-CH=CH_2$ (*trans*)), 5.65 (ddd, 1H, *J* 8.1, 10.3 and 17.2 Hz, $-CH=CH_2$). ^{13}C NMR ($CDCl_3$, ppm): δ 18.2 (CH_3-), 29.4 ($-COCH_3$), 38.2 ($-CH-CH(COCH_3)_2$), 75.3 ($-CH(C)CH_3)_2$) 115.5 ($-CH=CH_2$), 139.6 ($-CH=CH_2$), 203.5 (C=O). MS (*m/z*): 154 (M^+). Anal. Found: C, 69.95; H, 9.08. Calc. for $C_9H_{14}O_2$: C, 70.09; H, 9.15%.

3.1.15. (E)-3-Acetyl-5-hepten-2-one (17) [6]

Kugelrohr distillation (80 ~ 85°C/0.4 mmHg). ^{1}H NMR ($CDCl_3$, ppm): δ 1.64 (d, 3H, *J* 6.6 Hz, $-CH_3$), 2.15 (s, 3H, $-COCH_3$), 2.54 (dd, 2H, *J* 6.6 and 7.3 Hz, $-CH_2-CH=$), 3.69 (t, 1H, *J* 7.3 Hz, $-CH(COCH_3)_2$), 5.34 (dt, 1H, *J* 15.4 and 6.6 Hz, $-CH_2-CH=CH-CH_3$), 5.53 (dq, 1H, *J* 15.4 and 6.6 Hz, $-CH_2-CH=CH-CH_3$).

3.1.16. Ethyl 2-ethoxycarbonyl-3-methyl-4-pentenoate (18)

Kugelrohr distillation (90°C/0.3 mmHg). ^{1}H NMR ($CDCl_3$, ppm): δ 1.10 (d, 3H, *J* 7.0 Hz, $-CH_3$), 1.26 (t, 6H, *J* 7.0 Hz, CH_3CH_2O-), 2.95 (ddq, 1H, *J* 8.1, 8.8 and 7.0 Hz, $-CH-CH(CO_2C_2H_5)_2$), 3.27 (d, 1H, *J* 8.8 Hz, $-CH(CO_2C_2H_5)_2$), 4.18 (q, 4H, 7.0 Hz, $-OCH_2CH_3$), 5.01 (d, 1H, *J* 10.3 Hz, $-CH=CH_2$ (*cis*)), 5.09 (d, 1H, *J* 17.2 Hz, $-CH=CH_2$ (*trans*)), 5.79 (ddd, 1H, *J* 8.1, 10.3 and 17.2 Hz, $-CH=CH_2$). ^{13}C NMR ($CDCl_3$, ppm): δ 14.1 ($-OCH_2CH_3$), 17.81 ($-CH_3$), 37.9 ($-CH-CH(CO_2C_2H_5)_2$), 52.2 ($-CH(CO_2C_2H_5)_2$), 61.1 ($-OCH_2CH_3$), 115.3 ($-CH=CH_2$), 139.8 ($-CH=CH_2$), 168.0 (C = O). Anal. Found: C, 61.62; H, 8.71. Calc. for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47%.

3.1.17. Ethyl (E)-2-ethoxycarbonyl-4-hexenoate (19)

Kugelrohr distillation (90°C/0.3 mmHg). ^{1}H NMR ($CDCl_3$, ppm): δ 1.28 (t, 6H, *J* 7.0 Hz, $-OCH_2CH_3$), 1.63 (d, 3H, *J* 7.7 Hz, CH_3-), 2.56 (dd, 2H, *J* 7.1 and 8.1 Hz, $-CH_2-CH=$), 3.37 (t, 1H, *J* 8.1 Hz, $-CH-$), 4.21 (q, 4H, 7.0 Hz, $-OCH_2CH_3$), 5.38 (dt, 1H, *J* 15.0 and 7.1 Hz, $-CH_2-CH=CH-CH_3$), 5.53 (dq, 1H, *J* 15.0 and 7.7 Hz, $=CH-CH_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 14.1 ($-OCH_2CH_3$), 17.9 ($-CH_3$), 31.8 ($-CH_2-CH=CH-$), 57.7 ($-CH(CO_2C_2H_5)_2$), 61.2 ($-OCH_2CH_3$), 126.5 ($-CH_2-CH=CH-CH_3$), 128.3 ($-CH_2-CH=CH-CH_3$), 169.0 (C = O).

