yield 390 mg (97%); yellow crystals; mp 305–306 °C. Anal. Calcd for $C_{26}H_{28}O_6$ (mol wt 436.51): C, 71.54; H, 6.47. Found: C, 71.93; H, 6.51.

Reduction of Tetra-*tert*-butylisoxindigo with Benzpinacol To Give 25a. A solution of **23a** (976 mg, 2 mmol) and benzpinacol (732 mg, 2 mmol) in DMF (10 mL) was heated under nitrogen to reflux temperature whereupon the deep red solution turned colorless. Addition of aqueous methanol at room temperature gave a colorless crystalline precipitate which was removed by filtration and washed with petroleum ether: yield 720 mg (73%); mp 162–165 °C. Recrystallization by dissolving in ether and precipitation with petroleum ether (bp 40–60 °C) did not change the melting point: ^{1}H NMR ($CDCl_3$) 1.20 (s, 9), 1.36 (s, 9), 4.45 (s, 1), 6.66 (d, J = 2 Hz, 1), 7.32 (d, J = 2 Hz, 1); IR (KBr) 1810 cm^{-1}. Anal. Calcd for $C_{32}H_{42}O_4$ (mol wt 490.69): C, 78.33; H, 8.63. Found: C, 78.38; H, 8.75.

Reduction of Tetra-*tert*-butyl-dibenzonaphthyrone 24a with Benzpinacol To Give 26a. A solution of **24a** (224 mg, 0.5 mmol) and benzpinacol (201 mg, 0.55 mmol) in DMF (4 mL) was heated under nitrogen to reflux temperature to give a colorless solution. Dilution of **Tetra-*tert*-butyldibenzonaphthyrone** reaction mixture with water and methanol gave a colorless crystalline precipitate of **26a**: 220 mg (90%); mp 210–211 °C; recrystallization from aqueous methanol did not change the melting point; ^{1}H NMR ($CDCl_3$) 1.2 (s, 9), 1.35 (s, 9), 4.43 (s, 1), 7.05 (d, J = 2 Hz, 1), 7.26 (d, J = 2 Hz, 1); IR (KBr) 1770 cm^{-1}. Anal. Calcd for $C_{32}H_{42}O_4$ (mol wt 490.69): C, 78.33; H, 8.63. Found: C, 78.25; H, 8.71.

Registry No. 5c, 65905-73-9; (*E*)-**14a**, 80360-46-9; (*E*)-**14b**, 66737-81-3; (*Z,Z*)-**15**, 64309-44-0; (*E,E*)-**16**, 64309-45-1; **17**, 64675-30-5; (*E*)-**23** ($R^1 = R^2$ = H), 80360-47-0; (*E*)-**23a**, 75540-64-6; (*E*)-**23b**, 80360-48-1; (*E*)-**23c**, 80360-49-2; **24** ($R^1 = R^2$ = H), 13225-81-5; **24a**, 80360-50-5; **24b**, 80360-51-6; **24c**, 80360-52-7; *meso*-**25a**, 80360-53-8; *dl*-**25a**, 80360-54-9; *trans*-**26a**, 80360-55-0; **31**, 80360-56-1; DDQ, 84-58-2.

New Synthesis of α-Benzoyloxy Aldehydes. Application to the Stereoselective Synthesis of Conjugated (*E,E*)-Dienoic Esters[1]

