Removal of the solvent in vacuo gave 29 mg (90%) of ketone **42** as a pale yellow solid, mp 206–209 °C. Recrystallization from ethyl acetate/hexanes afforded analytically pure material as white needles, mp 217–219 °C: IR ($CHCl_3$) 1760, 1740 cm^{-1}; ^1H NMR δ 1.01 (d, 3 H, J = 7), 1.27 (s, 3 H), 1.46 (s, 9 H), 1.50–1.85 (m, 6 H), 2.04 (dm, 1 H, J = 16), 2.22 (dd, 1 H, J = 18, 5), 2.28 (br d, 1 H, J = 20), 2.31 (dd, 1 H, J = 20, 6), 2.69 (m, 1 H), 3.02 (dd, 1 H, J = 16, 13), 3.09 (br t, 1 H, J = 4), 3.78 (s, 3 H), 3.79 (dd, 1 H, J = 9, 1), 3.87–4.03 (m, 4 H), 4.68 (d, 1 H, J = 9), 5.42 (m, 1 H); ^{13}C NMR δ 9.82, 18.32, 28.45 (3C), 29.23, 29.31, 30.73, 36.31, 37.64, 40.84, 43.94, 44.80, 44.94, 49.98, 52.44, 64.97, 65.36, 81.12, 88.95, 110.77, 117.22, 142.14, 167.92, 170.57, 205.58; mass spectrum (70 eV), m/z 490 (M^+), 434, 419, 389, 327, 345. Anal. Calcd for $C_{27}H_{38}O_8$: C, 66.10; H, 7.81. Found: C, 65.92; H, 7.76.

Acknowledgment. This work was supported by a research grant from the United States Public Health Service (CA 21163) and by a NATO Fellowship to Dr. Axel Paul. We thank Dr. Dariush Davalian for assistance in developing the conditions for the preparation of intermediate **5**.

Palladium-Complex-Catalyzed Reactions of Ketenes with Allylic Carbonates or Acetates. Novel Syntheses of α-Allylated Carboxylic Esters and 1,3-Dienes

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Diphenylketene and ethylphenylketene react with allylic carbonates or acetates in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium to give α-allylated esters or 1,3-dienes, respectively. For example, the reaction of diphenylketene with allyl methyl carbonate in DMF at 0 °C gave methyl 2,2-diphenyl-4-pentenoate in 67% yield. The reaction of diphenylketene with allyl acetate in benzene at 25 °C gave 1,1-diphenyl-1,3-butadiene in 72% yield. Marked solvent effects were observed.

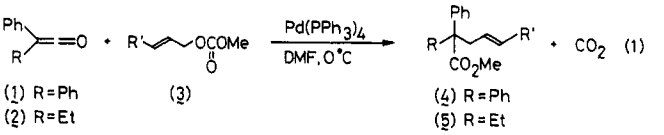
In organic syntheses catalyzed by palladium, π- or σ-allyl palladium complexes have often been recognized as important intermediates.[1] For example, nucleophilic attack of a carbonucleophile on a π-allyl ligand on a palladium complex has been revealed to be a key step in several important carbon–carbon bond-formation reactions.[1]

On the other hand, ketenes are known to undergo a variety of characteristic reactions due to their high reactivity. However, catalytic processes using a transition-metal complex are rare.[2] In the course of our study on the development of catalytic reactions utilizing ketenes, we have found palladium-catalyzed reactions of ketenes with terminal acetylenes[3] or acid halides[4] to give disubstituted acetylenes or α,β-unsaturated ketones, respectively.

In this paper, along with the concept to build up a catalytic cycle involving the reaction of ketene with a π- or σ-allyl palladium complex as a key step, reactions of ketenes with allylic carbonates or acetates have been investigated; products were expected α-allylated carboxylic esters or unexpected 1,3-dienes, respectively. Preliminary results appear in a previous paper.[5]

Results and Discussion

Reaction of Ketenes with Allylic Carbonates. The reaction of ketene **1** or **2** with allylic carbonate **3** in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium gives α-allylated carboxylic ester **4** or **5** in high yields by alkoxy allylation of the ketene accompanied by decarboxylation (eq 1). The reaction

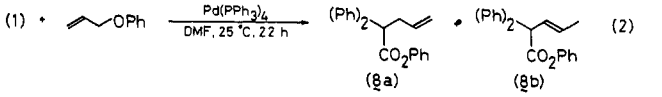


(1) R=Ph (2) R=Et (3) (4) R=Ph (5) R=Et

proceeds rapidly under mild conditions (0 °C, 0.5 h, in DMF). Results using various carbonates are summarized in Table I.

A usual allyl rearrangement was observed in the ester formation reaction. Both crotyl (**3c**) and 1-methylallyl carbonate (**3d**) gave products **4c** and **4d** in ratios of 94:6 and 80:20, respectively (Table I, runs 3 and 4). 2-Hexenyl (**3e**) or cinnamyl carbonate (**3f**), having a large substituent, gave **4e** or **4f** selectively (Table I, runs 5 and 6). The ester from geranyl carbonate (**3i**) kept the E configuration during the reaction; however, that from neryl carbonate (**3j**) was a mixture of isomers (Z:E = 8:2). Myrtenyl (**3k**) and perillyl carbonate (**3l**), which have terpene skeletones, also gave esters in high yields. The reaction using ethylphenylketene **2** proceeded similarly, affording the corresponding esters in moderate yields (runs 13 and 14).

The reaction using allyl phenyl ether as an allyl moiety instead of the carbonate also gave allylated phenyl ester **8a** and its isomer **8b** in 66% yield (**8a**:**8b** = 1:1) (eq 2).



(8a) (8b)

However, use of allyl phenyl ether required a longer reaction time than that for the carbonate. Allyl alkyl ether did not react at all. When N,N-dimethylallylamine was allowed to react with diphenylketene in DMF or THF, allylated amide was not obtained but N,N-dimethyl-2,2-

(1) For a recent review, see: Heck, R. F. *Palladium Reagents in Organic Syntheses*; Academic: New York, 1985; Chapter 5. Tsuji, J. In *The Chemistry of the Metal–Carbon Bond*; Patai, S., Ed.; Wiley: New York, 1985; Vol. 3, p 163.

