***trans*-7,8-Dihydroxy-7,8-dihydro-1-isopropylbenzo[*a*]pyrene (2d).** Oxygen gas was bubbled into a stirred solution of **15** (400 mg, 1.23 mmol) and $NaBH_4$ (1.5 g, 40 mmol) in 200 mL of ethanol for 8 h. The solution was partitioned between CH_2Cl_2 and water, and the aqueous layer was extracted twice with CH_2Cl_2. The combined organic extracts were washed with water, dried, and concentrated to a small volume until the dihydro diol **2d** began to crystallize. Filtration gave **2d** (352 mg, 87%): mp 211-212 °C dec, NMR (500 MHz) δ 1.48 (d, 6, CH_3), 4.07 (m, 1, methine), 4.48 (d, 1, H_7), 4.91 (m, 1, H_8, $J_{7,8}$ = 10.6 Hz), 6.22 (m, 1, H_9, $J_{9,10}$ = 10.1 Hz), 7.50 (d, 1, H_{10}, $J_{9,10}$ = 10.2 Hz), 7.9-8.5 (m, 7, Ar); UV λ_{max} (ethanol) 373 nm (ϵ 48 260), 354 (40 800), 337 (20 500), 295 (27 900), 283 (24 960), 255 (45 800).

***trans*-7,8-Dihydroxy-*anti*-9,10-epoxy-1-isopropyl-7,8,9,10-tetrahydrobenzo[*a*]pyrene (3d).** A solution of **2d** (100 mg, 0.3 mmol) in anhydrous THF (20 mL) was stirred with *m*-chloroperbenzoic acid (540 mg, 3 mmol) for 2 h under N_2. The solution was diluted with ether and washed twice with ice-cold 2 N NaOH and once with ice water. The solvent was removed under reduced pressure at 40 °C bath temperature. The solid residue (101 mg) was triturated with dry ether to yield **3d** (61 mg): mp 175-177 °C; NMR (500 MHz) (Me_2SO-d_6) δ 1.49 (d, 6, CH_3), 4.09 (m, 1, methine), 4.13 (m, 1, H_8), 4.26 (m, 1, H_9), 4.91 (m, 1, H_7), 5.03 (dd, 1, H_{10}), 7.99-8.58 (m, 7, Ar); UV λ_{max} (ethanol) 350 nm (ϵ 34 700), 334 (24 200), 281 (37 500), 269 (22 350), 248 (60 250), 239 (39 400), 202 (31 260).

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Registry No. **1d**, 4648-83-3; **2d**, 107616-95-5; **3d**, 107616-96-6; **4**, 3331-46-2; **5**, 107616-82-0; **6**, 107616-83-1; **7**, 107616-84-2; **8**, 107616-85-3; **9**, 107616-86-4; **10**, 107616-87-5; **11**, 107616-88-6; **12**, 107616-90-0; **13**, 107616-91-1; **14a**, 107616-93-3; **14b**, 107616-92-2; **15**, 107616-94-4; *trans*-7,8-dihydroxy-1-isopropenyl-7,8,9,10-tetrahydrobenzo[*a*]pyrene dibenzoate, 107616-89-7.

Ruthenium-Catalyzed Selective Addition of Carboxylic Acids to Alkynes. A Novel Synthesis of Enol Esters

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Carboxylic acids react with alkynes in the presence of a catalytic amount of bis(η^5-cyclooctadienyl)ruthenium/trialkylphosphine/maleic anhydride in toluene at 60-80 °C to give enol esters having a terminal methylene group in good to excellent yields with high regioselectivity. The deuterium distributions in the products of the reaction of acetic acid-*d* with 1-hexyne and ethyl propargyl carbonate were examined. Kinetic measurements revealed that the rate has first-order dependence on carboxylic acid, alkyne, and the initial concentration of the ruthenium catalyst.

Introduction

Enol esters are well-known intermediates for carbon-carbon bond formation in organic synthesis.[1] Three major methods are available for the synthesis of enol carboxylates: (1) the treatment of aldehydes or ketones under either acid or basic conditions with appropriate acid anhydride or chloride;[2] (2) the acetoxylation of olefins promoted by palladium acetate;[3,4] (3) the addition reaction of carboxylic acids to alkynes,[5] in which mercury salts are very useful catalysts. However, since the mercury salts are very toxic, development of safer catalysts has been required. On the other hand, characteristic organic syntheses catalyzed by ruthenium complexes have been developed in recent years.[6] Rotem and Shvo reported the first example of the addition of carboxylic acids to acetylenes catalyzed by $Ru_3(CO)_{12}$.[6b] In the course of our study on characteristic ruthenium-catalyzed organic syntheses,[7] a novel selective addition of carboxylic acids to alkynes catalyzed by bis(η^5-cyclooctadienyl)ruthenium (A)/PR_3/maleic anhydride (eq 1) was found and reported briefly.[7a,b] In this report, the scope of this reaction is described in detail. On the basis of kinetic studies and reactions with

(1) For example: (a) Rozen, S.; Lerman, O. *J. Am. Chem. Soc.* **1979**, *101*, 2782. (b) Wexler, A.; Balchunis, R. J.; Swenton, J. S. *J. Chem. Soc., Chem. Commun.* **1975**, 601. (c) Schmitt, G.; Warwel, S.; Homminga, E.; Meltzow, W. *Justus Liebigs Ann. Chem.* **1972**, *763*, 75. (d) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1972; p 313. (e) Tsuji, J.; Minami, I.; Shimizu, I. *Tetrahedron Lett.* **1983**, *24*, 4713.

(2) For example: (a) House, H. O.; Kramar, V. *J. Org. Chem.* **1963**, *28*, 3362. (b) Cousineau, T. J.; Cook, S. L.; Secrist, J. A., III. *Synth. Commun.* **1979**, *9*, 157.

(3) Kitching, W.; Rapport, Z.; Winstein, S.; Young, W. G. *J. Am. Chem. Soc.* **1966**, *88*, 2054.

(4) Schultz, R. G.; Gross, D. E. *Adv. Chem. Ser.* **1968**, *No. 70*, 97.

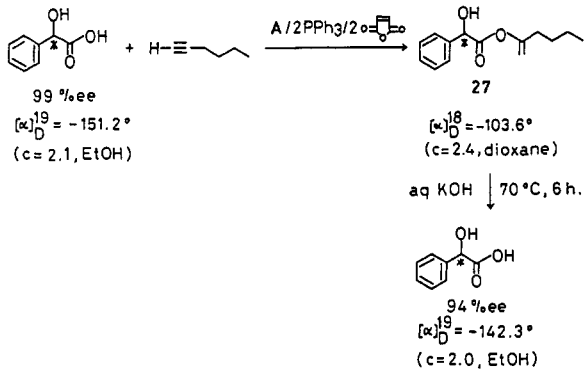
(5) For example: (a) Fahey, R. C.; Lee, D. J. *J. Am. Chem. Soc.* **1966**, *88*, 5555. (b) Hudrlic, P. F.; Hudrlic, A. M. *J. Org. Chem.* **1973**, *38*, 4254. (c) Krafft, G. A.; Katzenellenbogen, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 5459. (d) Lemaire, H.; Lucas, H. J. *J. Am. Chem. Soc.* **1955**, *77*, 939. (e) Hennion, G. F.; Nieuwland, J. A. *J. Am. Chem. Soc.* **1934**, *56*, 1802. (f) Larock, R. C.; Oertle, K.; Beatty, K. M. *J. Am. Chem. Soc.* **1980**, *102*, 1966. (g) Gack, R. D.; Woodward, R. A.; Anderson, T. J.; Glick, M. D. *J. Org. Chem.* **1982**, *47*, 3707. (h) Lambert, C.; Utimoto, K.; Nozaki, H. *Tetrahedron Lett.* **1984**, *25*, 5323. (i) Ishino, Y.; Hirashima, T. *Nippon Kagaku Kaishi* **1985**, *2*, 198.

(6) For example: (a) Bennett, M. A.; Matheson, T. W. *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, 1982; Vol. 4, p 931. (b) Rotem, M.; Shvo, Y. *Organometallics* **1983**, *2*, 1689. (c) Blum, Y.; Shvo, J. *J. Organomet. Chem.* **1985**, *282*, C7. (d) Nakano, T.; Ohkawa, K.; Ikemori, S.; Matsumoto, H.; Nagai, Y. *Nippon Kagaku Kaishi* **1983**, *12*, 1778. (e) Kamigata, N.; Ozaki, J.; Kobayashi, M. *J. Org. Chem.* **1985**, *50*, 5045. (f) Nagashima, H.; Ara, K.; Wakamatsu, H.; Itoh, K. *J. Chem. Soc., Chem. Commun.* **1985**, 518. (g) Smith, T. A.; Aplin, R. P.; Maitlis, P. M. *J. Organomet. Chem.* **1985**, *291*, C13. (h) McKinney, R. J.; Colton, M. C. *Organometallics* **1986**, *5*, 1080. (i) Sasaki, Y.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1986**, 790.

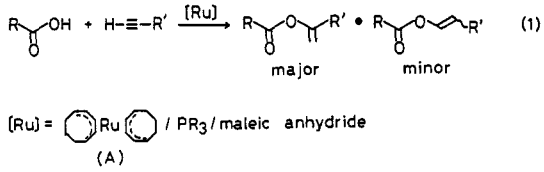
(7) (a) Mitsudo, T.; Hori, Y.; Watanabe, Y. *J. Org. Chem.* **1985**, *50*, 1566. (b) Mitsudo, T.; Hori, Y.; Yamakawa, Y.; Watanabe, Y. *Tetrahedron Lett.* **1986**, *27*, 2125. (c) Mitsudo, T.; Nakagawa, Y.; Watanabe, K.; Hori, Y.; Misawa, H.; Watanabe, H.; Watanabe, Y. *J. Org. Chem.* **1985**, *50*, 565. (d) Tsuji, Y.; Huh, K. T.; Ohsugi, Y.; Watanabe, Y. *J. Org. Chem.* **1985**, *50*, 1365 and references cited therein.

