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RUTHENIUM-CATALYZED ADDITION REACTION OF ACETIC ACID TO PROPARGYL ALCOHOL DERIVATIVES: REAGENTS FOR PALLADIUM-CATALYZED 2-ACETOXYALLYLATION OF CARBONUCLEOPHILES

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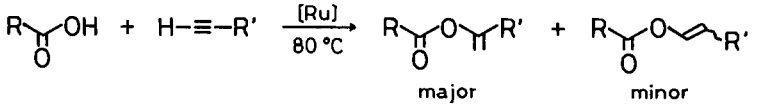
Summary

A bis(η^5-cyclooctadienyl)ruthenium/PCy_3/maleic anhydride system catalyzes the addition reaction of acetic acid to propargyl alcohol derivatives at 80°C to give 2-acetoxyallyl derivatives with high selectivity in high yields. The 2-acetoxyallyl carbonates prepared react with carbonucleophiles in the presence of a catalytic amount of $Pd(PPh_3)_4$ to give a series of novel polyfunctional enol esters in good to excellent yields.

Introduction

Quite recently characteristic organic syntheses catalyzed by ruthenium complexes have undergone rapid development [1,2]. In the course of our study on ruthenium complex catalyst [2a–2c], a selective addition reaction of carboxylic acids to terminal acetylenes catalyzed by bis(η^5-cyclooctadienyl)ruthenium (A)/PR_3/maleic anhydride [2a,2b] has been found (eq. 1) [3].



(1)

[Ru]= bis(η^5-cyclooctadienyl)ruthenium/PR_3/maleic anhydride

On the other hand, allylic derivatives have been found to be useful reagents for palladium-catalyzed allylation of carbonucleophiles [4–6].

Here we report on an example which shows that the combination of the chemistries of ruthenium and palladium would provide a fruitful field in organic synthesis. Combination of the ruthenium-catalyzed selective addition of acetic acid to propargyl compounds affording 2-acetoxyallyl derivatives and the palladium-

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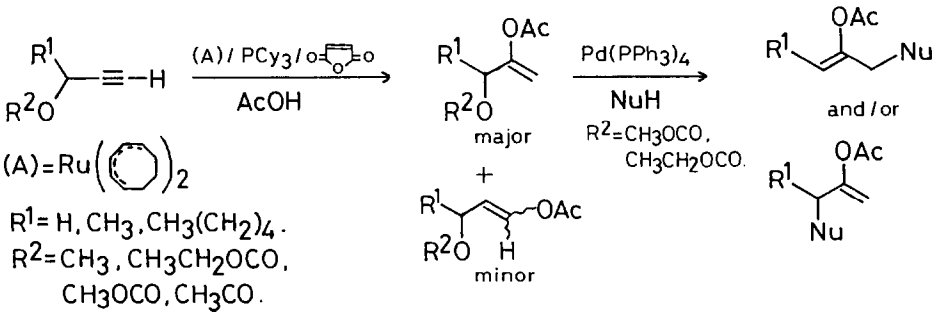


SCHEME 1

catalyzed 2-acetoxyallylation of carbonucleophiles provides a new method for the synthesis of novel polyfunctional enol esters (Scheme 1), the preliminary results of which have been described [7].