(2) (a) Hong, P.; Sonogashira, K.; Hagihara, N. *Tetrahedron Lett.* **1971**, 1105. (b) Hong, P.; Yamazaki, H.; Sonogashira, K.; Hagihara, N. *Chem. Lett.* **1978**, 535.

(3) Mitsudo, T.; Kadokura, M.; Watanabe, Y. *Tetrahedron Lett.* **1985**, *26*, 3697.

(4) (a) Mitsudo, T.; Kadokura, M.; Watanabe, Y. *Tetrahedron Lett.* **1985**, *26*, 5143. (b) Kadokura, M.; Mitsudo, T.; Watanabe, Y. *J. Chem. Soc., Chem. Commun.* **1986**, 252.

(5) Mitsudo, T.; Kadokura, M.; Watanabe, Y. *J. Chem. Soc., Chem. Commun.* **1986**, 1539.

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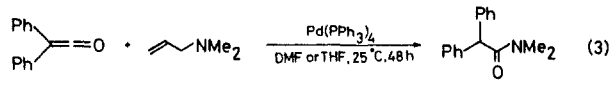
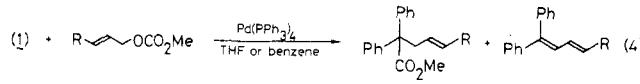
diphenylacetamide was formed (eq 3).

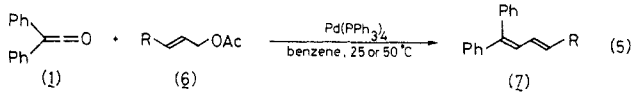


This ester formation reaction was significantly affected by solvents. In the reaction of diphenylketene with allyl carbonate (**3a**), effects of the solvents were examined (Table II). Consequently, it was revealed that more polar solvent was preferable for the reaction. Esters were obtained selectively in DMF, and the selectivity for ester decreased in the order DMF ≫ THF > benzene. When THF or benzene was used, a considerable amount of 1,3-diene was formed along with the expected ester (eq 4); in

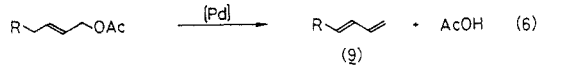


the reaction of diphenylketene with methyl cinnamyl carbonate (**3f**) in THF or benzene, the main product was the corresponding diene (Table II, runs 5 and 6). The selective diene synthesis was achieved by the reaction using allylic acetate in nonpolar solvent (vide infra).

Reaction of Diphenylketene with Allylic Acetates. The reaction of diphenylketene **1** with allylic acetate **6** in the presence of a catalytic amount of $Pd(PPh_3)_4$ in benzene gives (*E*)-1,1-diphenyl-1,3-butadiene derivatives **7** selectively under very mild conditions (25 or 50 °C, 1–2 h) (eq 5). Results are listed in Table III. Allyl rearrangement

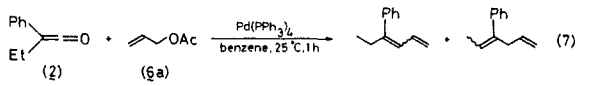


was also observed in the diene formation reaction. Both crotyl (**6c**) and 1-methylallyl acetate (**6d**) gave 1,1-diphenyl-1,3-pentadiene (**7c**) as a sole product in 65% and 55% yield, respectively. Reactions with crotyl (**6c**), 1-methylallyl (**6d**), *trans*-2-hexenyl (**6e**), and myrtenyl (**6g**) acetate gave the corresponding dienes **7** in moderate yields, because of a side reaction. It is well-known that allylic acetate is converted into the corresponding conjugated diene **9** by elimination of acetic acid catalyzed by palladium (eq 6).[6] Geranyl acetate did not react with di-



phenylketene at 25 °C; however, at higher temperature (50–100 °C) (*Z*)-3,7-dimethyl-1,3,6-octatriene was produced by the elimination reaction. In this case, diphenylketene was catalytically decomposed to tetraphenylethylene and tetraphenylethane by decarbonylation reaction.[7] Allylic acetates, which cannot release acetic acid by (eq 6) such as **6a**, **6b**, and **6f**, gave the 1,3-dienes **7** derived from ketene in high yields.

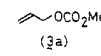
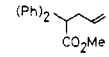
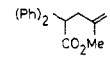
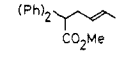
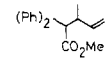
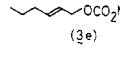
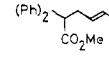
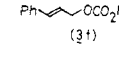
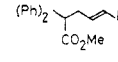
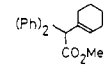
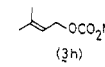
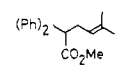
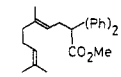
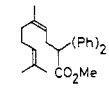
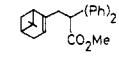
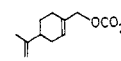
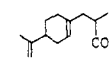
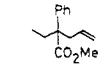
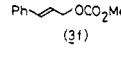
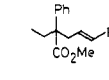
The reaction of ethylphenylketene **2** with allyl acetate (**6a**) gave a mixture of dienes in 26% of total yield (eq 7).



Although the dienes were not isolated in pure form, ^1H NMR and GC-MS analyses of the products proved to be a mixture of isomers of the dienes.

(6) Tsuji, J.; Yamakawa, T.; Kaito, M.; Mandai, T. *Tetrahedron Lett.* **1978**, 2075.
(7) Hong, P.; Sonogashira, K.; Hagihara, N. *Nippon Kagaku Zasshi* **1968**, *89*, 74.