0022-3263/87/1952-2230$01.50/0

Scheme I



deuteriated reagents, a mechanism of the reaction is proposed.



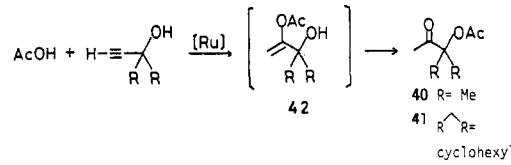
Results and Discussion

Synthesis of Enol Esters. Carboxylic acids readily reacted with acetylene and terminal alkynes in the presence of a catalytic amount of bis(η^5-cyclooctadienyl)ruthenium (A)/PR_3/maleic anhydride in toluene at 60–80 °C to give the corresponding enol esters (eq 1) selectively. The reaction was highly regioselective; the enol ester having the methylene group was a major product, and *E* and *Z* isomers were minor products. Maleic anhydride was essential for the saturated carboxylic acid and the phosphine was essential for the regioselectivity (vide infra). The results are summarized in Tables I–III.

Octadecanoic acid reacted with acetylene to give vinyl octadecanoate (**1**) in 77% yield (run 1). The addition reaction of saturated carboxylic acids to alkynes gave the enol esters **2** and **5**–**11** in 69–99% yields with 90–99% regioselectivity [(major ester/total esters) × 100%] (runs 3–10). In the reaction of acetic acid with 1-hexyne, 1-hexen-2-yl acetate (**2**) was obtained in benzene (yield 88%, regioselectivity 88%), in acetone (93%, 94%), and in 1,2-dimethoxyethane (DME) (76%, 94%) (run 39), respectively.[8] Alkyl substituents on the α-carbon of the carboxylic acids had no effect on the yields and the selectivities (runs 3–10). α,β-Unsaturated carboxylic acids and benzoic acid reacted with alkynes in the presence of a catalytic amount of the complex A/PBu_3 without maleic anhydride to give the products **12**, **15**–**17**, **19**, **20**, and **28** in 50–99% yields with 93–99% regioselectivity (runs 13–16, 18, 19 and 27). The addition of 3-butenoic acid to 1-pentyne gave 1-penten-2-yl 3-butenoate (**18**) and its isomer **15** in 40% and 26% yields (run 17). The reaction of 2,4-hexadienoic acid with an equimolar of 1,7-octadiyne gave 1-octen-7-yn-2-yl (*E*,*E*)-2,4-hexadienoate (**21**) in 30% yield (run 20). Ruthenium-catalyzed cyclization of 4-pentynoic acid gave γ-methylene-γ-butyrolactone (α'-angelica lactone) (**22**) in 52% yield (run 21).

In the absence of maleic anhydride, saturated carboxylic acids did not react with alkynes at all, and the starting materials were recovered. These results show that electron-deficient olefins (π-acid ligands) such as maleic anhydride are required in the addition reaction; α,β-unsaturated carboxylic acids and benzoic acid play a role of π-acid ligand by themselves.[9] On the other hand, in the absence of tributylphosphine, the reaction of acetic acid with 1-hexyne afforded the three isomers **2**–**4** of enol esters in low selectivity; the regioselectivity was contrary of run 3 (run 2). The reaction of 2-methyl-2-propenoic acid with 1-pentyne also afforded the three isomers **12**–**14** (run 12). These results show that the phosphine ligands control the regioselectivity of enol esters.

Scheme II



To elucidate the effect of the functional groups on the reactivity of the carboxylic acid, reactions of α- and γ-keto acids, *N*-acetylamino acid, and α-hydroxy carboxylic acid were performed (runs 22–26). These acids also gave satisfactory results when an appropriate phosphine ligand and solvent such as DME were selected. (*R*)-(−)-Mandelic acid of 99% ee [$[\alpha]^{19}_D$ −151.2° (*c* 2.1, EtOH)] reacted with 1-hexyne to give optically active enol ester **27** [$[\alpha]^{18}_D$ −103.6° (*c* 2.4, 1,4-dioxane)] in yield of 77% (run 26) (Scheme I). The enol ester **27** was treated with 0.56% aqueous KOH at 70 °C for 6 h to afford (*R*)-(−)-mandelic acid of 94% ee. Only a slight racemization occurred during this procedure.

Para-substituted benzoic acids reacted with 1-pentyne and 1-hexyne to give enol esters **28**–**34** with high regioselectivity (94–99%) (runs 27–33). No evident relation between the acidity of benzoic acids and the yields of enol esters was observed.

Alkynes containing various functional groups such as phenylacetylene, propargyl alcohol derivatives, and 2-methyl-1-buten-3-yne also reacted with acetic acid to afford enol acetates **35**–**39** (runs 34–38). Ethyl propargyl carbonate reacted with acetic acid to give enol ester **36** in 63% yield with 99% selectivity (run 35). In this case tricyclohexylphosphine was preferable. When tributylphosphine was used in place of tricyclohexylphosphine, enol ester **36** was formed in lower yield (23%) with lower regioselectivity (90%). In the reaction of acetic acid with 2-methyl-1-buten-3-yne, the 100% of regioselectivity for enol ester **39** was realized by using triphenylphosphine as a ligand. In this case, tributylphosphine (regioselectivity 86%) and tricyclohexylphosphine (regioselectivity 94%) were less favorable. Thus, the most suitable phosphine ligand depends on the substituents of the acids and alkynes. These results suggest that both electronic and steric effects of the phosphines affect the reactivity and regioselectivity.

Propargyl alcohols such as 3-methyl-1-butyn-3-ol and 1-ethynylcyclohexanol reacted with acetic acid to afford acyloin acetates **40** (yield 61%, run 39) and **41** (yield 54%, run 40), respectively. These products **40** and **41** may be produced through an intramolecular rearrangement of enol ester **42** (Scheme II).

Various ruthenium complexes have catalytic activity (Table III). The complex A/PBu_3/maleic anhydride system was the best catalyst precursor (run 41). Complex A/PPh_3/maleic anhydride and $Ru(CO)_2(PPh_3)_2$-

(8) Coordinative solvents such as tetrahydrofuran and pyridine were unfavorable, probably because of the disturbance of the coordination of acetylene.

(9) The π-acid such as maleic anhydride may be effective (i) to enhance the attack of carboxylate anion to the coordinated acetylene (eq 6) and/or (ii) to accelerate the reductive elimination (eq 7) to give the enol ester.

Table I. Addition of Carboxylic Acids to Alkynes Catalyzed by Ruthenium Complex (A)[a]

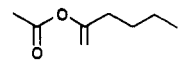
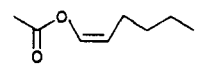
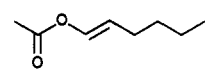
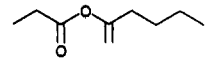
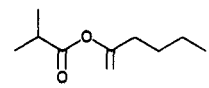
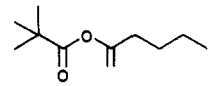
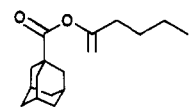
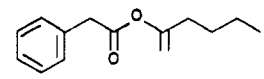
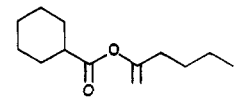
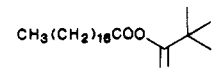
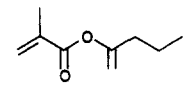
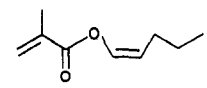
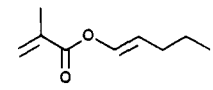
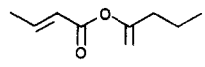
run	acid	alkyne	complex A, mmol	PR_3 (mmol)	MA,[b] mmol	time, h	product	yield,[c] %	selectivity,[d] %
1[e]	octadecanoic acid	acetylene	0.2	PBu_3 (0.4)	0.4	96	$CH_3(CH_2)_{16}CO_2CH{=}CH_2$ **1**	77	
2	acetic acid	1-hexyne	0.1		0.3	4	 **2**	11	
							 **3**	24	
							 **4**	32	
3	acetic acid	1-hexyne	0.1	PBu_3 (0.2)	0.2	4	**2**	(99)	99
4	propanoic acid	1-hexyne	0.1	PBu_3 (0.2)	0.2	4	 **5**	72	97
5	2-methylpropanoic acid	1-hexyne	0.1	PBu_3 (0.2)	0.2	4	 **6**	77	96
6	2,2-dimethyl-propanoic acid	1-hexyne	0.1	PBu_3 (0.2)	0.2	4	 **7**	69	90
7	1-adamantane-carboxylic acid	1-hexyne	0.1	PBu_3 (0.2)	0.2	4	 **8**	80	98
8	phenylacetic acid	1-hexyne	0.1	PBu_3 (0.2)	0.2	4	 **9**	80	97
9	cyclohexane-carboxylic acid	1-hexyne	0.1	PBu_3 (0.2)	0.2	4	 **10**	84	95
10	octadecanoic acid	3,3-dimethy-l-1-butyne	0.1	PBu_3 (0.2)	0.2	4	 **11**	88	99
11	2-methyl-2-propenoic acid	1-pentyne		PBu_3 (0.2)		4		0	
12	2-methyl-2-propenoic acid	1-pentyne	0.1			4	 **12**	5 (8)	
							 **13**	13 (18)	
							 **14**	12 (18)	
13	2-methyl-2-propenoic acid	1-pentyne	0.1	PBu_3 (0.2)		4	**12** **13** **14**	66 (93) (2) (2)	96
14	2-butenoic acid	1-pentyne	0.1	PBu_3 (0.2)		4	 **15**	50 (69)	96