Results and discussion

Selective addition of acetic acid to propargyl alcohol derivatives

Ethyl propargyl carbonate was treated with a large exces of acetic acid in the presence of a catalytic amount of complex A/PCy_3/maleic anhydride at 80°C for 8 h to give ethyl 2-acetoxy-2-propenyl carbonate (**1**) in 63% yield with 99% regioselectivity (Table 1, run 1); the remaining 1% was ethyl 3-acetoxy-2-propenyl carbonate. The reactions of propargyl carbonate with an equivalent mole of acetic acid in toluene gave the corresponding carbonate **1** in 42% yield (run 2). A large excess of acetic acid accelerated the addition reaction and suppressed decomposition of propargyl carbonate. When tributylphosphine was used in place of tricyclohexylphosphine, carbonate **1** was formed in lower yield (23%) with lower regioselectivity (90%) (run 3). Reaction of methyl 1-butyn-3-yl carbonate or methyl 1-octyn-3-yl carbonate with acetic acid gives methyl 2-acetoxy-1-buten-3-yl carbonate (**2**) (44% yield) or methyl 2-acetoxy-1-octen-3-yl carbonate (**3**) (40% yield), respectively (runs 4 and 5). Although the yields were moderate, the regioselectivities were excellent. Ethyl 1-ethynylcyclohexyl carbonate did not react with acetic acid and only decomposition of the carbonate occurred (run 6). Propargyl acetate reacts with acetic acid to give 2-acetoxy-2-propen-1-yl acetate (**4**) in a yield of 47% with regioselectivity of 95% when triphenylphosphine was used (run 7). In this reaction, triphenylphosphine is more suitable than tricyclohexylphosphine (regioselectivity, 84%) with respect to the regioselectivity of the products. Furthermore the reaction of propargyl methyl ether with acetic acid gives methyl 2-acetoxy-2-propen-1-yl ether (**5**) in a yield of 70% with regioselectivity of 74% (run 9). Propargyl trimethylsilyl ether did not react with acetic acid and the starting material was recovered (run 10). Thus the most suitable phosphine ligand for excellent regioselectivity depends upon the substituents at the 3-position of propargyl derivatives, which suggests that both electronic and steric effects of the phosphine ligands and the substituents on the propargyl derivatives would affect the selectivity. A preliminary study on the mechanism of the addition reaction of carboxylic acid to various acetylenes sug-

gested that the nucleophilic attack of acetate anion or acetic acid on the propargyl compounds coordinated to the ruthenium would occur [8].

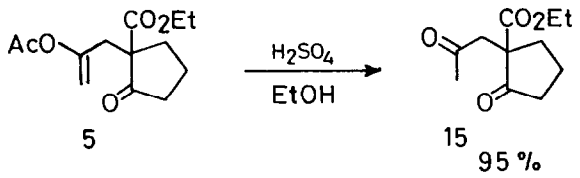
The successful selective synthesis of 2-acetoxyallyl carbonates which have not been synthesized by other methods led us to apply these reagents to palladium-catalyzed allylation of carbonucleophiles found by Tsuji and his co-workers [5,6].

2-Acetoxyallylation catalyzed by tetrakis(triphenylphosphine)palladium

In the presence of a catalytic amount of $Pd(PPh_3)_4$, the reaction of 2-acetoxyallyl carbonates with carbonucleophiles is facile. Results are summarized in Table 2. 2-Acetoxyallyl carbonate **1** when treated with ethyl 2-oxopentanecarboxylate, 2-acetylbutanolide, diethyl malonate, or diethyl 2-methylmalonate gave the corresponding 2-acetoxyallylated compounds **6–9** in yields of 92–34% (runs 11–14). Ethyl acetoacetate reacts smoothly with two equivalents of carbonate **1** selectively to give doubly acetoxyallylated compound **10** in 86% yield (run 15). Since the reaction of 2-acetoxyallylated compound **14** with carbonate **1** is faster than for ethyl acetoacetate, it is difficult to obtain compound **14** selectively (Scheme 2).

Reaction of carbonate **2** with dimethyl malonate gives the corresponding products **11** and **12** (yield 53%, **11**/**12** = 2, run 16). The regioselectivity of **11**/**12** = 2 is almost the same as that observed for the reaction of methyl 1-buten-3-yl carbonate with methyl 2-methyl-3-oxobutanoate in the presence of a catalytic amount of $Pd_2(dba)_3 \cdot CHCl_3/4\ PPh_3$ [6]; the acetoxy group in **2** did not affect the regioselectivity. The reaction of carbonate **3** with dimethyl malonate gave compound **13** as the sole product (run 17). It seems that the steric effect of the $CH_3(CH_2)_4$ group in **3** controlled the regioselectivity. The products **1–13** are novel polyfunctional enol esters and can be utilized as intermediates for further organic syntheses such as the precursors of enolate anions [9].

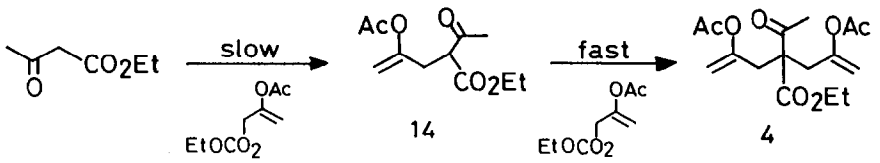
Ethanolysis of **6** in the presence of a catalytic amount of 95% H_2SO_4 gave the 1,4-diketone **15** in 95% yield (eq. 2) [10].