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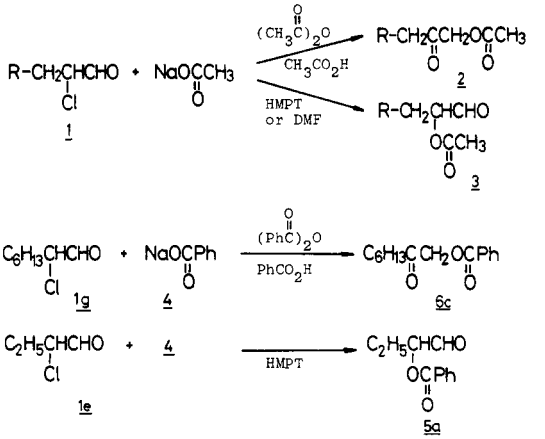
A new synthetic method for the preparation of secondary α-benzoyloxy aldehydes (**5a–d**) and its use in the stereoselective synthesis of conjugated (*E,E*)-dienone (**14**) and dienoic esters (**9b, 9c, 11, 15b,** and **15c**) were studied. Two-phase (benzene–H_2O) reaction of $RCH_2CHXCHO$ (R = CH_3, C_3H_7, C_5H_{11}, C_7H_{15}; X = Cl, Br) with sodium benzoate (**4**) in the presence of a catalytic amount of tetrabutylammonium bromide gave the corresponding α-benzoyloxy aldehydes (**5a–d**) in moderate yields. Compounds **5a–d** were converted to γ-benzoyloxy-α,β-unsaturated carbonyl compounds or esters (**7b, 7c, 10, 12, 13b,** and **13c**) either by the $TiCl_4$/py-catalyzed condensation with malonate or acetoacetate or by the Wittig reaction with $Ph_3P{=}CHC(O)CH_3$ and $Ph_3P{=}CHCO_2Et$. Treatment of these compounds with 5 mol % of $(Ph_3P)_4Pd$ in refluxing THF afforded the corresponding conjugated (*E,E*)-dienones and dienoic esters stereoselectively. The reaction sequence was further extended to the stereoselective synthesis of ethyl (2*E*,4*E*,6*E*)-2,4,6-dodecatrienoate (**18**) and pellitorine (**21**).

α-Acyloxy aldehydes are important class of starting materials for the synthesis of heterocycles such as furans[2] and γ-butyrolactones.[3] The known methods of α-acyloxy aldehyde synthesis are as follows: (a) the hydroformylation (CO/H_2) of 1-alkenyl acetates,[4a] (b) the acylation of 2-(α-hydroxyalkyl)-1,3-dithianes,[4b] (c) the oxidative cleavage of aldehydes[4c] or glycidates[5a] with lead tetraacetate, (d) the reaction of silyl enol ethers with lead tetrabenzoate,[4d] (e) the reaction of α-chloro aldehydes with sodium acetate in polar, aprotic solvents,[4e] (f) the reaction of tertiary α-bromo aldehydes with potassium phenylacetate in the presence of 18-crown-6.[5b]

Scheme I



In this paper we report a simple and convenient procedure for the preparation of α-benzoyloxy aldehydes, which involves the reaction of an α-halo aldehyde (**1**) with sodium benzoate (**4**) in a two-phase system consisting of

(1) Present partly at the 37th Annual Meeting of the CSJ (Chemical Society of Japan), Yokohama, April 1978, Abstr. Vol. 2, p 810 and at the 43rd Annual Meeting of CSJ, Tokyo, March 1981, Abstr. Vol. 2, p 799.

(2) (a) Merkle, H. R.; Siegel, H. DOS Patent 2 207 098, 1972; *Chem. Abstr.* **1976**, *85*, 142972. (b) Siegel, H.; Himmele, W. *Angew. Chem. Int., Ed. Engl.* **1980**, *19*, 178.

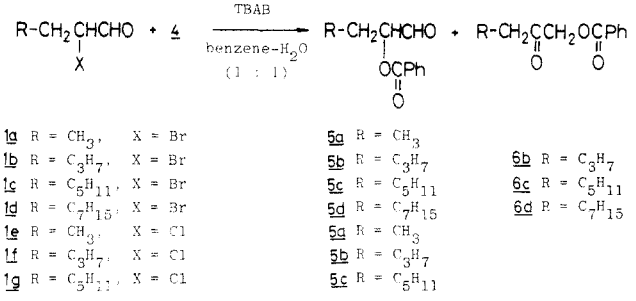
(3) Corbet, J. P.; Benezra, C. *Tetrahedron Lett.* **1979**, 4003.

(4) For secondary α-acyloxy aldehydes: (a) Merkle, H. R.; Siegel, H. DOS Patent 2 227 547, 1972, BASF; *Chem. Abstr.* **1974**, *80*, 70681. (b) Ross, W. J.; Harrison, R. G.; Jolley, R. J.; Naville, M. C.; Todd, A.; Verge, J. P. *J. Med. Chem.* **1979**, *22*, 412. (c) Riehl, J. J. *C. R. Acad. Sci.* **1960**, *250*, 4174. (d) Carlson, R. M.; Oyler, A. R. *J. Org. Chem.* **1976**, *41*, 4065. (e) Riehl, J. J.; Fougerousse, A. *Bull. Soc. Chim. Fr.* **1968**, 4083.