Table I (Continued)

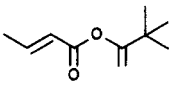
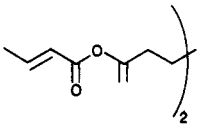
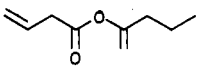
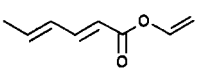
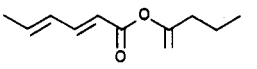
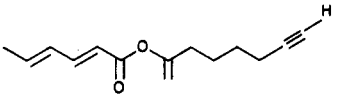
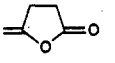
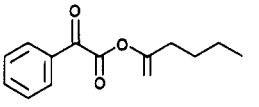
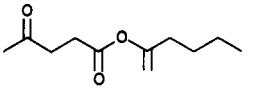
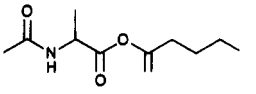
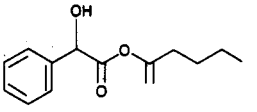
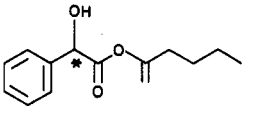
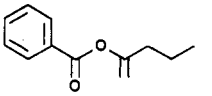
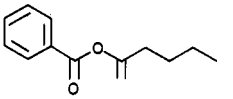
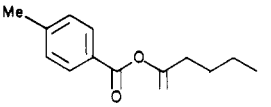
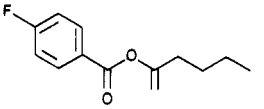
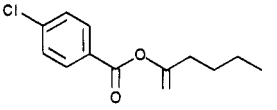
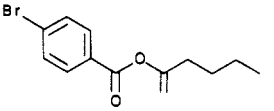
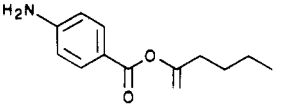
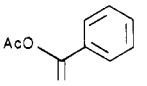
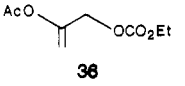
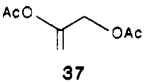
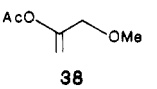
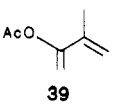
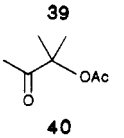
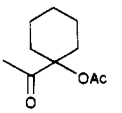
run	acid	alkyne	complex A, mmol	PR_3 (mmol)	MA,[b] mmol	time, h	product	yield,[c] %	selectivity,[d] %
15	2-butenoic acid	3,3-dimethyl-1-butyne	0.1	PBu_3 (0.2)		4	 **16**	68	93
16[f]	2-butenoic acid	1,7-octadiyne	0.2	PBu_3 (0.2)		4	 **17**	63	94
17	3-butenoic acid	1-pentyne	0.2	PBu_3 (0.4)		8	 **18**	40	
18	2,4-hexadienoic acid	acetylene	0.2	PBu_3 (0.4)		96	 **19**	15 26 67	
19	2,4-hexadienoic acid	1-pentyne	0.1	PBu_3 (0.2)		4	 **20**	79 (97)	99
20	2,4-hexadienoic acid	1,7-octadiyne	0.1	PBu_3 (0.2)		4	 **21**	30	99
21	4-pentynoic acid		0.2	PBu_3 (0.4)		4	 **22**	52	100
22	benzoylformic acid	1-hexyne	0.1	PPh_3 (0.2)	0.2	8	 **23**	59 (88)	89
23	4-oxopentanoic acid	1-hexyne	0.1	PBu_3 (0.2)	0.2	8	 **24**	(60)	94
24	*N*-acetylalanine	1-hexyne	0.2	PBu_3 (0.4)	0.4	24	 **25**	31	89
25	*dl*-mandelic acid	1-hexyne	0.2	PPh_3 (0.4)	0.4	4	 **26**	(77)	89
26	(*R*)-(−)-mandelic acid	1-hexyne	0.2	PPh_3 (0.4)	0.4	10	 **27**	(77)	93
27	benzoic acid	1-pentyne	0.1	PBu_3 (0.2)		4	 **28**	75 (99)	99
28	benzoic acid	1-hexyne	0.1	PBu_3 (0.2)	0.2	8	 **29**	64 (76)	95

Table I (Continued)

run	acid	alkyne	complex A, mmol	PR_3 (mmol)	MA,[b] mmol	time, h	product	yield,[c] %	selectivity,[d] %
29	4-methylbenzoic acid	1-hexyne	0.1	PBu_3 (0.2)	0.2	8	 **30**	64 (79)	94
30	4-fluorobenzoic acid	1-hexyne	0.1	PBu_3 (0.2)	0.2	27	 **31**	39	98
31	4-chlorobenzoic acid	1-hexyne	0.1	PBu_3 (0.2)	0.2	24	 **32**	53 (73)	97
32	4-bromobenzoic acid	1-hexyne	0.1	PBu_3 (0.2)	0.2	24	 **33**	63 (93)	99
33	4-aminobenzoic acid	1-hexyne	0.1	PBu_3 (0.2)	0.2	28	 **34**	53	96

[a] Reactions were carried out by using acid (10 mmol) and alkyne (10 mmol) in toluene (5.0 mL) (runs 1–10, 18, 22, 23), benzene (5.0 mL) (runs 11–17, 19–21, 27), 1,2-dimethoxyethane (5.0 mL) (5.0 mL) (runs 24–26, 28–33) at 80 °C under argon. [b] MA = maleic anhydride. [c] Isolated yield (GLC yield). [d] Selectivity is (major ester/total esters) × 100%. [e] Under atmospheric pressure of acetylene. [f] 20 mmol of 2-butenoic acid was used.

Table II. Addition of Acetic Acid to Substituted Alkynes[a]

run	alkyne	catalyst, mmol	PR_3, mmol	MA,[b] mmol	time, h	product	yield,[c] %	selectivity[d] %
34	phenylacetylene	0.1	PBu_3 (0.2)	0.2	12	 **35**	52	76
35	ethyl propargyl carbonate	0.1	PCy_3 (0.2)	0.2	8	 **36**	63	99
36	propargyl acetate	0.1	PPh_3 (0.2)	0.2	22	 **37**	(47)	95
37[e]	methyl propargyl ether	0.2	PBu_3 (0.4)	0.4	24	 **38**	(70)	74
38[f]	2-methyl-1-buten-3-yne	0.2	PPh_3 (0.4)	0.4	8	 **39**	60	100
39[g]	3-methyl-1-butyn-3-ol	0.1	PBu_3 (0.2)	0.2	5	 **40**	61	
40[h]	1-ethynylcyclohexanol	0.2	PBu_3 (0.4)	0.4	5	 **41**	54	

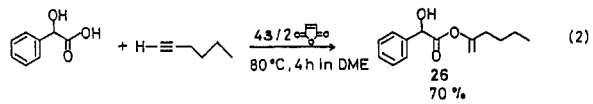
[a] Reactions were carried out by using alkyne (10 mmol) and acetic acid (5.0 mL) at 80 °C under argon. [b] MA = maleic anhydride. [c] Isolated yield (GLC yield). [d] Selectivity is (major ester/total esters) × 100%. [e] Acetic acid, 10 mmol; methyl propargyl ether, 10 mmol; benzene, 5.0 mL as solvent. [f] 2-Methyl-1-buten-3-yne, 20 mmol. [g] Acetic acid, 10 mmol; 3-methyl-1-butyn-3-ol, 10 mmol; small amounts of hydroquinone; toluene, 5.0 mL as solvent. [h] Acetic acid, 10 mmol; 1-ethynylcyclohexanol, 10 mmol; toluene, 5.0 mL as solvent.

Table III. Addition of Acetic Acid to 1-Hexyne Catalyzed by Various Ruthenium Complexes[a]

run	catalyst (mmol)	product	yield, %	selectivity,[b] %
41	complex A (0.2)/2PBu_3/2MA[c]	2	76	94
42	complex A (0.2)/2PPh_3/2MA	2	41	86
43	$Ru(CO)_2(PPh_3)_2(CH_3CO_2)_2$ (0.2)/2MA	2	43	88
44	$Ru(CO)_3(PPh_3)_2$ (0.2)/2MA	2	5	94
45	$RuCl_3 \cdot nH_2O$ (0.2)/2PBu_3/2MA	2	8	94
46	$Ru_3(CO)_{12}$ (0.067)/6PBu_3/6MA	2	48	94
47	$Ru_3(CO)_{12}$ (0.067)	2	11	
		3	18	
		4	30	
2	complex A (0.1)	2	11	
		3	24	
		4	32	
48	$RuCl_3 \cdot nH_2O$ (0.2)	2	6	
		3	10	
		4	12	

[a] Reactions were carried out by using acetic acid (10 mmol) and 1-hexyne (10 mmol) in 1,2-dimethoxyethane (5.0 mL) at 80 °C for 4 h. [b] Selectivity is [2/(2 + 3 + 4)] × 100%. [c] MA = maleic anhydride.