(2)

Thus the combination of the ruthenium-catalyzed selective addition of acetic acid to propargyl carbonates and the palladium-catalyzed 2-acetoxyallylation reaction provides a novel synthetic method for the new and useful polyfunctional enol esters.

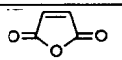
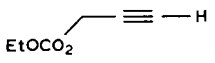
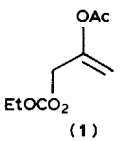
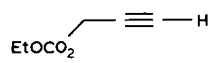
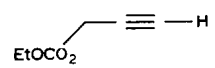
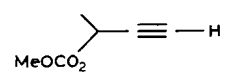
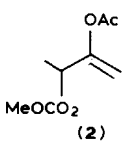
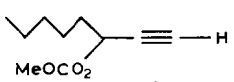
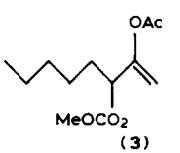
(*Continued on p. 404*)

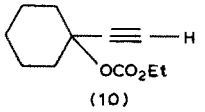
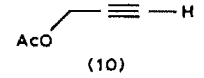
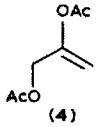
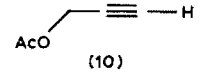
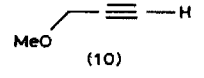
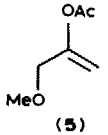
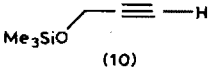


SCHEME 2

TABLE 1

SELECTIVE ADDITION OF ACETIC ACID TO PROPARGYLALCOHOL DERIVERTIVES [a]

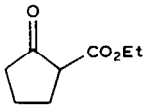
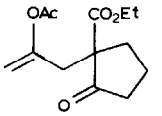
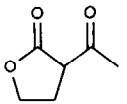
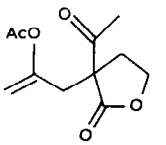
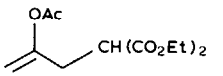
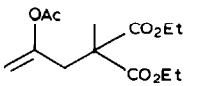
Run	Acetylene (mmol)	Cat. (mmol)	PR_3 (mmol)	 (mmol)	Temp. (°C)	Time (h)	Product	Yield [b] (%)	Regio-selectivity (%)
1	 (10)	0.1	PCy_3 (0.2)	0.2	80	8	 (1)	63 (65)	99
2 [c]	 (10)	0.3	PCy_3 (0.6)	0.6	80	24	1	42	99
3 [d]	 (10)	0.1	PBu_3 (0.2)	0.2	80	6	1	23	90
4	 (10)	0.1	PCy_3 (0.2)	0.2	80	8	 (2)	44	100
5	 (10)	0.1	PCy_3 (0.2)	0.2	80	10	 (3)	40	100

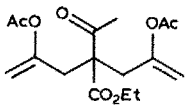
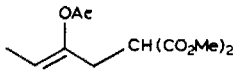
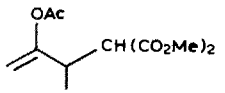
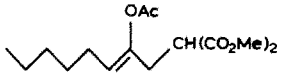
6	 (10)	0.1	PCy_3 (0.2)	0.2	80	4	—	0	–
7 [d]	 (10)	0.2	PPh_3 (0.4)	0.4	80	24	 (4)	(47)	95
8 [d]	 (10)	0.2	PCy_3 (0.4)	0.4	80	24	4	(47)	84
9 [e]	 (10)	0.2	PBu_3 (0.4)	0.4	80	24	 (5)	(70)	74
10	 (10)	0.2	dppe (0.2)	0.4	80	28	—	0	–

[a] Reactions were carried out in acetic acid (5.0 cm^3) under argon. [b] Isolated yield (GLC yield). [c] Acetic acid (30 mmol), toluene (15.0 cm^3) as solvent in a 50 cm^3 autoclave. [d] Acetic acid (10 mmol), toluene (5.0 cm^3) as solvent. [e] Acetic acid (10 mmol), benzene (5.0 cm^3) as solvent in a heavy-walled sealed tube.