Table I. Reaction of Ketenes with Allylic Carbonates To Give Allylated Esters[a]

run	ketene	carbonate	product	yield,[b] %
1	 (1)	 (3a)	 (4a)	67 (65)
2	1	 (3b)	 (4b)	80 (75)
3	1	 (3c)	 (4c)	78 (66)
			 (4d)	5
4	1	 (3d)	**4c**	64 (58)
			4d	16
5	1	 (3e)	 (4e)	85 (75)
6	1	 (3f)	 (4f)	87 (78)
7	1	 (3g)	 (4g)	80 (53)
8	1	 (3h)	 (4h)	67 (50)
9[c]	1	 (3i)	 (4i)	78 (77)
10[c]	1	 (3j)	 (4j)	48 (46)
			(4i)	12
11[c]	1	 (3k)	 (4k)	80 (44)
12[c]	1	 (3l)	 (4l)	90 (61)
13	 (2)	 (3a)	 (5a)	41 (32)
14	2	 (3f)	 (5f)	58 (38)

[a] Ketene (3 mmol), carbonate (3 mmol), $Pd(PPh_3)_4$ (0.09 mmol), DMF (9 mL), 0 °C, 0.5 h. [b] Determined by GLC using an internal standard. Isolated yields are given in parentheses. [c] At 25 °C, 1 h.

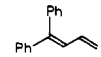
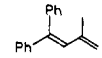
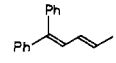
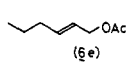
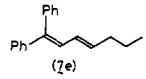
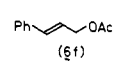
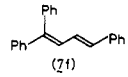
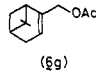
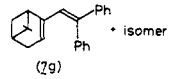
Table II. Reaction of Diphenylketene with Allyl or Cinnamyl Carbonate:[a] Effects of Solvents

run	carbonate	solvent	ester/diene[b]	ester yield,[c] %
1	**3a**	DMF	99/1	67
2	**3a**	THF	54/46	23
3	**3a**	benzene	50/50	23
4	**3f**	DMF	95/5	87
5	**3f**	THF	39/61	31
6	**3f**	benzene	36/64	33

[a] Diphenylketene (1 mmol), carbonate (1 mmol), $Pd(PPh_3)_4$ (0.03 mmol), solvent (3 mL), 0 °C, 0.5 h. [b] Determined by GLC. [c] Determined by GLC using an internal standard based on diphenylketene charged.

In the reaction of diphenylketene **1** with allyl acetate (**6a**), effects of solvents were examined (Table IV). Consequently, benzene was revealed to be favorable, and more polar solvents, such as DMF and Me_2SO, were not

Table III. Reaction of Diphenylketene with Allylic Acetates To Give 1,3-Dienes[a]

run	acetate	product	yield,[b] %
1	 (6a)	 (7a)	72 (40)
2	 (6b)	 (7b)	84 (51)
3[c]	 (6c)	 (7c)	65 (41)
4	 (6d)	**7c**	55
5[c]	 (6e)	 (7e)	68 (57)
6	 (6f)	 (7f)	86
7[c]	 (6g)	 + isomer (7g)	46

[a] Diphenylketene (3.6 mmol), acetate (3 mmol), $Pd(PPh_3)_4$ (0.09 mmol), benzene (9 mL), 25 °C, 1 h. [b] Determined by GLC using an internal standard based on acetate charged. Isolated yields are in parentheses. [c] At 50 °C, 2 h.

Table IV. Reaction of Diphenylketene with Allyl Acetate To Give 1,1-Diphenyl-1,3-butadiene:[a] Effects of Solvents

run	solvent	yield,[b] %
1	benzene	72
2	THF	59
3	dioxane	55
4	DMF	48
5	Me_2SO	43

[a] Diphenylketene (1.2 mmol), allyl acetate (1 mmol), $Pd(PPh_3)_4$ (0.03 mmol), solvent (3 mL), 25 °C, 1 h. [b] Determined by GLC using an internal standard based on allyl acetate charged.

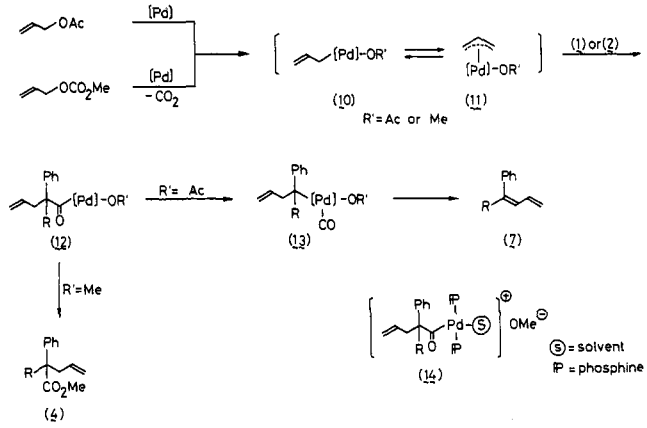
appropriate. This tendency is quite in contrast to the ester formation using allylic carbonate.

Mechanistic Consideration. On the basis of the results mentioned above, we propose a possible mechanism (Scheme I). It is evident that both the ester formation reaction and the diene synthesis proceed via a π-allyl intermediate (**11**). The π-allyl palladium complex is in equilbrium with a σ-allyl complex (**10**). Insertion of ketene into the σ-allyl–Pd bond forms an acyl complex (**12**). When the OR′ in **12** is a methoxy or a phenoxy group in DMF, reductive elimination or rapid nucleophilic attack of the alkoxide ion on the acyl group prior to decarbonylation would give the allylated ester.[8] In less polar or less coordinative solvent such as THF or benzene, the decarbonylation reaction competes with the attack of the alkoxide to give a homoallyl palladium intermediate (**13**) which affords the 1,3-dienes by β-hydrogen elimination reaction. This fact suggests that the formation of the ester may proceed via a palladium cation complex such as **14**.

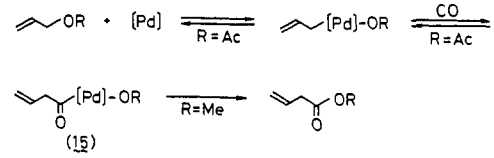
When OR′ in **12** is acetate, the decarbonylation reaction occurs to give **13** and 1,3-diene is obtained selectively. During this reaction, no evolution of carbon monoxide was observed. In order to elucidate the fate of acetoxy anion and carbon monoxide, ^{13}C NMR, IR, and GC-MS analyses of the reaction mixture of **1** with **6f** were carried out. Consequently, formations of acetic anhydride[9] (80% yield) and a trace amount of carbon dioxide were confirmed; neither acetic acid nor the anhydride that can be formed by addition of acetic acid to ketene was detected.