(5) For tertiary α-acyloxy aldehydes: (a) Kulkarni, B. O.; Rao, A. S. *Synthesis* **1976**, 454. (b) Padwa, A.; Dehm, D. *J. Org. Chem.* **1975**, *40*, 3139.

0022-3263/82/1947-1101$01.25/0

Scheme II

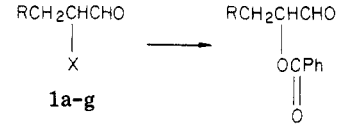


benzene and water in the presence of tetrabutylammonium bromide (TBAB).[6] Investigated further was the use of α-benzoyloxy aldehyde in the stereoselective syntheses of conjugated (*E,E*)-dienones,[7] dienoic esters,[8] and amides,[9] which are widely distributed in nature as the active principle of flavors and as insecticidal substances. The methodology of constructing the conjugated (*E,E*)-diene systems consists of Pd(0)-catalyzed elimination of benzoic acid from appropriate γ-benzoyloxy-α,β-unsaturated carbonyl compounds or esters, which were readily prepared from α-benzoyloxy aldehydes either by a Knoevenagel condensation (malonate or acetoacetate) or by a Wittig reaction.

Riehl[4e] has reported that reaction of α-chloro aldehydes with sodium acetate in a mixed solution of acetic anhydride and acetic acid gave acetoxymethyl alkyl ketone (**2**) as the sole products. A similar reaction, when carried out in highly polar, aprotic solvents, i.e., hexamethylphosphoric triamide (HMPT) and dimethylformamide (DMF), afforded α-acetoxy aldehydes (**3**, R = C_4H_9) as the principal products in 38–76% yields along with a small amount of **2** (Scheme I). It has been suggested that the initial attack of acetoxy anion on the carbonyl carbon predominates over nucleophilic substitution[4e] in protic solvents. We also found that the treatment of 2-chlorooctanal (**1g**) with sodium benzoate (**4**) in a mixture of benzoic anhydride and benzoic acid afforded 1-(benzoyloxy)octan-2-one (**6c**), while the treatment of 2-chlorobutanal (**1e**) with **4** in HMPT gave 2-(benzoyloxy)butanal (**5a**).

The rate of nucleophilic substitution tends to be accelerated under two-phase reaction conditions.[10] Therefore, it was decided to investigate the two-phase reaction (benzene–H_2O, 1:1) of α-halo aldehydes with sodium benzoate in the presence of TBAB (5 mol % based on **4**), in which the benzoate anion might be activated to induce nucleophilic substitution at the α-position to give α-benzoyloxy aldehydes rather than to attack the carbonyl carbon.

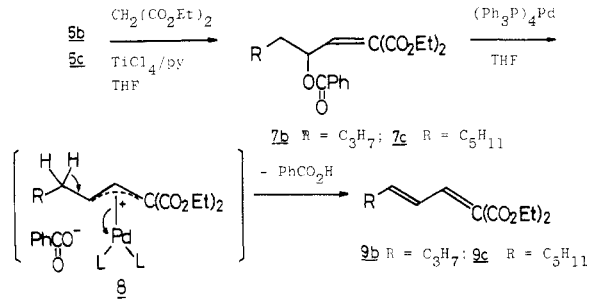
Table I. Syntheses of α-Benzoyloxy Aldehydes



α-halo aldehyde			molar ratio	%
compd	R	X	1:4	yield[a]
1a	CH_3	Br	1:2	40
1b	C_3H_7	Br	1:2	43[b]
1c	C_5H_{11}	Br	1:2	58[c]
1d	C_7H_{15}	Br	1:2	55[d]
1e	CH_3	Cl	1:1	24
			1:1 (TEBA)[e]	14
			1:2	28
1f	C_3H_7	Cl	1:1	22
			1:2	32
1g	C_5H_{11}	Cl	1:1	26
			1:2	47

[a] Isolated yield by column chromatography. [b] **6b** was obtained in 4% yield. [c] **6c** was obtained in 5% yield. [d] **6d** was obtained in 1% yield. [e] Triethylbenzylammonium bromide.