$(CH_3CO_2)_2$[10]/maleic anhydride system showed less activity (runs 42 and 43). Bis(mandelate)dicarbonylbis(triphenylphosphine)ruthenium $[Ru(CO)_2(PPh_3)_2(PhCH(OH)CO_2)_2]$ (**43**) was obtained in 62% yield from the reaction mixture of *dl*-mandelic acid with 1-hexyne (run 25); in the presence of complex **43** (1.6 mol %)/maleic anhydride (3.2 mol %), the reaction of *dl*-mandelic acid with 1-hexyne gave 1-hexen-2-yl *dl*-mandelate (**26**) in 70% yield with 91% regioselectivity (eq 2). Thus the complex Ru-



(2)

43 = $Ru(CO)_2(PPh_3)_2(PhCH(OH)CO_2)_2$

$(CO)_2(PR''_3)_2(RCO_2)_2$/maleic anhydride system is suggested to be the active intermediate of the catalyst. $Ru(CO)_3(PPh_3)_2$/maleic anhydride, $RuCl_3 \cdot nH_2O$/PBu_3/maleic anhydride, and $RuCl_3 \cdot nH_2O$ showed low catalytic activity (runs 44, 45, and 48). Catalytic activity of the $Ru_3(CO)_{12}$/PBu_3/maleic anhydride is lower than the complex A/PBu_3/maleic anhydride (runs 41 and 46). $Ru_3(CO)_{12}$[11] showed the same catalytic activity using complex A (runs 2 and 47). $RuCl_2(PPh_3)_3$/maleic anhydride had no catalytic activity. (η^4-Cyclooctadiene)(η^6-cyclooctatriene)ruthenium [Ru(COD)(COT)]/PBu_3 had no catalytic activity.[12] The reaction of 2,4-hexadienoic acid with ethyl propargyl carbonate was slow and regioselectivity of enol esters was low. No enol ester was obtained in the reactions of acetic acid with propargyl trimethylsilyl ether and the starting alkyne was recovered. The addition reaction of acetic acid to methyl propiolate was not successful; polymerization occurred. Under the present reaction conditions, the rate of the addition reaction of carboxylic acids to internal alkynes, 3-hexyne, and diphenylacetylene was very slow.

Addition of Acetic Acid-*d* to Alkynes. To investigate the reaction mechanism, addition reactions of acetic acid-*d* to 1-hexyne and ethyl propargyl carbonate were performed. When the reactions of acetic acid-*d* with an equivalent mole of 1-hexyne in benzene, acetone, and DME were carried out, the deuterium completely scrambled to afford

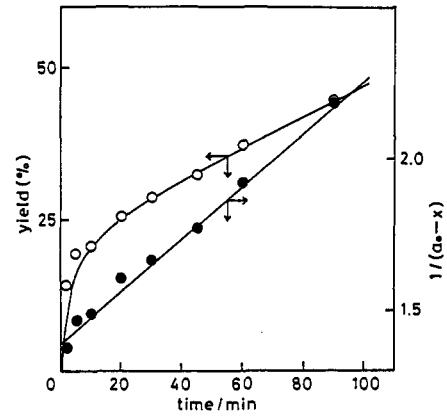
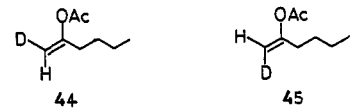
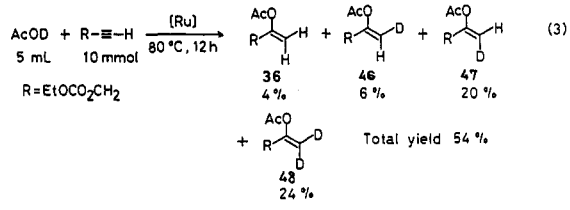


Figure 1. Determination of total order with respect to benzoic acid and 1-octyne: (○) yield of enol ester, (●) second plot; a_0 = [benzoic acid]$_0$ = [1-octyne]$_0$ = 0.756 mol·dm^{-3}, [Ru]$_0$ = 1.55 × 10^{-2} mol·dm^{-3}, DME (5.0 mL), [triphenylmethane] = 0.182 mol·dm^{-3} as an internal standard at 83 °C.

the same proportion of (*Z*)- (**44**) and (*E*)-1-hexen-2-yl-*1-d* acetate (**45**). The reaction of a large excess of acetic acid-*d*



with ethyl propargyl carbonate gave the four enol esters **36** and **46**–**48** (total yield 54%) (eq 3). The yields of **36**, **46**, **47**, and **48** were 4%, 6%, 20%, and 24%, respectively. This result shows that the trans addition was predominant and, therefore, suggests that a nucleophilic attack of an acetate anion to a coordinated alkyne occurred.



(3)

Kinetic Measurement. The kinetic features of the addition reaction were investigated by employing benzoic acid and 1-octyne as the reactants. Since benzoic acid and 1-octyne behave in a similar manner as other acids and alkynes employed in the addition reaction, generalities of the reaction system will not suffer in the kinetic measurements. The first reaction was carried out with an equimolar mixture of benzoic acid and 1-octyne (each a_0 = 0.756 mol·dm^{-3}). Plots of the $1/(a_0 - x)$ value vs. time

(10) In the case of the complex A/PPh_3/AcOH/1-pentyne system, $Ru(CO)_2(PPh_3)_2(AcO)_2$ was isolated from the reaction solution in a fairly good yield.

(11) Shvo et al. reported that in the reaction with the $Ru_3(CO)_{12}$ catalyst the active species were binuclear ruthenium complexes: Rotem, M.; Shvo, Y.; Goldberg, I.; Shmueli, U. *Organometallics* **1984**, *3*, 1758.

(12) Frequently, crude Ru(COD)(COT) contains a small amount of complex A. Of course, the mixture has catalytic activity, however, pure Ru(COD)(COT) has no catalytic activity in the present reaction.

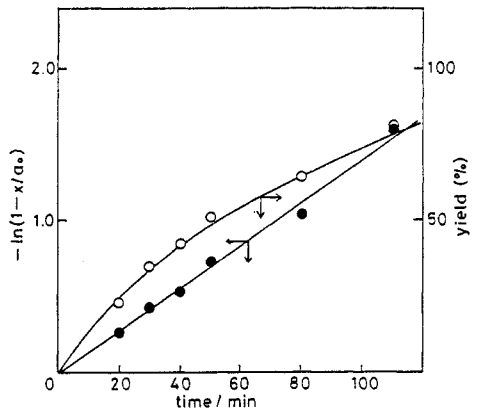


Figure 2. First-order dependence on benzoic acid concentration: (○) yield, (●) first plot; a_0 = [benzoic acid]$_0$ = 0.518 mol·dm^{-3}, [1-octyne]$_0$ = 3.505 mol·dm^{-3}, [Ru]$_0$ = 1.16 × 10^{-2} mol·dm^{-3}, DME (5.0 mL), [triphenylmethane] = 0.151 mol·dm^{-3} as an internal standard at 83 °C.

show a linear relationship (Figure 1), where x is the amount (mol·dm^{-3}) of 1-octen-2-yl benzoate (**49**) formed. This result indicates that the total order with respect to these two reactants is two.

Furthermore, with the amount of 1-octyne in large molar excess and held relatively constant, plots of the $-\ln(1 - x/a_0)$ value vs. time show a linear relationship (Figure 2). This phenomenon clearly shows that the reaction is of first-order dependence on the benzoic acid concentration. Therefore, the rate of the addition reaction is first order on the acid and first order on the alkyne concentration.

When the addition reactions were carried out with different initial catalyst concentrations, a straight line was obtained on plotting the observed rate constants against the different initial catalyst concentrations ([Ru]$_0$ = 1.55 × 10^{-2}, 2.32 × 10^{-2}, and 3.24 × 10^{-2} mol·dm^{-3}). Therefore, there is a first-order dependence on the initial concentration of the catalyst. Thus the rate law of the present reaction is expressed by eq 4.

$$\text{rate} = k[\text{Ru}]_0^1[\text{RCO}_2\text{H}]^1[\text{R'C}{\equiv}\text{CH}]^1 \quad (4)$$

The reaction rates were measured at three temperatures ranging from 61 to 83 °C; k_{obsd} = 1.51 × 10^{-1} mol^{-2}·dm^6·min^{-1} at 61 °C, 1.87 × 10^{-1} mol^{-2}·dm^6·min^{-1} at 71 °C, and 5.05 × 10^{-1} mol^{-2}·dm^6·min^{-1} at 83 °C. From the Arrhenius plot of ln k_{obsd} against $1/T$, the activation energy E_a of 57.0 kJ mol^{-1} was obtained; $\Delta H^{\ddagger}$ = 54.1 kJ·mol^{-1} and $\Delta S^{\ddagger}$ = −135 J·mol^{-1}·K^{-1}.