3.1.18. Ethyl (E)-2-acetyl-2-methyl-4-hexenoate (21)

Kugelrohr distillation (80°C/0.9 mmHg). ^{1}H NMR ($CDCl_3$, ppm): δ 1.25 (t, 3H, *J* 7.0 Hz, $-OCH_2CH_3$), 1.30 (s, 3H, $-CH_3$), 1.63 (dd, 3H, *J* 6.2 and 1.8 Hz, $-CH=CH-CH_3$), 2.14 (s, 3H, CH_3CO-), 2.45 (dd, 1H, *J* 14.3 and 6.6 Hz, $-CH_2-$) and 2.55 (dd, 1H, *J* 14.3 and 7.0 Hz, $-CH_2-$), 4.20 (q, 2H, *J* 7.0 Hz, $-OCH_2CH_3$), 5.26 (dddq, 1H, *J* 15.2, 7.0, 6.6 and 1.8 Hz, $-CH_2-CH=CH-$), 5.50 (dq, 1H, *J* 15.2 and 6.2 Hz, $-CH=CH-CH_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 14.0 ($-OCH_2CH_3$), 17.9 ($-CH=CH-CH_3$), 26.6 ($-COCH_3$), 38.1 ($-CH_2-$), 59.6 ($-C-$), 61.2 ($-OCH_2CH_3$), 124.9 ($-CH=CH-CH_2$), 132.2 ($-CH_3-CH=CH$). Anal. Found: C, 66.57; H, 9.37. Calc. for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15%.

3.1.19. Ethyl 2-acetyl-2-allyl-4-pentenoate (23)

Kugelrohr distillation (75°C/0.65 mmHg). IR (neat): 1741, 1714, 1641 cm^{-1}. ^{1}H NMR ($CDCl_3$, ppm): δ 1.27 (t, 3H, *J* 7.3 Hz, $-OCH_2(CH_3)$, 2.14 (s, 3H, $-COCH_3$), 2.59 (dd, 2H, *J* 14.5 and 7.3 Hz, one of $-CH_2-$), 2.63 (dd, 2H, *J* 14.5 and 7.3 Hz, one of $-CH_2-$), 4.20 (q, 2H, *J* 7.3 Hz, $-OCH_2CH_3$), 5.09 (d, 2H, *J* 11.4 Hz, $-CH=CH_2$ (*cis*)), 5.10 (d, 2H, *J* 15.8 Hz, $-CH=CH_2$ (*trans*)), 5.60 (ddt, 1H, *J* 15.8, 11.4 and 7.3 Hz, and ddt, 1H, *J* 15.8, 11.4 and 6.9 Hz, $-CH=CH_2$). ^{13}C NMR ($CDCl_3$, ppm): δ 14.1 ($-OCH_2CH_3$), 26.9 ($-COCH_3$), 35.9 ($-CH_2-$), 61.4 ($-OCH_2CH_3$), 63.2 ($-C-$), 119.1 ($-CH=CH_2$), 132.2 ($-CH=CH_2$), 171.4 ($-COOC_2H_5$), 204.0 ($-COCH_3$). MS (*m/z*): 210 (M^+). Anal. Found: C, 68.72; H, 8.84. Calc. for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63%.

3.1.20. Ethyl 2-acetyl-2-methyl-4-pentenoate (24)

Kugelrohr distillation (70°C/1.0 mmHg). ^{1}H NMR ($CDCl_3$, ppm): δ 1.27 (t, 3H, *J* 7.0 Hz, $-OCH_2CH_3$), 1.33 (s. 3H, $-CH_3$), 2.15 (s, 3H, $-COCH_3$), 2.50 (dd, 1H, *J* 14.3 and 7.7 Hz, $-CH_2-$) and 2.63 (dd, 1H, *J* 14.3 and 7.0 Hz, $-CH_2-$), 4.20 (q 2H, *J* 7.0 Hz, $-OCH_2CH_3$), 5.08 (d, 2H, *J* 9.9 Hz, $-CH=CH_2$ (*cis*)), 5.09 (d, 1H, *J* 17.2 Hz, $-CH=CH_2$ (*trans*)), 5.65 (ddt, 1H, *J* 17.2, 9.9 and 7.3 Hz, $-CH=CH_2$): ^{13}C NMR ($CDCl_3$, ppm): δ 14.0 ($-OCH_2CH_3$), 18.8 ($-CH_3$), 26.2 ($-COCH_3$), 39.3 ($-CH_2-$), 59.4 ($-C-$), 61.3 ($-OCH_2CH_3$), 118.9 ($-CH=CH_2$), 132.6 ($-CH=CH_2$), 172.5 ($-COOC_2H_5$), 205.0 ($-COCH_3$).