Scheme III



The α-benzoyloxy aldehydes **5a–d** were obtained in moderate yields by reacting appropriate α-halo aldehydes (**1a–g**) with **4** in the presence of TBAB (5 mol % based on **4**;[11] Scheme II). The results are summarized in Table I. Better yields were obtained when α-bromo aldehydes with a longer alkyl chain reacted with excess of **4**. Triethylbenzylammonium bromide (TEBA) was less effective than TBAB. In the case of the bromo aldehydes **1b–d**, the resulting α-benzoyloxy aldehydes **5b–d** were accompanied by the ketones **6b–d** as minor byproducts. The spectral and analytical data for **5a–d** and **6b–d** are listed in Table II. The present two-phase reaction technique adapted for the preparation of α-benzoyloxy aldehydes can avoid the use of costly highly polar, aprotic solvents such as HMPT and DMF.

The α-benzoyloxy aldehydes **5b** and **5c** were then converted to γ-benzoyloxy-α,β-unsaturated ketones and esters by known methods. The $TiCl_4$/py-catalyzed condensation[12] of α-benzoyloxy aldehydes **5b** and **5c** with ethyl malonate (THF) gave ethyl 4-(benzoyloxy)-2-(ethoxy-

(6) We previously reported the efficient synthesis of *d,l*-avenaciolide by the adaptation of two-phase reaction: Sakai, T.; Horikawa, H.; Takeda, A. *J. Org. Chem.* **1980**, *45*, 2039.

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(8) (a) Hudryashow, L. I.; Kochetkov, N. K. *Zh. Obshch. Khim.* **1959**, *28*, 2448. (b) Howe, R. K. *J. Am. Chem. Soc.* **1971**, *93*, 3457. (c) Baldev, V.; Chander, M. A.; Ram, B.; Lal, K. G. *Indian J. Chem.* **1973**, *11*, 207. (d) Ohloff, G.; Pawlak, M. *Helv. Chim. Acta* **1974**, *57*, 1309. (e) Oberhaensli, P. German Patent 2 439 059, 1975; *Chem. Abstr.* **1975**, *82*, 155405c. (f) Gill, G. B.; Wallace, B. *J. Chem. Soc., Chem. Commun.* **1977**, 380. (g) Rickards, G.; Weiler, L. *J. Org. Chem.* **1978**, *43*, 3607. (h) Amos, R. A.; Katzenellenbogen, J. A. *Ibid.* **1978**, *43*, 555. (i) Rickards, G.; Weiler, L. *Ibid.* **1978**, *43*, 3607. (j) Tanikawa, R.; Nishida, M.; Ono, N.; Kaji, A. *Chem. Lett.* **1980**, 781.

(9) (a) Jacobson, M. *J. Am. Chem. Soc.* **1953**, *75*, 2584. (b) Crombie, L. *J. Chem. Soc.* **1955**, 999. (c) Crombie, L. *Ibid.* **1955**, 1007. (d) Burden, R. S.; Crombie, L. *J. Chem. Soc. C* **1969**, 2477. (e) Viswanathan, N.; Balakrishnan, V.; Joshi, B. S.; Philipsborn, W. *Helv. Chem. Acta* **1975**, *58*, 2026. (f) Tsuji, J.; Nagashima, H.; Takahashi, T.; Masaoka, K. *Tetrahedron Lett.* **1977**, 1917. (g) Sharma, S. D.; Aggarwal, R. C.; Soni, B. R.; Sharma, M. L. *Indian J. Chem., Sect. B.* **1979**, 81. (h) Mandai, T.; Gotoh, J.; Otera, J.; Kawada, M. *Chem. Lett.* **1980**, 313. (i) Nokami, J.; Nishiguchi, K.; Wakabayashi, S. *Tetrahedron Lett.* **1980**, 4455. (j) Ono, N.; Miyake, H.; Tanabe, Y.; Tanaka, K.; Kaji, A. *Chem. Lett.* **1980**, 1365. (k) Miyakado, M.; Nakayama, I.; Yoshioka, H. *Agric. Biol. Chem.* **1980**, *44*, 1701. (l) Tanaka, K.; Terauchi, M.; Kaji, A. *Chem. Lett.* **1981**, 315.