In order to derive the rate equation (eq 4), the sequences of the elemental reactions in eq 5–7 (Scheme III) are considered. We assume that first the alkyne coordinates

Scheme III

$$\text{R'C}{\equiv}\text{CH} + \text{RuLn} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (\text{R'C}{\equiv}\text{CH})\text{RuLn} \quad (5)$$

$$(\text{R'C}{\equiv}\text{CH})\text{RuLn} + \text{RCO}_2\text{H} \xrightarrow{k_2} (\text{RCO}_2\text{C(R')}{=}\text{CH})\text{RuLnH} \quad (6)$$

$$(\text{RCO}_2\text{C(R')}{=}\text{CH})\text{RuLnH} \xrightarrow{k_3} \text{RCO}_2\text{C(R')}{=}\text{CH}_2 + \text{RuLn} \quad (7)$$

the ruthenium, and then the nucleophilic addition reaction of carboxylic acid (probably carboxylate anion) to the coordinated alkyne and the attack of the proton on the ruthenium occur. This assumption can reasonably explain the trans addition of acetic acid-*d* to ethyl propargyl carbonate described above. From eq 7, the rate is expressed as is eq 8. When steady-state concentration for

$$\text{rate} = k_3[(\text{RCO}_2\text{C(R')}{=}\text{CH})\text{RuLnH}] \quad (8)$$

(R'C≡CH)RuLn and (RCO$_2$(R')C=CH)RuLnH is assumed, the rate equation for Scheme III would be eq 9, where eq 10 obtains. [Ru]$_0$ is the initial catalyst con-

$$\text{rate} = k_2K[\text{Ru}]_0[\text{RCO}_2\text{H}][\text{R'C}{\equiv}\text{CH}]/\{1 + (k_2/k_{-1}) \times [\text{RCO}_2\text{H}] + K[\text{R'C}{\equiv}\text{CH}](1 + (k_2/k_3)[\text{RCO}_2\text{H}])\} \quad (9)$$

$$[\text{Ru}]_0 = [\text{RuLn}] + [(\text{R'C}{\equiv}\text{CH})\text{RuLn}] + [(\text{RCO}_2\text{C(R')}{=}\text{CH})\text{RuLnH}] \quad (10)$$

centration. If $k_2 \ll k_{-1}$, $K \ll 1$, and $k_2 \ll k_3$ the rate equation becomes eq 11. Thus, by simplifying the

$$\text{rate} = k_2K[\text{Ru}]_0[\text{RCO}_2\text{H}][\text{R'C}{\equiv}\text{CH}] \quad (11)$$

equations according to the assumptions, we could obtain the observed rate dependence on the substrates and the initial catalyst concentration.

Conclusion

The novel bis(η^5-cyclooctadienyl)ruthenium/trialkylphosphine/maleic anhydride system is an extremely versatile catalyst precursor for the preparation of enol esters through the addition of carboxylic acids to terminal alkynes. This catalytic system is easy to use and easy to design by using appropriate phosphine ligands for high activity and high regioselectivity.

Experimental Section

All boiling points and melting points were uncorrected. Infrared spectra were recorded on a Hitachi Model 215 or a NICOLET 5-MX spectrometer as films or KBr plates. Proton nuclear magnetic resonance spectra were obtained on a JNM-FX-100 or a NICOLET NT-300NB spectrometer as 5–10% solutions with tetramethylsilane as an internal reference. Carbon-13 nuclear magnetic resonance spectra were obtained on a JNM-FX-100 (25.05 MHz) spectrometer as 40–50% solutions with tetramethylsilane as an internal reference. Mass spectra were taken on 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 analysis (GLC) were carried out on a 3 m × 3 mm diameter column with OV 17. All carboxylic acids, acetylene, 1-pentyne, 1-hexyne, 1-octyne, phenylacetylene, maleic anhydride, PBu_3, PPh_3, PCy_3, toluene, benzene, 1,2-dimethoxyethane (DME), $RuCl_3{\cdot}nH_2O$, and $Ru_3(CO)_{12}$ were commercial samples and were purified by distillation or by recrystallization under an atmosphere of argon before use. 4-Pentynoic acid,[13] 3,3-dimethyl-1-butyne,[14] 2-methyl-1-buten-3-yne,[15] ethyl propargyl carbonate,[16] propargyl acetate,[17] and methyl propargyl ether[18] were prepared by methods described in the literature. The complexes, bis(η^5-cyclooctadienyl)ruthenium (complex A),[19] Ru(COD)(COT),[20] $Ru(CO)_2(PPh_3)_2(CH_3CO_2)_2$,[21] $Ru(CO)_3(PPh_3)_2$,[22] and $RuCl_2(PPh_3)_3$[23] were prepared by the reported methods. All the catalytic reactions were carried out under an atmosphere of argon.

Kinetic Measurements. The reactions were performed in a two-necked flask under an argon atmosphere. DME was used as a solvent, and triphenylmethane was employed as an internal

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standard. A small amount of the reaction mixture was sampled at suitable intervals and was subjected to GLC analysis.

Bis(*dl*-mandelato)dicarbonylbis(triphenylphosphine)-ruthenium (43). Microcrystals of **43** precipitated from the reaction mixture of *dl*-mandelic acid, 1-hexyne, complex A, PPh_3, and maleic anhydride. The crystals were washed with methanol (3 × 2 mL) at 0 °C, water (2 × 2 mL), and methanol (2 × 2 mL) at 0 °C and then dried in vacuo at 100 °C for 4 h. Colorless crystal of the complex was obtained (0.122 g, yield 62%): mp 208.7–209.3 °C; IR (KBr) 3478, 3356, 2058, 1998, 1620, 1599, 1360 cm^{-1}. Anal. Calcd for $C_{54}H_{44}O_8P_2Ru$: C, 65.92; H, 4.51. Found: C, 65.73; H, 4.41.

Addition of Carboxylic Acids to Acetylene. The reaction of octadecanoic acid with acetylene is representative. A mixture of octadecanoic acid (2.85 g, 10 mmol), complex A (0.063 g, 0.2 mmol), tributylphosphine (0.081 g, 0.4 mmol), maleic anhydride (0.039 g, 0.4 mmol), and toluene (5.0 mL) was heated at 80 °C for 96 h under an atmospheric pressure of acetylene. Careful vacuum distillation of the reaction mixture afforded 2.40 g (yield 77%) of vinyl octadecanoate (**1**). The reaction of 2,4-hexadienoic acid with acetylene was carried out in a similar manner.

Addition of Carboxylic Acids to Alkynes. The reaction of octadecanoic acid with 3,3-dimethyl-1-butyne is representative. A mixture of octadecanoic acid (2.85 g, 10 mmol), 3,3-dimethyl-1-butyne (0.82 g, 10 mmol), complex A (0.032 g, 0.1 mmol), tributylphosphine (0.040 g, 0.2 mmol), maleic anhydride (0.020 g, 0.2 mmol), and toluene (5.0 mL) was heated in a heavy-walled sealed tube at 80 °C for 4 h. Careful vacuum distillation of the reaction mixture afforded 3.24 g (yield 88%) of 3,3-dimethyl-1-buten-2-yl octadecanoate (**11**). Other reactions were carried out in a similar manner. The catalysts used were cited in Tables I–III. Spectral data of **1** and **19** were the same as those of the authentic samples. Enol esters except for **2**,[5e] **3**,[24] **4**,[24] **22**,[25] **29**,[5e] **35**,[5i] **39**,[26] **44**,[24] and **45**[24] are new compounds.

1-Hexen-2-yl propanoate (5): colorless liquid; bp 84 °C (30 mmHg); IR (neat) 1667, 1761 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.69 (s, 2 H), 2.40 (q, J = 7.6 Hz, 2 H), 2.21 (t, J = 7.1 Hz, 2 H), 1.28–1.57 (m, 4 H), 1.17 (t, J = 7.6 Hz, 3 H), 0.91 (t, J = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 172.2 (s), 156.8 (s), 100.7 (t), 33.3 (t), 28.9 (t), 27.8 (t), 22.3 (t), 13.9 (q), 9.2 (q); MS, m/z 156 (M^+). Anal. Calcd for $C_9H_{16}O_2$: C, 69.20; H, 10.32. Found: C, 69.12; H, 10.49.

1-Hexen-2-yl 2-methylpropanoate (6): colorless liquid; bp 75 °C (17 mmHg); IR (neat) 1667, 1753 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.70 (s, 2 H), 2.64 (hep, J = 7.1 Hz, 1 H), 2.22 (t, J = 7.1 Hz, 2 H), 1.29–1.58 (m, 4 H), 1.24 (d, J = 7.1 Hz, 6 H), 0.93 (t, J = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 175.1 (s), 156.6 (s), 100.7 (t), 34.2 (d), 33.1 (t), 28.7 (t), 22.1 (t), 19.0 (q), 13.9 (q); MS, m/z 170 (M^+). Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.23; H, 10.98.

1-Hexen-2-yl 2,2-dimethylpropanoate (7): colorless liquid; bp 81 °C (16 mmHg); IR (neat) 1660, 1738 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.63–4.72 (m, 2 H), 2.20 (t, J = 7.2 Hz, 2 H), 1.27–1.56 (m, 4 H), 1.25 (s, 9 H), 0.91 (t, J = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 176.3 (s), 156.8 (s), 100.5 (t), 39.0 (s), 33.0 (t), 28.7 (t), 27.1 (q), 22.1 (t), 13.9 (q); MS, m/z 184 (M^+). Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 71.64; H, 11.05.

1-Hexen-2-yl 1-adamantanecarboxylate (8): colorless liquid; bp 108 °C (0.3 mmHg); IR (neat) 1667, 1746 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.67 (m, 1 H), 4.64 (m, 1 H), 2.19 (t, J = 7.1 Hz, 2 H), 1.90–2.10 (m, 9 H), 1.73 (br, 6 H), 1.25–1.54 (m, 4 H), 0.91 (t, J = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 175.3 (s), 156.8 (s), 100.5 (t), 40.9 (s), 38.9 (t), 36.6 (t), 33.1 (t), 28.7 (t), 28.1 (d), 22.1 (t), 13.9 (q); MS, m/z 262 (M^+). Anal. Calcd for $C_{17}H_{26}O_2$: C, 77.82; H, 9.99. Found: C, 77.62; H, 10.09.