TABLE 2

REACTION OF 2-ACETOXYALLYL CARBONATES WITH CARBONUCLEOPHILES [a]

Run	Carbonate (mmol)	nucleophile (mmol)	Cat. (mmol)	Temp (°C)	Time (h)	Product	Yield [b] (%)
11	**1** (5)	 (5)	0.2	23	6	 (**6**)	92
12	**1** (10)	 (10)	0.2	28	1	 (**7**)	83
13	**1** (5)	$CH_2(CO_2Et)_2$ (15)	0.1	17	3	 (**8**)	77
14	**1** (10)	$CH_3CH(CO_2Et)_2$ (5)	0.2	60	53	 (**9**)	34

15	**1** (10)	$CH_3COCH_2CO_2Et$ (5)	0.1	60	7	 **(10)**	86
16	**2** (5)	$CH_2(CO_2Me)_2$ (15)	0.1	50	6	 **(11)**	53 **11/12** = 2
						 **(12)**	
17	**3** (5)	$CH_2(CO_2Me)_2$ (15)	0.2	60	7	 **(13)**	56

[a] Reactions were carried out using $Pd(PPh_3)_4$ in THF (10.0 cm^3) as solvent under argon. [b] Isolated yield.

Experimental

All boiling points were uncorrected. Infrared spectra were recorded on a Nicolet 5-MX spectrometer as films. ^{1}H NMR spectra were obtained by use of a JNM-FX-100 spectrometer as 10% solutions with tetramethylsilane as an internal reference. ^{13}C NMR spectra were recorded with a JNM-FX-100 (25.05 MHz) spectrometer as 40% solutions with tetramethylsilane as an internal reference. Mass spectra were recorded with a JMS-01SG mass spectrometer. Microanalyses were performed by the Laboratory for Organic Elemental Microanalysis at the Faculty of Pharmaceutical Science at Kyoto University. Gas chromatographic analyses (GLC) were carried out on a 3 m × 3 mm diameter column with OV 17. Propargyl carbonates [5], propargyl acetate [11], and propargyl methyl ether [12] were prepared by methods described in the literature. The complex bis(η^5-cyclooctadienyl)ruthenium (complex **A**) [13] was prepared from (η^4-1,5-cyclooctadiene)(η^6-1,3,5-cyclooctatriene) ruthenium [14]. The complex $Pd(PPh_3)_4$ was prepared by a published method [15]. PCy_3, PBu_3, ethyl acetoacetate, ethyl 2-oxocyclopentanecarboxylate, diethyl malonate, dimethyl malonate, diethyl 2-methylmalonate, 2-acetylbutanolide, acetic acid, toluene, benzene, and THF were commercial samples and were purified by distillation or by recrystallization under argon before use. All the catalytic reactions were carried out under argon.

Addition of acetic acid to propargyl alcohol derivatives

The reaction of ethyl propargyl carbonate is representative. A mixture of ethyl propargyl carbonate (1.28 g, 10 mmol), acetic acid (5.0 cm^3), complex **A** (0.032 g, 0.1 mmol), tricyclohexylphosphine (0.056 g, 0.2 mmol), and maleic anhydride (0.020 g, 0.2 mmol) was stirred under argon at 80°C for 8 h. Careful vacuum distillation of the reaction mixture afforded 1.18 g (63% yield) of ethyl 2-acetoxy-2-propenyl carbonate **1**. Other reactions were carried out in a similar manner.

Ethyl 2-acetoxy-2-propen-1-yl carbonate (1). Colorless liquid; b.p. 90°C (3 mmHg); IR (neat) 1674, 1759vs, br cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.11 (dt, J 2.0, 0.8 Hz, 1H), 5.03 (d, J 2.0 Hz, 1H), 4.66 (d, J 0.8 Hz, 2H), 4.21 (q, J 7.1 Hz, 2H), 2.15 (s, 3H), 1.31 (t, J 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 168.6 (s), 154.8 (s), 150.0 (s), 105.7 (t), 65.8 (t), 64.3 (t), 20.7 (q), 14.3 (q); MS, m/z 188 (M^+). Anal. Found: C, 51.31; H, 6.56. $C_8H_{12}O_5$ calc: C, 51.06; H, 6.43%.