These observations are closely related to the palladium-catalyzed carbonylation reaction of allylic acetates and carbonates. Although the carbonylation of allylic acetate is not well achieved catalytically, that of carbonates is easily peformed.[10] When the ligand on the key intermediate is OAc, decarbonylation of **15** occurs and the starting materials are recovered. In contrast, when the ligand is an alkoxide, reductive elimination affords the corresponding ester (Scheme II). Thus, our findings in the reaction of ketenes are quite consistent with the carbonylation of allylic compounds.

Scheme I. Proposed Mechanism



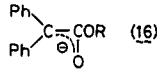
Scheme II



Concluding Remarks

Some palladium-mediated diene formation reactions have been known.[11] Representative is the direct coupling reaction of vinyl halides with vinyl organometallics, such as vinylic alanes,[12] Grignard reagents,[13] zirconium deriv-

(8) An alternative mechanism, which includes a nucleophilic attack of alkoxide on the carbonyl group in ketene followed by a nucleophilic attack of the carbon atom of the enolate (**16**) on the π-allyl ligand, can be assumed. However, it has been reported that the oxygen atom, not the carbon atom, in enolate **16** derived from diphenylketene and alkoxide


(16)

attacks a π-allyl ligand on palladium. Thus the present ester formation reaction must proceed via the insertion of ketenes into a σ-allyl–Pd bond followed by nucleophilic attack of alkoxide: Fujinami, T.; Suzuki, T.; Ito, N.; Fukuzawa, S.; Sakai, S. *Abstracts of Papers*, 32nd Symposium on Organometallic Chemistry, Japan; 1985; Abstract B101.

(9) The mechanism of the formation of acetic anhydride from the ligands of the complex **13** is confusing. It would be formed by the subsequent reaction of the primary product such as acetic formic anhydride; the reaction of acetic formic anhydride with $Pd(PPh_3)_4$ gave a small amount of acetic anhydride under the reaction conditions employed.

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(12) Baba, S.; Negishi, E. *J. Am. Chem. Soc.* **1976**, *98*, 6729.

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atives,[14] boranes,[15] and copper reagents.[16] Another typical procedure is Heck reaction of olefins with aryl or vinyl halides.[17] Conjugated diene synthesis by decomposition of 3-acetoxy-2-alkyl-4-alkenoate salts catalyzed by palladium has been achieved by Trost.[18] This decomposition reaction is considered to proceed via a π-allyl intermediate. The present reaction is, to our knowledge, the first example of palladium-catalyzed 1,3-diene synthesis from an allyl moiety involving carbon–carbon bond-formation reaction.

In conclusion, palladium-catalyzed reaction of ketenes with allylic carbonates or acetates via a π-allyl intermediate has been revealed. Versatile novel synthetic methods for σ-allylated carboxylic esters and 1,3-dienes have been achieved by the present reactions.

Experimental Section

Materials. Allyl acetate, cinnamyl acetate, *trans*-2-hexenyl acetate, and geranyl acetate were commercial products and used after distillation. Other allylic acetates[19] and carbonates,[19] diphenylketene,[20] and ethylphenylketene[20] were prepared by published methods. The optical rotations ($[\alpha]^{25}$) of (*R*)-(−)-myrtenyl carbonate (**3k**) and (*S*)-(−)-perillyl carbonate (**3l**) were −42.2° and −39.8°, respectively. Benzene, tetrahydrofuran (THF), and *N*,*N*-dimethylformamide (DMF) were dried and distilled just before use. $Pd(PPh_3)_4$ was prepared according to the method in the literature.[21]

Analytical Procedures. Identification of all products was confirmed by ^{13}C NMR, ^1H NMR, FT-IR, GC-MS, and elemental analysis. All boiling points are uncorrected.

^{13}C NMR spectra were recorded on a JEOL FX-100 spectrometer at 25.05 MHz in $CDCl_3$. ^1H NMR spectra were recorded on a JEOL FX-100 or a Nicolet NT-300NB spectrometer at 100 MHz or 300 MHz, respectively. FT-IR spectra were measured on a Nicolet 5-MX spectrometer as films or Nujol mulls. GC-MS analyses were performed on a Hitachi RM-50 GC-MS spectrometer. Elemental analyses were performed at the Laboratory for Organic Elemental Microanalysis at the Faculty of Pharmaceutical Science at Kyoto University. GLC analyses were performed on a Shimadzu GC-4C equipped with a column packed with silicone SE-30 (5% on Chromosorb W) or silicone OV-17 (2% on Chromosorb W).

General Procedure. 1. Synthesis of α-Allylated Carboxylic Esters. The reaction of diphenylketene with allyl methyl carbonate is representative. To a solution of diphenylketene (3 mmol, 0.582 g) and $Pd(PPh_3)_4$ (0.09 mmol, 0.11 g) in 9 mL of dry degassed DMF was added allyl carbonate (3 mmol, 0.35 g) at 0 °C, and the mixture was stirred under an argon atmosphere for 0.5 h. During that time gentle evolution of carbon dioxide was observed. After evolution of the gas was over, the solvent was removed in vacuo followed by extraction with ether (3 mL × 3). Yellow precipitates were filtered, and the filtrate was subjected to Kugelrohr distillation (150 °C/0.15 mmHg), giving 0.52 g of methyl 2,2-diphenyl-4-pentenoate (65%). All other reactions were carried out in the same manner unless otherwise noted (see Table I).