1-Hexen-2-yl phenylacetate (9): colorless liquid; bp 105 °C (1.5 mmHg); IR (neat) 1667, 1753 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.28 (s, 5 H), 4.68 (m, 2 H), 3.65 (s, 2 H), 2.15 (t, J = 7.1 Hz, 2 H), 1.04–1.47 (m, 4 H), 0.84 (t, J = 6.4 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 169.3 (s), 156.6 (s), 133.8 (s), 129.2 (d), 128.6 (d), 127.2 (d), 100.9 (t), 41.5 (t), 33.0 (t), 28.5 (t), 22.1 (t), 13.8 (q); MS, m/z 218 (M^+). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.93; H, 8.39.

1-Hexen-2-yl cyclohexanecarboxylate (10): colorless liquid; bp 110 °C (5 mmHg); IR (neat) 1665, 1752 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.67 (m, 2 H), 2.20 (t, J = 7.2 Hz, 2 H), 1.10–2.45 (m, 15 H), 0.91 (t, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 173.8 (t), 156.6 (s), 100.6 (t), 43.3 (d), 33.1 (t), 29.1 (t), 28.7 (t), 25.9 (t), 25.5 (t), 22.2 (t), 13.9 (q); MS, m/z 210 (M^+). Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.03; H, 10.71.

3,3-Dimethyl-1-buten-2-yl octadecanoate (11): colorless crystal; mp 35–36 °C; bp 158 °C (0.2 mmHg); IR (neat) 1655, 1761 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.85 (d, J = 2.0 Hz, 1 H), 4.62 (d, J = 2.0 Hz, 1 H), 2.42 (t, J = 7.4 Hz, 2 H), 1.26 (br, 30 H), 1.09 (s, 9 H), 0.88 (t, J = 7.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 171.7 (s), 162.5 (s), 98.8 (t), 36.1 (s), 34.6 (t), 32.06 (t), 29.8 (t), 29.5 (t), 29.4 (t), 27.9 (t), 25.1 (t), 22.8 (t), 14.2 (q); MS, m/z 366 (M^+). Anal. Calcd for $C_{24}H_{46}O_2$: C, 78.62; H, 12.65. Found: C, 78.43; H, 12.83.

1-Penten-2-yl 2-methyl-2-propenoate (12): colorless liquid; bp 82 °C (33 mmHg); IR (neat) 1660, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.16 (s, 1 H), 5.65 (s, 1 H), 4.74 (s, 2 H), 2.24 (t, J = 7.0 Hz, 2 H), 1.96 (s, 3 H), 1.48 (qt, J = 7.0, 7.0 Hz, 2 H), 0.93 (t, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 164.9 (s), 156.1 (s), 135.8 (s), 125.8 (t), 100.6 (t), 35.0 (t), 19.4 (t), 17.9 (q), 13.0 (q); MS, m/z 154 (M^+). Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.16; H, 9.21.

(*Z*)-1-Penten-1-yl 2-methyl-2-propenoate (13): colorless liquid; IR (neat) 1655, 1715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.10 (dt, J = 6.4, 1.5 Hz, 1 H), 6.22 (qd, J = 1.1, 1.6 Hz, 1 H), 5.66 (qd, J = 1.6, 1.6 Hz, 1 H), 4.92 (td, J = 7.4, 6.4 Hz, 1 H), 2.16 (td, J = 7.1, 7.4 Hz, 2 H), 1.99 (dd, J = 1.1, 1.6 Hz, 3 H), 1.43 (qt, J = 7.1, 7.1 Hz, 2 H), 0.93 (t, J = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 164.3 (s), 135.7 (s), 134.2 (d), 126.6 (t), 114.3 (d), 26.6 (t), 22.4 (t), 18.2 (q), 13.7 (q).

(*E*)-1-Penten-1-yl 2-methyl-2-propenoate (14): colorless liquid; IR (neat) 1655, 1715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.13 (dt, J = 12.4, 1.4 Hz, 1 H), 6.19 (m, 1 H), 5.64 (m, 1 H), 5.48 (td, J = 7.4, 12.4 Hz, 1 H), 2.01 (td, J = 7.1, 7.4 Hz, 2 H), 1.97 (s, 3 H), 1.42 (qt, J = 7.1, 7.1 Hz, 2 H), 0.92 (t, J = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 164.7 (s), 135.7 (s), 135.7 (d), 126.6 (t), 115.2 (d), 29.4 (t), 22.8 (t), 18.2 (q), 13.5 (q). Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.35; H, 9.35.

1-Penten-2-yl (*E*)-2-butenoate (15): colorless liquid; bp 85 °C (13 mmHg); IR (neat) 1650, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.08 (qd, J = 7.0, 15.5 Hz, 1 H), 5.90 (dq, J = 15.5, 1.5 Hz, 1 H), 4.76 (s, 2 H), 2.23 (t, J = 7.0, 2 H), 1.90 (dd, J = 7.0, 2.0 Hz, 3 H), 1.50 (qt, J = 7.0, 7.0 Hz, 2 H), 0.93 (t, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 164.4 (s), 156.2 (s), 145.8 (d), 122.4 (d), 101.0 (t), 35.5 (t), 19.8 (t), 18.0 (q), 13.5 (q); MS, m/z 154 (M^+). Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.81; H, 9.25.

3,3-Dimethyl-1-buten-2-yl (*E*)-2-butenoate (16): colorless liquid; bp 89 °C (18 mmHg); IR (neat) 1657, 1742 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.05 (qd, J = 6.8, 15.5 Hz, 1 H), 5.91 (dq, J = 15.5, 1.7 Hz, 1 H), 4.86 (d, J = 1.8 Hz, 1 H), 4.66 (d, J = 1.8 Hz, 1 H), 1.91 (dd, J = 6.8, 1.7 Hz, 3 H), 1.10 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 164.2 (s), 162.3 (s), 145.4 (d), 122.6 (d), 98.8 (t), 36.2 (s), 27.8 (q), 18.0 (q); MS, m/z 168 (M^+). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.38; H, 9.70.

1,7-Octadiene-2,7-diyl (*E*)-2-butenedioate (17): colorless liquid; bp 150 °C (0.4 mmHg); IR (neat) 1650, 1720 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.01 (qd, J = 6.9, 15.6 Hz, 2 H), 5.87 (dd, J = 15.6, 1.5 Hz, 2 H), 4.72 (s, 2 H), 4.70 (s, 2 H), 2.24 (t, J = 6.6 Hz, 4 H), 1.88 (dd, J = 6.9, 1.5 Hz, 6 H), 1.50 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 163.9 (s), 156.0 (s), 145.7 (d), 122.4 (d), 100.9 (t), 33.1 (t), 25.8 (t), 17.9 (q); MS, m/z 278 (M^+). Anal. Calcd for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 68.89; H, 7.79.

1-Penten-2-yl 3-butenoate (18): colorless liquid; bp 81 °C (25 mmHg); IR (neat) 1660, 1750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.01 (tdd, J = 7.0, 17.5, 10.0 Hz, 1 H), 4.90–5.50 (m, 2 H), 4.75 (s, 2 H), 3.17 (d, J = 6.5 Hz, 2 H), 2.22 (t, J = 7.0 Hz, 2 H), 1.48 (qt, J = 7.0, 7.0 Hz, 2 H), 0.93 (t, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 169.4 (s), 156.3 (s), 130.0 (d), 118.7 (t), 101.2 (t), 39.2 (t), 35.4 (t), 19.8 (t), 13.5 (q); MS, m/z 154 (M^+). Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.00; H, 9.37.

1-Penten-2-yl (*E*,*E*)-2,4-hexadienoate (20): colorless liquid; bp 89 °C (7 mmHg); IR (neat) 1635, 1715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.00–7.70 (m, 1 H), 6.02–6.50 (m, 2 H), 5.82 (d, J = 15.5 Hz, 1

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H), 4.76 (br, 2 H), 2.24 (t, J = 7.0 Hz, 2 H), 1.87 (d, J = 5.0 Hz, 3 H), 1.50 (qt, J = 7.0, 7.0 Hz, 2 H), 0.94 (t, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 164.4 (s), 155.8 (s), 145.5 (d), 139.3 (d), 129.3 (d), 118.1 (d), 100.3 (t), 29.0 (t), 19.3 (t), 18.1 (q), 13.0 (q); MS, m/z 180 (M^+). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.00; H, 9.13.

1-Octen-7-yn-2-yl (*E,E*)-2,4-hexadienoate (21): colorless liquid; bp 117 °C (6 mmHg); IR (neat) 1617, 1645, 1726 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (dd, J = 9.6, 15.0 Hz, 1 H), 6.11–6.27 (m, 2 H), 5.81 (d, J = 15.6 Hz, 1 H), 4.76 (s, 1 H), 4.75 (s, 1 H), 2.27 (t, J = 6.9 Hz, 2 H), 2.20 (td, J = 6.6, 2.4 Hz, 2 H), 1.94 (t, J = 2.4 Hz, 1 H), 1.87 (d, J = 5.1 Hz, 3 H), 1.52–1.62 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 164.6 (s), 155.7 (s), 145.8 (d), 139.6 (d), 129.6 (d), 118.2 (d), 100.9 (t), 83.8 (s), 68.6 (d), 32.9 (t), 27.7 (t), 25.4 (t), 18.6 (q), 18.2 (t); MS, m/z 218 (M^+). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.26; H, 8.51.