(10) Starks, C. M.; Liotta, C. "Phase Transfer Catalysis"; Academic Press; New York, 1978; Chapter 4.

(11) The two-phase reaction (benzene–H_2O, 1:1; TBAB) of **1a** with sodium acetate and that of tertiary α-halo aldehydes such as 2-chloro-2-methylpropanal with sodium benzoate failed to give corresponding α-acyloxy aldehydes, and resulted in the formation of a complex mixture.

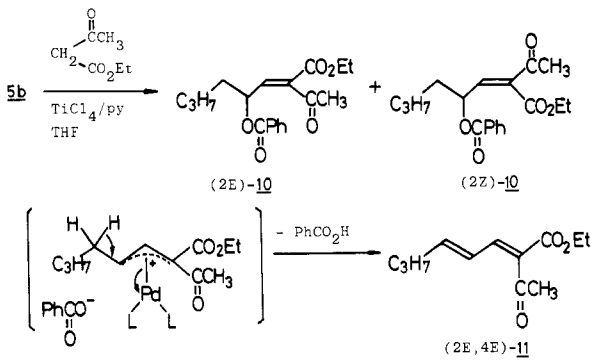
(12) Lehnert, W. *Tetrahedron Lett.* **1970**, 4723.

Table II. Physical and Spectral Data of α-Benzoyloxy Aldehydes 5a-d[a] and α-Benzoyloxy Ketones 6b-d[a]

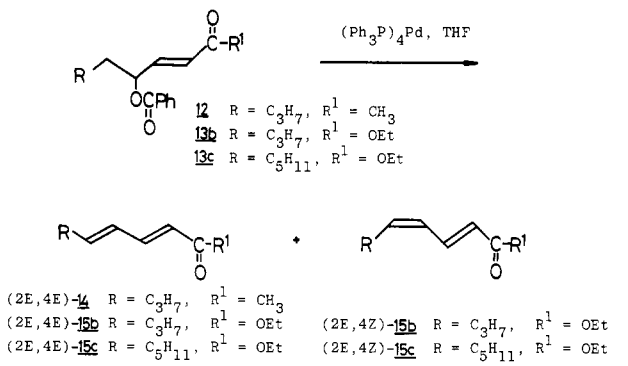
compd	bp, °C (mmHg)	IR, cm^{-1}	^1H NMR (CCl_4) δ
5a	105-108 (5)	1715 1600 1585	1.03 (br t, 3, 7 Hz), 2.85 (m, 2), 5.02 (t, 1, 6 Hz), 7.25-8.15 (m, 5), 9.52 (s, 1)
5b	106-125 (4)	1720 1600 1583	0.94 (br t, 3, 6 Hz), 1.1-2.2 (m, 6), 5.11 (t, 1, 6 Hz), 7.2-8.2 (m, 5), 9.51 (s, 1)
6b	95-116 (5)	1721 1600 1582	0.7-2.2 (m, 9), 4.76 (s, 2), 7.2-8.3 (m, 5)
5c	130-147 (0.5)	1720 1603 1582	0.88 (br t, 3, 6 Hz), 1.0-2.4 (m, 10), 5.15 (t, 1, 6 Hz), 7.2-8.2 (m, 5), 9.58 (s, 1)
6c	125-136 (0.5)	1723 1604 1585	0.86 (br t, 3, 5 Hz), 1.0-2.0 (m, 8), 2.0-2.7 (m, 2), 4.72 (s, 2), 7.1-8.25 (m, 5)
5d	*c*	1720 1602 1582	0.86 (br t, 3, 5 Hz), 1.0-2.4 (m, 14), 5.14 (t, 1, 6 Hz), 7.2-8.2 (m, 5), 9.56 (br s, 1)
6d	*c*	1721 1601 1582	0.6-2.6 (m, 17), 4.75 (s, 2), 7.3-8.2 (m, 5)

[a] Satisfactory analytical data (±0.4% for C, H) were reported for all new compounds listed in the table. [b] Kugelrohr distillation gave the analytical sample. [c] Isolated by column chromatography (silica gel, hexane-ether-methanol, 20:2:1).