Methyl 2-acetoxy-1-buten-3-yl carbonate (2). Colorless liquid; b.p. 78°C (3 mmHg); IR (neat) 1667, 1753, 1765 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.24 (qd, J 6.7, 0.6 Hz, 1H), 5.14 (dd, J 2.2, 0.6 Hz, 1H), 5.00 (d, J 2.2 Hz, 1H), 3.78 (s, 3H), 2.17 (s, 3H), 1.43 (d, J 6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 168.6 (s), 155.0 (s), 152.9 (s), 104.0 (t), 73.1 (d), 54.8 (q), 20.8 (q), 17.9 (q); MS, m/z 188 (M^+). Anal. Found: C, 51.15; H, 6.51. $C_8H_{12}O_5$ calc: C, 51.06; H. 6.43%.

Methyl 2-acetoxy-1-octen-3-yl carbonate (3). Colorless liquid; b.p. 90°C (0.7 mmHg); IR (neat) 1667, 1753, 1767 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.01–5.15 (m, 3H), 3.78 (s 3H), 2.16 (s, 3H), 1.15–1.88 (m, 8H), 0.89 (t, J 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 168.3 (s), 155.2 (s), 151.8 (s), 104.7 (t), 77.1 (d), 54.7 (q), 31.7 (t), 31.5 (t), 24.8 (t), 22.6 (t), 20.8 (q), 14.0 (q); MS, m/z 244 (M^+). Anal. Found: C, 59.24; H, 8.50. $C_{12}H_{20}O_5$ calc: C, 59.00; H, 8.25%.

2-Acetoxy-2-propen-1-yl acetate (4). Colorless liquid; b.p. 107°C (26 mmHg); IR (neat) 1674, 1759vs, br cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.08 (td, J 2.0, 0.7 Hz, 1H), 5.01

(d, *J* 2.0 Hz, 1H). 4.62 (d *J* 0.7 Hz, 2H), 2.16 (s, 3H), 2.09 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 170.1 (s), 168.7 (s), 150.4 (s), 105.3 (t), 62.8 (t), 20.8 (q), 20.6 (q); MS, *m/z* 158 (M^+). Anal. Found: C, 52.93; H, 6.49. $C_7H_{10}O_4$ calc: C, 53.16; H, 6.37%.

2-Acetoxy-2-propen-1-yl methyl ether (5). Colorless liquid; b.p. 82°C (47 mmHg); IR (neat) 1119, 1674, 1757 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.00 (m, 1H), 4.95 (d, *J* 1.5 Hz, 1H), 3.95 (s, 2H), 3.35 (s, 3H), 2.14 (s, 3H); ^{13}C NMR($CDCl_3$) δ 174.5 (s), 152.1 (s), 103.6 (t), 71.2 (t), 58.0 (q), 20.8 (q); MS, *m/z* 130 (M^+). Anal. Found: C, 55.82; H, 8.30. $C_6H_{10}O_3$ calc: C, 55.37; H, 7.75%.

Reaction of 2-acetoxyallyl carbonates with carbonucleophiles

The reaction of ethyl 2-acetoxy-2-propen-1-yl carbonate (**1**) with ethyl 2-oxocyclopentanecarboxylate is representative. A mixture of **1** (0.94 g, 5mmol), ethyl 2-oxocyclopentanecarboxylate (0.78 g, 5 mmol) and $Pd(PPh_3)_4$ (0.23 g, 0.2 mmol), in THF (10.0 cm^3) was stirred under argon at 23°C for 6 h. Careful vacuum distillation of the reaction mixture afforded 1.17 g (92%) of ethyl 1-(2-acetoxy-2-propen-1-yl)-2-oxocyclopentanecarboxylate (**6**). Other reactions were carried out in a similar manner.