1-Hexen-2-yl benzoylformate (23): colorless liquid; (Kugelrohr) 180 °C (0.2 mmHg); IR (neat) 1692, 1748 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.04 (d, J = 7.2 Hz, 2 H), 7.66 (d, J = 7.2 Hz, 1 H), 7.52 (dd, J = 7.2, 7.2 Hz, 2 H), 4.97 (d, J = 1.8 Hz, 1 H), 4.90 (s, 1 H), 2.34 (t, J = 7.4 Hz, 2 H), 1.53 (tt, J = 7.4, 7.2 Hz, 2 H), 1.39 (qt, J = 7.2, 7.2 Hz, 2 H), 0.92 (t, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 185.1 (s), 161.8 (s), 156.1 (s), 135.1 (d), 132.3 (s), 130.0 (d), 129.0 (d), 102.2 (t), 32.9 (t), 28.4 (t), 22.0 (t), 13.8 (q); MS, m/z 121, 95. Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.21; H, 6.93.

1-Hexen-2-yl 4-oxopentanoate (24): colorless liquid; bp 115 °C (5 mmHg); IR (neat) 1665, 1721, 1753 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.69 (s, 2 H), 2.74 (t, J = 5.0 Hz, 2 H), 2.69 (t, J = 5.0 Hz, 2 H), 2.19 (s, 3 H), 2.19 (t, J = 7.0 Hz, 2 H), 1.16–1.63 (m, 4 H), 0.90 (t, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 206.1 (s), 170.8 (s), 156.6 (s), 100.9 (t), 37.9 (t), 33.0 (t), 29.7 (q), 28.6 (t), 28.1 (t), 22.1 (t), 13.9 (q); MS, m/z 198 (M^+). Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.66; H, 9.29.

1-Hexen-2-yl 2-(*N*-acetylamino)propanoate (25): colorless liquid; bp 118 °C (0.8 mmHg); IR (neat) 1545, 1655, 1661, 1759 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.40 (br, 1 H), 4.75 (s, 2 H), 4.62 (q, J = 7.2 Hz, 1 H), 2.21 (t, J = 7.3 Hz, 2 H), 2.03 (s, 3 H), 1.47 (d, J = 7.2 Hz, 3 H), 1.30–1.50 (m, 4 H), 0.91 (t, J = 7.0, 3 H); ^{13}C NMR ($CDCl_3$) δ 171.4 (s), 169.9 (s), 156.3 (s), 101.3 (t), 48.2 (d), 32.8 (t), 28.5 (t), 23.0 (q), 22.0 (t), 18.4 (q), 13.8 (q); MS, m/z 114, 86. Anal. Calcd for $C_{11}H_{19}O_3N$: C, 61.95; H, 8.98. Found: C, 62.02; H, 9.14.

1-Hexen-2-yl *dl*-mandelate (26): colorless crystal; mp 36.6–37.9 °C, bp 96 °C (0.2 mmHg); IR (neat) 1667, 1752 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.26–7.50 (m, 5 H), 5.23 (s, 1 H), 4.68 (s, 2 H), 4.28 (br, 1 H), 2.08 (t, J = 7.0 Hz, 2 H), 1.04–1.33 (m, 4 H), 0.77 (t, J = 5.7 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 171.8 (s), 156.2 (s), 138.0 (s), 128.5 (d), 126.6 (d), 101.4 (t), 73.0 (d), 32.6 (t), 28.2 (t), 21.9 (t), 13.7 (q); MS, m/z 107, 79, 77, 58. Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.79; H, 7.69.

1-Hexen-2-yl (*R*)-(−)-mandelate (27): colorless crystal; mp 35.2–36.8 °C; $[\alpha]^{18}_D$ −103.6° (c 2.4, 1,4-dioxane).

1-Penten-2-yl benzoate (28): colorless liquid; bp 91 °C (4 mmHg); IR (neat) 1668, 1738 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.07 (dm, J = 7.9 Hz, 2 H), 7.28–7.51 (m, 3 H), 4.89 (d, J = 1.5 Hz, 1 H), 4.79 (d, J = 1.2 Hz, 1 H), 2.30 (t, J = 7.2 Hz, 2 H), 1.52 (qt, J = 7.2, 7.2 Hz, 2 H), 0.94 (t, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 164.5 (s), 156.6 (s), 133.2 (d), 129.9 (d), 129.4 (s), 128.5 (d), 101.4 (t), 35.6 (t), 20.0 (t), 13.6 (q); MS, m/z 190 (M^+). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.51; H, 7.63.

1-Hexen-2-yl benzoate (29): colorless liquid; bp 92 °C (0.5 mmHg); IR (neat) 1667, 1738 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.08 (dm, J = 8.0 Hz, 2 H), 7.42–7.57 (m, 3 H), 4.82–4.87 (m, 2 H), 2.34 (t, J = 7.3 Hz, 2 H), 1.16–1.69 (m, 4 H), 0.91 (t, J = 7.4 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 164.6 (s), 156.8 (s), 133.2 (d), 129.9 (d), 129.4 (s), 128.4 (d), 101.2 (t), 33.2 (t), 28.8 (t), 22.2 (t), 13.9 (q); MS, m/z 204 (M^+). Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.15; H, 7.98.

1-Hexen-2-yl 4-methylbenzoate (30): colorless liquid; bp 89 °C (0.2 mmHg); IR (neat) 1667, 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.97 (dt, J = 8.2, 1.7 Hz, 2 H), 7.24 (d, J = 8.2 Hz, 2 H), 4.79–4.85 (m, 2 H), 2.41 (s, 3 H), 2.34 (t, J = 7.4 Hz, 2 H), 1.17–1.84 (m, 4 H), 0.91 (t, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 164.5 (s), 156.9 (s), 143.8 (s), 129.9 (d), 129.1 (d), 127.4 (s), 101.0 (t), 33.3 (t), 28.8 (t), 22.3 (t), 21.6 (q), 13.9 (q); MS, m/z 218 (M^+). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.79; H, 8.48.

1-Hexen-2-yl 4-fluorobenzoate (31): colorless liquid; bp 55 °C (0.2 mmHg); IR (neat) 1667, 1732, 1736 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.10 (dd, J = 8.9 Hz, J_{H-F} = 5.4 Hz, 2 H), 7.13 (dd, J = 8.9 Hz, J_{H-F} = 8.6 Hz, 2 H), 4.84 (s, 2 H), 2.33 (t, J = 7.3 Hz, 2 H), 1.19–1.69 (m, 4 H), 0.92 (t, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 166.2 (d, J_{C-F} = 254.4 Hz), 163.9 (s), 157.0 (s), 134.4 (s), 132.7 (dd, J_{C-F} = 10.3 Hz), 115.9 (dd, J_{C-F} = 22.3 Hz), 101.6 (t), 33.4 (t), 29.0 (t), 22.4 (t), 14.1 (q); MS, m/z 222 (M^+). Anal. Calcd for $C_{13}H_{15}O_2F$: C, 70.25; H, 6.80. Found: C, 70.35; H, 6.88.

1-Hexen-2-yl 4-chlorobenzoate (32): colorless liquid; bp 107 °C (1.2 mmHg); IR (neat) 1667, 1732, 1738 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.01 (d, J = 8.8 Hz, 2 H), 7.42 (d, J = 8.8 Hz, 2 H), 4.85 (s, 1 H), 4.84 (s, 1 H), 2.34 (t, J = 7.1 Hz, 2 H), 1.18–1.69 (m, 4 H), 0.91 (t, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 163.6 (s), 156.6 (s), 139.7 (s), 131.2 (d), 128.8 (d), 128.3 (s), 101.3 (t), 33.1 (t), 28.7 (t), 22.1 (t), 13.9 (q); MS, m/z 239 (M^+). Anal. Calcd for $C_{13}H_{15}O_2Cl$: C, 65.41; H, 6.33. Found: C, 65.66; H, 6.43.

1-Hexen-2-yl 4-bromobenzoate (33): colorless liquid; bp 108 °C (0.3 mmHg); IR (neat) 1667, 1732, 1738 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.94 (d, J = 8.5 Hz, 2 H), 7.58 (d, J = 8.5 Hz, 2 H), 4.85 (s, 2 H), 2.33 (t, J = 7.0 Hz, 2 H), 1.13–1.67 (m, 4 H), 0.91 (t, J = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 163.9 (s), 156.6 (s), 131.8 (d), 131.3 (d), 128.8 (s), 128.4 (s), 101.4 (t), 33.1 (t), 28.7 (t), 22.1 (t), 13.9 (q); MS, m/z 282 (M^+), 284 (M^+). Anal. Calcd for $C_{13}H_{15}O_2Br$: C, 55.14; H, 5.34. Found: C, 55.78; H, 5.56.

1-Hexen-2-yl 4-aminobenzoate (34): colorless crystal; mp 65.8–66.8 °C; bp 155 °C (0.8 mmHg); IR (KBr) 1667, 1701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.76 (d, J = 8.8 Hz, 2 H), 6.70 (d, J = 8.8 Hz, 2 H), 5.49 (br, 2 H), 4.75 (s, 2 H), 2.32 (t, J = 7.1 Hz, 2 H), 1.15–1.69 (m, 4 H), 0.90 (t, J = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 164.9 (s), 157.0 (s), 151.5 (s), 132.0 (d), 119.0 (s), 113.8 (d), 100.9 (t), 33.4 (t), 28.8 (t), 22.2 (t), 13.9 (q); MS, m/z 219 (M^+). Anal. Calcd for $C_{13}H_{17}O_2N$: C, 71.20; H, 7.81. Found: C, 70.69; H, 7.68.