3.1.21. Methyl 2-acetyl-2-allyl-4-pentenoate (26) [12]

Kugelrohr distillation (85°C/0.8 mmHg). IR (neat): 1745, 1713, 1641 cm^{-1}. ^{1}H NMR ($CDCl_3$, ppm): δ2.11 (s, 3H, $-COCH_3$), 2.57 (dd, 2H, *J* 14.5 and 7.3 Hz, one

of $-CH_2-$), 2.61 (dd, 2H, J 14.5 and 7.3 Hz, one of $-CH_2-$), 3.71 (s, 3H, $-COOCH_3$), 5.07 (d, 2H, J 10.6 Hz, $-CH=CH_2$ (*cis*)), 5.08 (d, 2H, J 15.4 Hz, $-CH=CH_2$ (*trans*)), 5.56 (ddt, 1H, J 15.4, 10.6 and 6.9 Hz, and ddt, 1H, J 15.4, 10.6 and 6.6 Hz, $-CH=CH_2$). ^{13}C NMR ($CDCl_3$, ppm): δ 26.9 ($-COCH_3$), 36.0 ($-CH_2-$), 52.3 ($-OCH_3$), 63.4 ($-C-$), 119.2 ($-CH=CH_2$), 132.1 ($-CH=CH_2$), 171.9 ($-COOCH_3$), 203.8 ($-COCH_3$). MS (m/z) 196 (M^+). Anal. Found: C, 67.53; H, 8.42. Calc. for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22%.

3.1.22. 3-Acetyl-3-allyl-5-hexen-2-one (28) [11]

Kugelrohr distillation (70°C/0.95 mmHg). IR (neat): 1697, 1641 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): δ 2.07 (s, 6H, $-COCH_3$), 2.62 (d, 4H, J 7.3 Hz, $-CH_2-$), 5.09 (d, 2H, J 9.9 Hz, $-CH=CH_2$ (*cis*)), 5.11 (d, 2H, J 17.2 Hz, $-CH=CH_2$ (*trans*)), 5.49 (ddt, 2H, J 17.2, 9.9 and 7.3 Hz, $-CH=CH_2$). ^{13}C NMR ($CDCl_3$, ppm): δ27.1 ($-COCH_3$), 34.9 ($-CH_2-$), 70.3 ($-C-$), 119.2 ($-CH=CH_2$), 131.9 ($-CH=CH_2$), 205.6 ($-COCH_3$). MS (m/z): 180 (M^+). Anal. Found: C, 73.32; H, 9.06. Calc. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95%.

3.1.23. Methyl 2-methoxycarbonyl-2-allyl-4-pentenoate (30)

Kugelrohr distillation (75°C/0.95 mmHg), IR (neat): 1732, 1641 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): δ 2.62 (d, 4H, J 7.3 Hz, $-CH_2-$), 3.69 (s, 6H, $-OCH_3$), 5.08 (d, 2H, J 11.0 Hz, $-CH=CH_2$ (*cis*)), 5.09 (d, 2H, J 15.4 Hz, $-CH=CH_2$ (*trans*)), 5.63 (ddt, 2H, J 15.4, 11.0 and 7.3 Hz, $-CH=CH_2$). ^{13}C NMR ($CDCl_3$, ppm): δ 36.9 ($-CH_2-$), 52.3 ($-COOCH_3$), 57.6 ($-C-$), 119.2 ($-CH=CH_2$), 132.2 ($-CH=CH_2$), 171.1 ($-COOCH_3$). MS (m/z): 212 (M^+). Anal. Found: C, 62.55; H, 7.41. Calc. for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60%.

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