Ethyl 1-(2-acetoxy-2-propen-1-yl)-2-oxocyclopentanecarboxylate (6). Colorless liquid; (Kugelrohr) 140°C (0.6 mmHg); IR (neat) 1667, 1726, 1759vs, br cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.84 (s, 2H), 4.16 (q, *J* 7.1 Hz, 2H), 2.81 (d, *J* 1.6 Hz, 2H), 1.78–2.67 (m, 6H), 2.06 (s, 3H), 1.25 (t, *J* 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 213.4 (s), 170.3 (s), 168.2 (s), 152.2 (s), 105.7 (t), 61.5 (t), 58.6 (s), 37.6 (t), 37.3 (t), 31.8 (t), 20.7 (q), 19.6 (t), 14.0 (q); MS, *m/z* 254 (M^+). Anal. Found: C, 61.46; H. 7.29. $C_{13}H_{18}O_5$ calc: C, 61.41; H, 7.13%.

2-Acetyl-2-(2-acetoxy-2-propen-1-yl)-butanolide (7). Colorless liquid; b.p. 118°C (0.6 mmHg); IR (neat) 1667, 1713, 1757, 1767 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.94 (d, *J* 2.0 Hz, 1H), 4.86 (dt, *J* 2.0, 0.9 Hz, 1H), 4.07–4.45 (m, 2H), 2.92 (s, 2H), 2.77–2.87 (m, 1H), 2.34 (s, 3H), 2.16–2.30 (m, 1H), 2.09 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 201.4 (s), 174.9 (s), 168.3 (s), 150.9 (s), 105.9 (t), 66.5 (t), 59.7 (s), 38.1 (t), 28.4 (t), 25.4 (q), 20.7 (q); MS, *m/z* 226 (M^+). Anal. Found: C, 58.60; H, 6.39. $C_{11}H_{14}O_5$ calc: C, 58.40; H. 6.24%.

Ethyl 4-acetoxy-2-ethoxycarbonyl-4-pentenoate (8). Colorless liquid; b.p. 90°C (0.15 mmHg); IR (neat) 1671, 1736, 1755 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.83 (s, 2H), 4.21 (q, *J* 7.1 Hz, 4H), 3.56 (t, *J* 7.7 Hz, 1H), 2.83 (d, *J* 7.7 Hz, 2H), 2.13 (s, 3H), 1.27 (t, *J* 7.1 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 168.4 (s), 168.3 (s), 152.8 (s), 103.5 (t), 61.5 (t), 50.0 (d), 32.9 (t), 20.8 (q), 14.1 (q); MS, m/z 258 (M^+). Anal. Found: C, 55.89; H. 7.07. $C_{12}H_{18}O_6$ calc: C, 55.81; H. 7.02%.

Ethyl 4-acetoxy-2-ethoxycarbonyl-2-methyl-4-pentenoate (9). Colorless liquid; (Kugelrohr) 100°C (0.2 mmHg); IR (neat) 1671, 1732, 1759 cm^{-1}; ^{1}H NMR($CDCl_3$) δ 4.89 (d, *J* 1.6 Hz, 1H), 4.83 (m, 1H), 4.19 (q, *J* 7.2 Hz, 4H), 2.89 (s, 2H), 2.07 (s, 3H), 1.44 (s, 3H), 1.25 (t, *J* 7.2 Hz, 6H); ^{13}C NMR($CDCl_3$) δ 171.4 (s), 168.3 (s), 151.5 (s), 105.7 (t), 61.4 (t), 52.5 (s), 39.4 (t), 21.0 (q), 19.5 (q), 14.0 (q); MS, *m/z* 272 (M^+). Anal. Found: C, 57.59; H, 7.57. $C_{13}H_{20}O_6$ calc: C, 57.34; H. 7.41%.

Ethyl 2-acetyl-4-acetoxy-2-(2-acetoxy-2-propen-1-yl)-4-pentenoate (10). Colorless liquid; (Kugelrohr) 160°C (0.15 mmHg); IR (neat) 1667, 1715, 1761 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.93 (d, *J* 1.7 Hz, 2H), 4.86 (m, 2H), 4.21 (q, *J* 7.1 Hz, 2H), 2.93 (s, 4H), 2.18 (s, 3H), 2.06 (s, 6H), 1.28 (t, *J* 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 202.3 (s), 170.6 (s), 168.2 (s), 150.8 (s), 106.1 (t), 61.8 (t), 60.5 (s), 36.3 (t), 26.4 (q), 20.9 (q),

13.9 (q); MS, *m/z* 326 (M^+). Anal. Found: C, 60.55; H. 6.79. $C_{16}H_{22}O_7$ calc: C, 58.89; H, 6.79%.