Ethyl 2-acetoxy-2-propen-1-yl carbonate (36): colorless liquid; bp 90 °C (3 mmHg); IR (neat) 1674, 1759 (vs, br) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.11 (dt, J = 2.0, 0.8 Hz, 1 H), 5.03 (d, J = 2.0 Hz, 1 H), 4.66 (d, J = 0.8 Hz, 2 H), 4.21 (q, J = 7.1 Hz, 2 H), 2.15 (s, 3 H), 1.31 (t, J = 7.1 Hz, 3 H); ^{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. Calcd for $C_8H_{12}O_5$: C, 51.06; H, 6.43. Found: C, 51.31; H, 6.56.

2-Acetoxy-2-propen-1-yl acetate (37): colorless liquid; bp 107 °C (26 mmHg); IR (neat) 1674, 1759 (vs, br) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.08 (td, J = 2.0, 0.7 Hz, 1 H), 5.01 (d, J = 2.0 Hz, 1 H), 4.62 (d, J = 0.7 Hz, 2 H), 2.16 (s, 3 H), 2.09 (s, 3 H); ^{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. Calcd for $C_7H_{10}O_4$: C, 53.16; H, 6.37. Found: C, 52.93; H, 6.49.

2-Acetoxy-2-propen-1-yl methyl ether (38): colorless liquid; bp 82 °C (47 mmHg); IR (neat) 1119, 1674, 1757 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.00 (m, 1 H), 4.95 (d, J = 1.5 Hz, 1 H), 3.95 (s, 2 H), 3.35 (s, 3 H), 2.14 (s, 3 H); ^{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. Calcd for $C_6H_{10}O_3$: C, 55.37; H, 7.75. Found: C, 55.82; H, 8.30.

2-Methyl-3-oxo-2-butyl acetate (40): colorless liquid; bp 63 °C (10 mmHg); IR (neat) 1723, 1738 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.10 (s, 3 H), 2.06 (s, 3 H), 1.46 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 206.7 (s), 170.3 (s), 83.7 (s), 23.5 (q), 23.4 (q), 21.1 (q); MS, m/z 144 (M^+). Anal. Calcd for $C_7H_{12}O_3$: C, 58.32; H, 8.39. Found: C, 58.41; H, 8.40.

1-Acetyl-1-cyclohexyl acetate (41): colorless liquid; bp 85 °C (3 mmHg); IR (neat) 1719, 1736 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.13 (s, 3 H), 2.09 (s, 3 H), 1.80–2.10 (m, 2 H), 1.31–1.75 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 206.7 (s), 170.0 (s), 85.1 (s), 30.9 (t), 25.2 (t), 23.5 (q), 21.3 (t), 21.0 (q); MS, m/z 184 (M^+). Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.76. Found: C, 65.48; H, 9.02.

Ethyl (*Z*)-2-Acetoxy-2-propen-1-yl-*3-d* Carbonate (46). ^{1}H NMR spectral data were the same as those of **36** except for the following signals: δ 5.10 (br, 1 H), 4.66 (s, 2 H) in the place of the signals δ 5.11 (dt, J = 2.0, 0.8 Hz, 1 H), 5.03 (d, J = 2.0 Hz, 1 H), 4.66 (d, J = 0.8 Hz, 2 H) in **36**.

Ethyl (*E*)-2-Acetoxy-2-propen-1-yl-*3-d* Carbonate (47). ^{1}H NMR spectral data were the same as those of **36** except for the following signals: δ 5.03 (s, 1 H), 4.66 (s, 2 H) in the place of the signals δ 5.11 (dt, J = 2.0, 0.8 Hz, 1 H), 5.03 (d, J = 2.0 Hz, 1 H),

4.66 (d, J = 0.8 Hz, 2 H) in **36**.

Ethyl 2-Acetoxy-2-propen-1-yl-3,3-d_2 Carbonate (48). ^{1}H NMR spectral data were the same as those of **36** except for the following signals: δ 4.66 (s, 2 H) in the place of the signals δ 5.11 (dt, J = 2.0, 0.8 Hz, 1 H), 5.03 (d, J = 2.0 Hz, 1 H), 4.66 (d, J = 0.8 Hz, 2 H) in **36**.

1-Octen-2-yl benzoate (49): colorless liquid; bp 80 °C (0.3 mmHg); IR (neat) 1667, 1732 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.09 (dm, J = 8.0 Hz, 2 H), 7.25-7.59 (m, 3 H), 4.86 (d, J = 1.5 Hz, 1 H), 4.83 (d, J = 1.1 Hz, 1 H), 2.34 (t, J = 7.1 Hz, 2 H), 1.16-1.74 (m, 8 H), 0.88 (t, J = 5.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 164.5 (s), 156.8 (s), 133.2 (d), 129.9 (d), 129.4 (s), 128.4 (d), 101.2 (t), 33.5 (t), 31.6 (t), 28.8 (t), 26.6 (t), 22.6 (t), 14.0 (q); MS, m/z 232 (M^+). Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.47; H, 8.70.

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Cross-Condensation Reactions of Cycloalkanones with Aldehydes and Primary Alcohols under the Influence of Zirconocene Complexes

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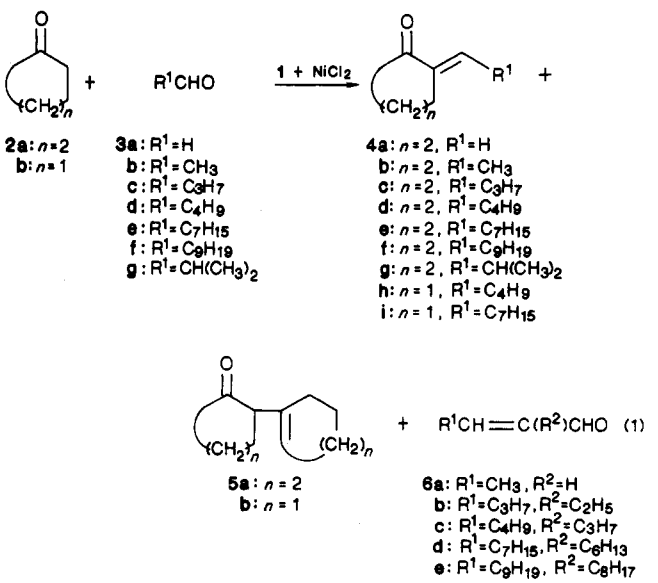
Under the influence of zirconocene complex, Cp_2ZrH_2 (**1**) or $Cp_2Zr(O\text{-}i\text{-}Pr)_2$ (**9**), cycloalkanones **2** condensed directly with aliphatic aldehydes **3** or primary alcohols **7** to form 2-alkylidenecycloalkanones **4** or 2-alkyl-2-cycloalken-1-ones **8**, respectively, in fair to substantial yields. The selectivity of the cross-condensations was slightly improved by using **1** in combination with a metal salt such as $NiCl_2$. Dihydrojasmone (**13**) was synthesized in 35% yield by one-step reaction from the commercially available 3-methylcyclopentanone (**2e**) with pentanol (**7b**) in the presence of **1** and $NiCl_2$.

Recently we reported that dicyclopentadienylzirconium dihydride, Cp_2ZrH_2 (**1**), catalyzes the hydrogen-transfer reaction from alcohols to carbonyl compounds: i.e., Meerwein-Ponndorf-Verley (MPV) type reduction of carbonyl compounds and Oppenauer (OPP) type oxidation of alcohols simultaneously proceeded under the influence of catalytic amount of **1**.[1,2] Primary alcohols, which are difficult to be oxidized by the OPP method using aluminum alkoxides, were easily oxidized by **1** to the corresponding aldehydes.[1] Furthermore, diols involving both primary and secondary hydroxy groups were oxidized chemoselectively to the corresponding hydroxy aldehydes.[2] In these reactions, the carbonyl compound having no α-hydrogen such as benzophenone or benzaldehyde served as a good hydrogen acceptor, while acetone, considered to be a suitable hydrogen acceptor in the OPP oxidation, was inadequate owing to the aldol condensation of acetone itself.

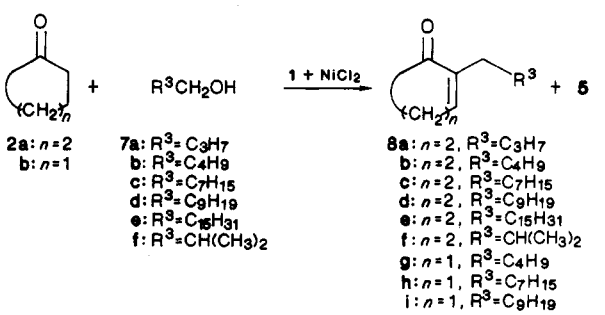
In the course of the study, it seemed of interest to investigate the cross-condensation between cycloalkanones and aldehydes, since the zirconocene dihydride **1** was found to catalyze aldol condensation of ketones. Thus, cycloalkanones **2** were allowed to react with aliphatic aldehydes **3** under the influence of **1** to give cross aldol condensation products, 2-alkylidenecycloalkanones **4**, in substantial yields with small amounts of self-condensates (eq 1).

Despite the fact that primary alcohols **7** in the presence of a carbonyl compound lacking α-hydrogen were only converted to the corresponding aldehydes by **1**, the same reaction of **7** employing cycloalkanones **2** as hydrogen acceptor in place of benzophenone or benzaldehyde gave



(1)

cross-condensation products 2-alkyl-2-cycloalken-1-ones **8** in fair yields (eq 2).



(2)

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