2. Synthesis of 1,3-Dienes. The reaction of diphenylketene with allyl acetate is representative. Allyl acetate (3 mmol, 0.30 g) was added to a solution of diphenylketene (3.6 mmol, 0.70 g) and $Pd(PPh_3)_4$ (0.09 mmol, 0.11 g) in 9 mL of dry degassed benzene under an argon atmosphere, and the mixture was stirred at 25 °C for 1 h. The resulting mixture was concentrated in vacuo and extracted with 10 mL of ether. Then precipitates were filtered off, and the filtrate was subjected to Kugelrohr distillation (130 °C/0.2 mmHg), giving 0.25 g of 1,1-diphenyl-1,3-butadiene (40%). All other reactions were carried out in the same manner unless otherwise noted (Table III).

Methyl 2,2-diphenyl-4-pentenoate (4a): colorless oil; Kugelrohr distillation (150 °C/0.15 mmHg); ^{13}C NMR ($CDCl_3$) δ 174.3 (s), 142.4 (s), 134.2 (d), 128.9 (d), 127.8 (d), 126.8 (d), 118.1 (t), 60.3 (s), 52.3 (q), 42.7 (t); ^1H NMR (100 MHz, $CDCl_3$) δ 7.25 (s, Ar, 10 H), 5.61 (ddt, J = 17.7, 9.4, 6.7 Hz, =CH–, 1 H), 4.92 (d, J = 9.4 Hz, $=CH_2$, 1 H), 4.90 (d, J = 17.7 Hz, $=CH_2$, 1 H), 3.65 (s, $-OCH_3$, 3 H), 3.17 (d, J = 6.9 Hz, $-CH_2-$, 2 H); IR (neat) 1732 cm^{-1}; MS, m/z 266 (M^+). Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.24; H, 6.70.

Methyl 2,2-diphenyl-4-methyl-4-pentenoate (4b): colorless oil; Kugelrohr distillation (110 °C/0.09 mmHg); ^{13}C NMR ($CDCl_3$) δ 174.0 (s), 143.2 (s), 141.8 (s), 128.8 (d), 127.6 (d), 126.6 (d), 115.2 (t), 60.1 (s), 52.0 (q), 45.8 (t), 24.2 (q); ^1H NMR (100 MHz, $CDCl_3$) δ 7.25 (s, Ar, 10 H), 4.69 (s, $=CH_2$, 1 H), 4.48 (s, $=CH_2$, 1 H), 3.65 (s, $-OCH_3$, 3 H), 3.18 (s, $-CH_2-$, 2 H), 1.35 (s, $-CH_3$, 3 H); IR (neat) 1732 cm^{-1}. MS, m/z 280 (M^+). Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 80.94; H, 7.12.

(*E*)-Methyl 2,2-diphenyl-4-hexenoate (4c): colorless oil; Kugelrohr distillation (120 °C/0.2 mmHg); ^{13}C NMR ($CDCl_3$) δ 174.5 (s), 142.6 (s), 134.0 (d), 128.9 (d), 127.6 (d), 126.6 (d), 126.3 (d), 60.6 (s), 52.1 (q), 41.6 (t), 18.0 (q); ^1H NMR (300 MHz, $CDCl_3$) δ 7.25 (s, Ar, 10 H), 5.27 (dq, J = 15, 5.1 Hz, $-CH_2CH=$, 1 H), 5.22 (dt, J = 15, 6 Hz, $=CHCH_3$, 1 H), 3.66 (s, $-OCH_3$, 3 H), 3.08 (d, J = 5.7 Hz, $-CH_2-$, 2 H), 1.50 (d, 4.8 Hz, $-CH_3$, 3 H); IR (neat) 1732 cm^{-1}; MS, m/z 280 (M^+). Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 81.16; H, 7.23.

(*E*)-Methyl 2,2-diphenyl-4-octenoate (4e): colorless oil; Kugelrohr distillation (160 °C/0.5 mmHg); ^{13}C NMR ($CDCl_3$) δ 174.4 (s), 142.7 (s), 134.4 (d), 128.9 (d), 127.7 (d), 126.6 (d), 125.3 (d), 60.6 (s), 52.1 (q), 41.7 (t), 34.7 (t), 22.4 (t), 13.6 (q); ^1H NMR (300 Mz, $CDCl_3$) δ 7.25 (s, Ar, 10 H), 5.25 (dt, J = 15.3, 5.7 Hz, =CH–, 1 H), 5.21 (dt, J = 15.3, 5.7 Hz, –CH=, 1 H), 3.66 (s, $-OCH_3$, 3 H), 3.09 (d, J = 5.7 Hz, 2 H), 1.82 (dt, J = 5.7, 7.2 Hz, 2 H), 1.20 (tq, J = 7.4, 7.2 Hz, 2 H), 0.75 (t, J = 7.4 Hz, 3 H); IR (neat) 1732 cm^{-1}; MS, m/z 308 (M^+). Anal. Calcd for $C_{21}H_{24}O_2$: C, 81.78; H, 7.84. Found: C, 81.98; H, 7.58.

(*E*)-Methyl 2,2,5-triphenyl-4-pentenoate (4f): colorless oil; Kugelrohr distillation (200 °C/0.1 mmHg); ^{13}C NMR ($CDCl_3$) δ 174.0 (s), 142.3 (s), 137.3 (d), 133.2 (d), 128.7 (d), 128.1 (d), 127.6 (d), 126.8 (d), 126.6 (d), 125.8 (d), 60.6 (s), 52.0 (q), 41.7 (t); ^1H NMR (100 MHz, $CDCl_3$) δ 7.26 (s, Ar, 10 H), 7.16 (s, Ar, 5 H), 6.23 (d, J = 15.9 Hz, =CHPh, 1 H), 5.93 (dt, J = 15.9, 6.5 Hz, $-CH_2CH=$, 1 H), 3.66 (s, $-OCH_3$, 3 H), 3.30 (d, J = 6.5 Hz, $-CH_2-$, 2 H); IR (neat) 1732 cm^{-1}; MS, m/z 342 (M^+). Anal. Calcd for $C_{24}H_{22}O_2$: C, 84.18; H, 6.48. Found: C, 83.29; H, 6.47.