Scheme IV



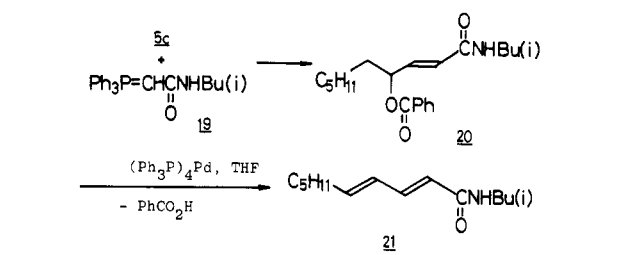
Scheme V



carbonyl)-2-octenoate (**7b**) in 73% yield and ethyl 4-(benzoyloxy)-2-(ethoxycarbonyl)-2-decenoate (**7c**) in 73% yield, respectively (Scheme III). Ethyl acetoacetate was reacted with **5b** in the similar way to give a 46:54 mixture[13] of ethyl (2*E*)-4-(benzoyloxy)-2-acetyl-2-octenoate (**10**)[14] and the 2*Z* isomer[14] in 67% yield. On the other hand, (3*E*)-5-(benzoyloxy)-3-nonen-2-one (**12**), ethyl (2*E*)-4-(benzoyloxy)-2-octenoate (**13b**), and ethyl (2*E*)-4-(benzoyloxy)-2-decenoate (**13c**) were obtained by the reaction of **5b** with (acetylmethylene)triphenylphosphorane[15] and by the reaction of **5b** and **5c** with [(ethoxycarbonyl)methylene]-triphenylphosphorane.[16] Wittig reaction of [(2*E*)-3-(ethoxycarbonyl)allylidene]triphenylphosphorane (**16**)[8b] with **5c** gave a 38:62 mixture[17] of ethyl (2*E*,4*E*)-6-(benzoyloxy)-2,4-dodecadienoate (**17**) and the 2*E*,4*Z* isomer in 40% yield.

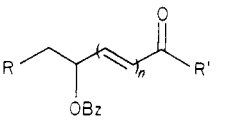
Elimination of benzoic acid from compounds **7b** and **7c** was effectively accomplished by heating with 5 mol % of

Scheme VI



tetrakis(triphenylphosphine)palladium [$(Ph_3P)_4Pd$] in THF to give the corresponding (4*E*)-dienoic esters **9b** (63% yield) and **9c** (68% yield). This reaction can be explained by a proton transfer to benzoate anion via the π-allyl complex (**8**)[18a,b] as shown in Scheme III. Furthermore,

(13) Based on ^1H NMR spectrum.
(14) Assigned by means of the ^{13}C NMR spectra. The signal of the carbonyl carbon (166.1 ppm) of the ester group in (2*E*)-**10** appeared at slightly lower field than that of 2*Z* isomer (165.9 ppm). The similar effect was also observed for the carbonyl carbon of acetyl group: Lippmaa, E.; Pehl, T.; Andersson, K.; Rappe, C. *Org. Magn. Reson.* **1970**, *2*, 109.
(15) Ramirez, F.; Dershowitz, S. *J. Org. Chem.* **1957**, *22*, 41.
(16) Isler, O.; Gutmann, H.; Montavon, M.; Ruegg, R.; Ryser, G.; Zeller, P. *Helv. Chem. Acta* **1957**, *40*, 1242.
(17) Based on high-performance liquid-chromatography (HPLC). Retention times of these compounds in HPLC were too close to be separable.
(18) (a) Tsuji, J.; Yamakawa, T.; Kaito, M.; Mandai, T. *Tetrahedron Lett.* **1978**, 2075. (b) Trost, B. M.; Verhoeven, T. R.; Fortunak, J. M. *Ibid.* **1979**, 2301.