In the reaction of **2** with dimethyl malonate, distillation of the reaction mixture gave the products as a mixture of two isomers (**11** and **12**) (Kugelrohr, 110°C (1 mmHg)). Spectral data and elemental analysis of the mixture gave the satisfactory results.

Methyl (Z)-4-acetoxy-2-methoxycarbonyl-4-hexenoate (11). Colorless liquid; ^{1}H NMR ($CDCl_3$) δ 5.21 (qt, *J*. 6.8, 0.8 Hz, 1H), 3.74 (s, 6H), 3.57 (t, *J* 7.6 Hz, 1H), 2.80 (d, *J* 7.6 Hz, 2H), 2.15 (s, 3H), 1.48 (dt, *J* 6.8, 1.1 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 168.9 (s), 168.2 (s), 145.4 (s), 113.9 (d), 52.6 (q), 49.8 (d), 33.1 (t), 20.4 (q), 10.8 (q); MS, *m/s* 244 (M^+). Anal. Found: C, 54.32; H. 6.74. $C_{11}H_{16}O_6$ calc: C, 54.10; H, 6.60%.

Methyl 4-acetoxy-3-methyl-2-methoxycarbonyl-4-pentenoate (12). Colorless liquid; ^{1}H NMR ($CDCl_3$) 4.86–4.92 (m, 2H), 3.74 (s, 6H), 3.52 (d, *J* 9.0 Hz, 1H), 3.12 (qd, *J* 6.8, 9.0 Hz, 1H), 2.15 (s, 3H), 1.18 (d, *J* 6.8 Hz, 3H); ^{13}C NMR($CDCl_3$) 168.9 (s), 168.2 (s), 155.7 (s), 102.6 (t), 55.4 (d), 52.4 (q), 38.8 (d), 21.0 (q), 16.0 (q).

Methyl (Z)-4-acetyl-2-methoxycarbonyl-4-decenoate (13). Colorless liquid; b.p. 111°C (0.15 mmHg); IR (neat) 1698, 1748, 1759 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.13 (t, *J* 7.3 Hz, 1H), 3.73 (s, 6H), 3.58 (t, *J* 7.7 Hz, 1H), 2.79 (t, *J* 7.7 Hz, 2H), 2.13 (s, 3H), 1.78–1.92 (m, 2H), 1.14–149 (m, 6H), 0.87 (t, *J* 6.2 Hz, 3H); ^{13}C NMR($CDCl_3$) δ 168.9 (s), 168.3 (s), 144.6 (s), 119.7 (d), 52.4 (q), 50.0 (d), 33.2 (t), 31.5 (t), 28.7 (t), 25.5 (t), 22.5 (t), 20.5 (q), 14.0 (q); MS, *m/z* 300 (M^+). Anal. Found C, 60.55; H, 8.18. $C_{15}H_{24}O_6$ calc: C, 59.99; H. 8.05%.

Ethanolysis of 6

A mixture of **6** (3.81 g, 15 mmol), ca. 0.1 cm^3 of 95% H_2SO_4, and ethanol (20.0 cm^3) was stirred at 56°C for 12 h. After removal of ethanol in vacuo, the residue was neutralized by addition of saturated aqueous $NaHCO_3$ and extracted with diethyl ether. The ether solution was dried with Na_2SO_4. Careful vacuum distillation of the solution afforded 3.02 g (95%) of ethyl 1-(2-oxopropyl)-2-oxocyclopentane carboxylate (**15**).

Ethyl 1-(2-oxopropyl)-2-oxocyclopentanecarboxylate (15). Colorless liquid; b.p. 104°C (0.6 mmHg); ^{1}H NMR ($CDCl_3$) δ 4.14 (q, *J* 7.1 Hz, 2H), 3.24 (d, *J* 18.6 Hz, 1H), 2.93 (d, *J* 18.6 Hz, 1H), 2.35–2.74 (m, 4H), 1.87–2.27 (m, 2H), 2.14 (s, 3H), 1.23 (t, *J* 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 214.4 (s), 205.1 (s), 170.4 (s), 61.5 (t), 57.4 (s), 47.4 (t), 37.6 (t), 33.2 (t), 29.9 (q), 19.8 (t), 14.0 (q).

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