Methyl 2-(2-cyclohexenyl)-2,2-diphenylacetate (4g): colorless viscous oil; Kugelrohr distillation (140 °C/0.2 mmHg); ^{13}C NMR ($CDCl_3$) δ 174.3 (s), 140.9 (s), 140.1 (s), 129.9 (d), 129.2 (d), 128.2 (d), 127.4 (d), 127.2 (d), 126.6 (d), 64.5 (s), 52.0 (q), 40.0 (d), 25.7 (t), 25.0 (t), 22.0 (t); ^1H NMR (300 MHz, $CDCl_3$) δ 7.14–7.32 (m, Ar, 10 H), 5.67 (d, J = 10.5 Hz, 1 H), 5.58 (dt, J = 10.5, 7.2 Hz, 1 H), 3.83 (s, 1 H), 3.55 (s, $-OCH_3$, 3 H), 0.97–1.92 (m, methylene, 6 H); IR (neat) 1732 cm^{-1}; MS, m/z 306 (M^+). Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.08; H, 7.22.

Methyl 2,2-diphenyl-5-methyl-4-hexenoate (4h): colorless oil; Kugelrohr distillation (110 °C/0.07 mmHg); ^{13}C NMR ($CDCl_3$) δ 174.5 (s), 142.7 (s), 134.5 (s), 128.9 (d), 127.6 (d), 126.5 (d), 119.6 (d), 66.6 (s), 52.9 (q), 36.9 (t), 25.8 (q), 17.4 (q); ^1H NMR (100 MHz, $CDCl_3$) δ 7.25 (s, Ar, 10 H), 5.01 (t, J = 6.9 Hz, –CH=, 1 H), 3.68 (s, $-OCH_3$, 3 H), 3.08 (d, J = 6.9 Hz, $-CH_2-$, 2 H), 1.57 (s, $-CH_3$, 3 H), 1.26 (s, $-CH_3$, 3 H); IR (neat) 1732 cm^{-1}; MS, m/z 294 (M^+). Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.54; H, 7.58.

(*E*)-Methyl 2,2-diphenyl-5,9-dimethyl-4,8-decadienoate (4i): pale yellow oil; Kugelrohr distillation (170 °C/1 mmHg); ^{13}C NMR ($CDCl_3$) δ 174.6 (s), 142.7 (s), 138.1 (s), 131.0 (s), 129.0 (d), 127.6 (d), 126.6 (d), 124.3 (d), 119.6 (d), 60.6 (s), 52.1 (q), 39.9 (t), 36.9 (t), 26.5 (t), 25.7 (q), 17.7 (q), 15.9 (q); ^1H NMR (300 MHz, $CDCl_3$) δ 7.25 (s, Ar, 10 H), 5.03 (t, J = 7.2 Hz, 1 H), 4.99 (t, J = 6.6 Hz,

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1 H), 3.67 (s, $-OCH_3$, 3 H), 3.09 (d, J = 6.9 Hz, 2 H), 1.84–1.93 (m, methylene, 4 H), 1.65 (s, $-CH_3$, 3 H), 1.55 (s, $-CH_3$, 3 H), 1.28 (s, $-CH_3$, 3 H); IR (neat) 1732 cm^{-1}; MS, m/z 362 (M^+). Anal. Calcd for $C_{25}H_{30}O_2$: C, 82.83; H, 8.34. Found: C, 82.85; H, 8.38.

(*Z*)-Methyl 2,2-diphenyl-5,9-dimethyl-4,8-decadienoate (4j): pale yellow oil; Kugelrohr distillation (150 °C/0.1 mmHg); ^{13}C NMR ($CDCl_3$) δ 174.7 (s), 142.7 (s), 137.9 (s), 131.8 (s), 128.9 (d), 127.6 (d), 126.6 (d), 124.3 (d), 120.2 (d), 60.5 (s), 52.1 (q), 36.6 (t), 31.8 (t), 26.1 (t), 25.7 (q), 23.5 (q), 17.6 (q); ^1H NMR (300 MHz, $CDCl_3$) δ 7.15–7.25 (m, Ar, 10 H), 5.03 (t, J = 6 Hz, 2 H), 3.63 (s, $-OCH_3$, 3 H), 3.13 (d, J = 6.9 Hz, 2 H), 1.75–1.88 (m, methylene, 4 H), 1.65 (s, $-CH_3$, 3 H), 1.56 (s, $-CH_3$, 6 H); IR(neat) 1732 cm^{-1}; MS, m/z 362 (M^+). Anal. Calcd for $C_{25}H_{30}O_2$: C, 82.83; H, 8.34. Found: C, 82.85; H, 8.32.

Methyl 2,2-diphenyl-2-myrtenylacetate (4k): pale yellow oil; Kugelrohr distillation (160 °C/0.2 mmHg); $[\alpha]^{25}$ −7.6° (*c* 5, MeOH); ^{13}C NMR ($CDCl_3$) δ 174.1 (s), 143.6 (s), 143.5 (s), 131.8 (s), 128.9 (d), 128.8 (d), 127.5 (d), 126.4 (d), 121.6 (d), 59.9 (s), 51.8 (q), 47.3 (d), 46.0 (t), 40.3 (d), 37.6 (s), 31.8 (t), 26.3 (q), 21.0 (q); ^1H NMR (300 Mz, $CDCl_3$) δ 7.13–7.32 (m, Ar, 10 H), 5.03 (s, $-CH=$, 1 H), 3.63 (s, $-OCH_3$, 3 H), 3.26 (d, J = 14.4 Hz, 1 H), 3.03 (d, J = 14.4 Hz, 1 H), 1.91–2.14 (m, methylene, 4 H), 1.49 (td, J = 5.4, 1.2 Hz, 1 H), 1.12 (s, $-CH_3$, 3 H), 0.96 (d, J = 8.4 Hz, 1 H), 0.77 (s, $-CH_3$, 3 H); IR (neat) 1732 cm^{-1}; MS, m/z 360 (M^+). Anal. Calcd for $C_{25}H_{28}O_2$: C, 83.29; H, 7.83. Found: C, 83.23; H, 7.97.