Table III. Pd(0)-Catalyzed Debenzoyloxylation of 

R′ = Me, OEt

entry	compd	R	n	product	% yield
1	7b	C_3H_7	1	ethyl (4*E*)-2-(ethoxycarbonyl)-2,4-octadienoate (**9b**)	63
2	7c	C_5H_{11}	1	ethyl (4*E*)-2-(ethoxycarbonyl)-2,4-decadienoate (**9c**)	63
3	10[a]	C_3H_7	1	(2*E*,4*E*)-2-acetyl-2,4-octadienoate (**11**)	42
4	12[b]	C_3H_7	1	(3*E*,5*E*)-3,5-nonadien-2-one (**14**)	84[c]
5	13b[b]	C_3H_7	1	ethyl (2*E*,4*E*)-2,4-octadienoate [(2*E*,4*E*)-**15b**]	74
				ethyl (2*E*,4*Z*)-2,4-octadienoate [(2*E*,4*Z*)-**15b**]	6
6	13c[b]	C_5H_{11}	1	ethyl (2*E*,4*E*)-2,4-decadienoate [(2*E*,4*E*)-**15c**]	73
				ethyl (2*E*,4*Z*)-2,4-decadienoate [(2*E*,4*Z*)-**15c**]	9
7	17[d]	C_5H_{11}	2	ethyl (2*E*,4*E*,6*E*)-2,4,6-dodecatrienoate (**18**)	52[e]

[a] 2*E*/2*Z* mixture. [b] 2*E* isomer. [c] Unidentified byproduct was obtained (5% by GLC). [d] 2*E*,4*Z*/2*E*,4*E* mixture. [e] Unidentified byproduct was obtained (8% by HPLC).

treatment of **10** (*E*/*Z* mixture[14]) with a Pd(0) catalyst stereospecifically afforded ethyl (2*E*,4*E*)-2-acetyl-2,4-octadienoate (**11**) in 42% yield (Scheme IV). It is reasonable to consider that the isomerization via the π-allyl complex formation is possible; hence the geometry of the double bond at the α and β positions of these products is thermodynamically controlled.[19] In accordance with the analogous geometry of the double bond, ^{1}H NMR signals of the acetyl group in (2*E*)-**10** and **11** appeared at δ 2.26 and 2.32, respectively. Compounds **12**, **13b**, **13c**, and **17** (2*E*,4*Z*/2*E*,4*E* mixture) also stereoselectively afforded the corresponding (2*E*,4*E*)- or (2*E*,4*E*,6*E*)-conjugated systems as shown in Scheme V and Table III.

Table IV (see paragraph at the end of paper regarding supplementary material) summarizes ^{13}C NMR spectral data of conjugated diene derivatives synthesized in this work. The geometry of 2*E*,4*E* and 2*E*,4*Z* isomers of **15b** and **15c** was elucidated by the consideration of the steric effects[20] observed in the ^{13}C NMR spectra. Signals for C_3, C_4, C_5, and C_6 of the 2*E*,4*Z* isomers appeared at higher fields than those of 2*E*,4*E* isomers.

The reaction sequence was further extended to the stereoselective synthesis of pellitorine (**21**),[9] an insecticidal substance isolated from *Anacyclus pyrethrum*[9a-c] (Scheme VI). The reaction of **5c** with [(*N*-isobutylcarbamoyl)-methylene]triphenylphosphorane (**19**)[21] gave *N*-isobutyl-(2*E*)-4-(benzoyloxy)-2-decenamide (**20**) in 86% yield. Treatment of the amide with Pd(0) catalyst in THF afforded *N*-isobutyl-(2*E*,4*E*)-2,4-decadienamide (pellitorine; **21**) in 70% yield.

Experimental Section

Melting points were determined on a Yamato Model MP-21 melting-point apparatus and are uncorrected. The evaporative bulb-to-bulb distillations were done with a Büchi Kugelrohrofen at the pressure and oven temperature indicated. Elemental analyses were carried out by Mr. Eiichiro Amano of our laboratory. IR spectra were taken on a Hitachi Model EPI-S2 or a JASCO Model A-102 spectrometer. Mass spectra were recorded at 70 eV with a Hitachi Model RMS-4 mass spectrometer. ^{1}H NMR spectra (60 MHz) were measured with a Hitachi Model R-24 spectrometer. Both ^{1}H NMR spectra (100 MHz) and ^{13}C NMR spectra (25 MHz) were taken on a JEOL Model FX-100 spectrometer equipped with FT facilities, using Me_4Si as an internal standard. The analytical determinations by GLC were performed on a Hitachi Model K-53 gas chromatography (N_2, 42 mL/min) using a column (3 mm o.d. × 1 m) packed with 10% Apiezone Grease L on Chromosorb W. The preparative isolations by GLC were done with a Yanagimoto Model G-80 gas chromatograph under the same conditions as those employed in the analytical determination. Preparative isolations by high-performance liquid chromatography (HPLC) were carried out with a Yanagimoto Model L-2000 chromatograph. Column chromatography was performed in a column containing silica gel (Wakogel C-200, Wako, Tokyo) or alumina (Aluminiumoxid 150 PF_{254}, E. Merck, Darmstadt).