Methyl 2,2-diphenyl-2-perillylacetate (4l): colorless oil; Kugelrohr distillation (160 °C/0.1 mmHg); $[\alpha]^{25}$ −28.7° (*c*, 5, MeOH); ^{13}C NMR ($CDCl_3$) δ 174.4 (s), 149.7 (s), 143.2 (s), 133.5 (s), 129.0 (d), 128.8 (d), 127.6 (d), 127.4 (d), 126.5 (d), 125.9 (d), 108.3 (t), 60.6 (s), 52.0 (q), 45.9 (d), 40.5 (d), 30.9 (t), 30.4 (t), 28.0 (t), 20.7 (q); ^1H NMR (100 MHz, $CDCl_3$) δ 7.17–7.27 (m, Ar, 10 H), 5.18 (s, $=CH-$, 1 H), 4.63 (s, $=CH_2$, 2 H), 3.63 (s, $-OCH_3$, 3 H), 2.92–3.27 (m, 2 H), 1.66 (s, $-CH_3$, 3 H), 1.14–1.85 (m, 7 H); IR (neat) 1732 cm^{-1}; MS/ m/z 360 (M^+). Anal. Calcd for $C_{25}H_{28}O_2$: C, 83.29; H, 7.83. Found: C, 83.46; H, 7.84.

Phenyl 2,2-Diphenyl-4-pentenoate (8a) and Phenyl 2,2-Diphenyl-3-pentenoate (8b). The products were obtained as a mixture of isomers **8a** and **8b**: colorless oil; Kugelrohr distillation (160 °C/0.15 mmHg); ^{13}C NMR ($CDCl_3$) δ 172.1 (s), 150.8 (s), 141.8 (s), 133.6 (d), 133.4 (d), 129.2 (d), 129.1 (d), 128.8 (d), 127.8 (d), 127.0 (d), 126.9 (d), 125.5 (d), 121.0 (d), 118.5 (t, **a**), 63.8 (s, **b**), 60.2 (s, **a**), 42.6 (t, **a**), 18.1 (q, **b**); ^1H NMR (100 MHz, $CDCl_3$) δ 7.30 (s, Ar, 10 H), 7.00 (q, J = 9.2 Hz, $=CHCH_3$, **b**), 6.56 (d, J = 15.7 Hz, $-CH=CHCH_3$, **b**), 5.70 (ddt, J = 17.6, 9.6, 6.8 Hz, $-CH=CH_2$, **a**), 5.03 (d, J = 17.3 Hz, $=CH_2$, **a**), 5.00 (d, J = 10 Hz, $=CH_2$ **a**), 3.29 (d, J = 7.0 Hz, $-CH_2-$, **a**), 1.79 (dd, J = 6.6, 1.6 Hz, $-CH_3$, **b**); IR (neat) 1753 cm^{-1}. Anal. Calcd for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14. Found: C, 83.86; H, 6.06.

Methyl 2-ethyl-2-phenyl-4-pentenoate (5a): colorless liquid; Kugelrohr distillation (100 °C/0.1 mmHg); ^{13}C NMR ($CDCl_3$) δ 175.5 (s), 141.9 (s), 133.3 (d), 128.0 (d), 126.4 (d), 126.2 (d), 117.8 (t), 53.9 (s), 51.5 (q), 38.4 (t), 26.8 (t), 8.1 (q); ^1H NMR (100 MHz, $CDCl_3$) δ 7.25 (s, Ar, 5 H), 5.52 (ddt, J = 16.9, 10, 6.9 Hz, $-CH=$, 1 H), 5.02 (d, J = 16.9 Hz, $=CH_2$, 1 H), 5.00 (d, J = 10 Hz, $-CH_2-$, 1 H), 3.62 (s, OCH_3, 3 H), 2.77 (d, J = 6.7 Hz, $-CH_2-$, 2 H), 2.05 (q, J = 7.3 Hz, $-CH_2CH_3$, 2 H), 0.75 (t, J = 7.5 Hz, $-CH_3$, 3 H); IR (neat) 1732 cm^{-1}; MS, m/z 218 (M^+). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.20; H, 8.36.

(*E*)-Methyl 2-ethyl-2,5-diphenyl-4-pentenoate (5f): colorless liquid; Kugelrohr distillation (140 °C/0.1 mmHg); ^{13}C NMR ($CDCl_3$) δ 175.6 (s), 142.0 (s), 137.2 (s), 132.9 (d), 128.1 (d), 126.9 (d), 126.5 (d), 126.3 (d), 125.9 (d), 125.1 (d), 54.5 (s), 51.7 (q), 37.9 (t), 27.1 (t), 8.4 (q); ^1H NMR (100 MHz, $CDCl_3$) δ 7.28 (s, Ar, 5 H), 7.22 (s, Ar, 5 H), 6.39 (d, J = 15.9 Hz, $=CHPh$, 1 H), 5.87 (dt, J = 15.9, 7.2 Hz, $-CH_2CH=$, 1 H), 2.93 (d, J = 7.6 Hz, $-CH_2CH=$, 2 H), 2.09 (q, J = 7.6 Hz, $-CH_2CH_3$, 2 H), 0.81 (t, J = 7.4 Hz, $-CH_3$, 3 H); IR (neat) 1732 cm^{-1}; MS, m/z 294 (M^+). Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.32; H, 7.45.

1,1-Diphenyl-1,3-butadiene (7a): colorless oil; Kugelrohr distillation (130 °C/0.2 mmHg); ^{13}C NMR ($CDCl_3$) δ 143.1 (s), 142.0 (s), 139.6 (d), 130.3 (d), 128.4 (d), 128.0 (d), 127.5 (d), 118.5 (t); ^1H NMR (100 MHz, $CDCl_3$) δ 7.05–7.45 (m, Ar, 10 H), 6.70 (d, J = 11 Hz, $-CH=C(Ph)_2$, 1 H), 6.44 (ddd, J = 9, 10, 16 Hz, $=CHCH=CH_2$, 1 H), 5.40 (dd, J = 16, 3 Hz, $=CH_2$, 1 H), 5.08 (dd, J = 9, 10 Hz, $=CH_2$, 1 H); IR (neat) 1662, 1618, 1494, 1444, 1590, 910 cm^{-1}; MS, m/z 206 (M^+). Anal. Calcd for $C_{16}H_{14}$: C, 93.16; H, 7.19. Found: C, 93.42; H, 6.58.

1,1-Diphenyl-3-methyl-1,3-butadiene (7b): colorless oil; Kugelrohr distillation (100 °C/0.1 mmHg); ^{13}C NMR ($CDCl_3$) δ 143.2 (s), 142.2 (s), 141.4 (s), 140.5 (s), 132.3 (d), 130.6 (d), 130.2 (d), 128.0 (d), 127.8 (d), 127.4 (d), 127.1 (d), 119.0 (t), 22.0 (q); ^1H NMR (100 MHz, $CDCl_3$) δ 7.22 (s, Ar, 10 H), 6.55 (s, $-CH=$, 1 H), 4.97 (s, $=CH_2$, 2 H), 1.47 (s, $-CH_3$, 3 H); IR (neat) 1660, 1599, 1494, 1444, 906, 896 cm^{-1}; MS, m/z 220 (M^+). Anal. Calcd for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.41; H, 7.34.

1,1-Diphenyl-1,3-pentadiene (7c): colorless oil; Kugelrohr distillation (100 °C/0.1 mmHg); ^{13}C NMR ($CDCl_3$) δ 142.3 (s), 139.9 (s), 131.4 (d), 130.3 (d), 129.6 (d), 128.0 (d), 127.2 (d), 126.9 (d), 18.4 (q); ^1H NMR (100 MHz, $CDCl_3$) δ 7.20 (s, Ar, 10 H), 6.66 (d, J = 10.5 Hz, $-CH=C(Ph)_2$, 1 H), 6.17 (dd, J = 10.5, 15 Hz, $-CH=CHCH_3$, 1 H), 5.84 (dq, J = 15, 6.6 Hz, $CH_3CH=$, 1 H), 1.69 (d, J = 6.3 Hz, $-CH_3$, 3 H); IR (neat) 1668, 1597, 1494, 1444, 972 cm^{-1}; MS, m/z 220 (M^+). Anal. Calcd for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.76; H, 7.26.

1,1-Diphenyl-1,3-heptadiene (7e): colorless oil; Kugelrohr distillation (120 °C/0.08 mmHg); ^{13}C NMR ($CDCl_3$) δ 142.4 (s), 140.2 (s), 140.0 (s), 136.9 (d), 130.3 (d), 128.4 (d), 128.3 (d), 128.0 (d), 127.3 (d), 127.0 (d), 126.9 (d), 35.0 (t), 22.5 (t), 13.7 (q); ^1H NMR (100 MHz, $CDCl_3$) δ 7.19 (s, Ar, 10 H), 6.66 (d, J = 10 Hz, $-CH=C(Ph)_2$, 1 H), 6.17 (dd, J = 10, 15 Hz, $-CH=CHCH=$, 1 H), 5.84 (dt, J = 15, 6.7 Hz, $-CH_2CH=$, 1 H), 2.00 (dt, J = 8.0, 7.5 Hz, $-CH_2CH=$, 2 H), 1.35 (dt, J = 7.3, 7.3 Hz, CH_3CH_2-, 2 H), 0.85 (t, J = 7.3 Hz, $-CH_3$, 3 H); IR (neat) 1668, 1597, 1494, 1444, 972 cm^{-1}; MS, m/z 248 (M^+). Anal. Calcd for $C_{19}H_{20}$: C, 91.88; H, 8.12. Found: C, 91.63; H, 8.05.

1,1,4-Triphenyl-1,3-butadiene (7f): colorless needle; mp 96.5–97.5 °C; ^{13}C NMR ($CDCl_3$) δ 143.0 (s), 142.2 (s), 139.7 (s), 137.4 (s), 133.8 (d), 130.4 (d), 128.5 (d), 128.1 (d), 127.5 (d), 127.4 (d), 126.4 (d); ^1H NMR (100 MHz, $CDCl_3$) δ 7.11–7.45 (m, Ar, 15 H), 6.91 (d, J = 12.4 Hz, 1 H), 6.87 (d, J = 4.2 Hz, 1 H), 6.68 (dd, J = 12.4, 4.2 Hz, 1 H); IR (Nujol) 1595, 1481, 1460, 1440, 970 cm^{-1}; MS, m/z 282 (M^+). Anal. Calcd for $C_{22}H_{18}$: C, 93.57; H, 6.43. Found: C, 93.40; H, 6.31.

6,6-Dimethyl-2-(2,2-diphenylethenyl)bicyclo[3.1.1]hept-2-ene (7g). **7g** was obtained as a mixture of isomers: pale yellow oil; Kugelrohr distillation (140 °C/0.15 mmHg); ^{13}C NMR ($CDCl_3$) δ 146.6 (s), 145.7 (s), 144.8 (s), 143.7 (s), 141.0 (s), 138.6 (s), 130.6 (d), 130.0 (d), 128.5 (d), 127.9 (d), 127.7 (d), 127.5 (d), 126.9 (d), 126.7 (d), 125.8 (d), 118.4 (d), 57.7 (d), 49.0 (d), 45.7 (d), 43.7 (d), 43.1 (d), 40.6 (d), 40.1 (d), 37.9 (s), 37.1 (s), 32.3 (t), 31.8 (t), 31.5 (t), 31.2 (t), 26.3 (q), 26.0 (q), 21.0 (q); ^1H NMR (100 MHz, $CDCl_3$) δ 7.21 (s, Ar, 10 H), 6.58 (s), 5.66 (s), 5.10 (s), 4.10 (t, J = 7.7 Hz), 1.62–2.75 (m), 1.22 (s), 1.11 (s), 1.00 (s), 0.87 (s), 0.67 (s); IR (neat) 1597, 1493, 1444, 908 cm^{-1}; MS, m/z 300 (M^+). Anal. Calcd for $C_{23}H_{24}$: C, 91.95; H, 8.05. Found: C, 91.84; H, 8.16.

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