Materials. α-Bromo aldehydes, such as **1a**[22] (30%), **1b**[23] (37%), **1c**[24] (52%), and **1d**[25] (64%), were prepared by the modifications of Favorskaya's procedure[26] (Br_2, $CaCO_3$, Et_2O). α-Chloro aldehydes, such as **1e**[27] (56%), **1f**[28] (60%), and **1g** (68%), were prepared by the modifications of Stevens' procedure[27] ($SOCl_2$, CH_2Cl_2).

Compound **1g**: bp 97–98 °C (27 mm); IR (neat) 1732 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.89 (br t, 3 H, J = 5 Hz, CH_3), 1.0–2.45 (m, 10 H, 5 CH_2), 4.05 (dt, 1 H, J = 3, 6 Hz, CHCl), 9.39 (d, 1 H, J = 3 Hz, CHO). Anal. Calcd for $C_8H_{15}OCl$: C, 59.07; H, 9.29. Found: C, 59.32; H, 9.16.

1-(Benzoyloxy)octan-2-one (6c). A mixture of 6.6 g (0.0421 mol) of 2-chlorooctanal (**1g**), 11.8 g (0.082 mol) of sodium benzoate (**4**), 5.7 g (0.025 mol) of benzoic anhydride, and 44 g (0.36 mol) of benzoic acid was heated at 150 °C for 40 h with stirring. The resulting mixture was diluted with ether and washed with aqueous $NaHCO_3$. The organic layer was dried over $MgSO_4$ and concentrated under vacuum. The residual oil was subjected to vacuum distillation to give 2.43 g of **6c**: yield 26%; bp 115–136 °C (0.18 mm).

Reaction of 2-Chlorobutanal (1e) with 4 in HMPT. 2-(Benzoyloxy)butanal (5a). A suspension of 5.1 g (0.048 mol) of 2-chlorobutanal and 1.8 g (0.012 mol) of **4** in 30 mL of hexamethylphosphoric triamide was stirred for 4 days at room temperature. The resulting mixture was diluted with water and the organic layer was extracted with several portions of ether, washed with water, aqueous $NaHCO_3$, and then with brine. After being dried over $MgSO_4$, the solvent was removed under vacuum. The residual oil was separated by column chromatography on silica gel (hexane–ether–methanol, 20:2:1) to give 0.72 g of **5a**, yield 29%.

Two-Phase Reaction of α-Halo Aldehyde. The following experiment of **5d** illustrates the manner in which two-phase reactions of α-halo aldehydes (**1a–g**) with sodium benzoate (**4**) were carried out. See also Tables I and II.

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2-(Benzoyloxy)decanal (5d). A suspension of 16.2 g (0.0689 mol) of freshly distilled 2-bromodecanal (**1d**) and 19.7 g (0.137 mol) of sodium benzoate in a two-phase system consisting of 2.2 g (0.006 46 mol) of TBAB and benzene–H_2O (100 mL/100 mL) was vigorously stirred under reflux for 40 h. The benzene layer was separated from the aqueous layer, which was further extracted with ether several times. The combined organic layer was washed with aqueous $NaHCO_3$, dried over $MgSO_4$, and concentrated under vacuum. The residual oil was separated by column chromatography on silica gel (hexane–ether–methanol, 20:2:1) to give 10.5 g (55%) of **5d** together with 0.2 g (1%) of 1-(benzoyloxy)decan-2-one (**6d**).

Ethyl 4-(Benzoyloxy)-2-(ethoxycarbonyl)-2-octenoate (7b). Titanium(IV) chloride[12] (2.32 g, 12.3 mmol) was carefully added to 25 mL of THF at 0 °C with stirring. Yellow precipitates[12] were immediately formed with fuming. To this suspension was added dropwise 1.50 g (6.82 mmol) of 2-(benzoyloxy)hexanal (**5b**), 1.20 g (7.50 mmol) of ethyl malonate, and then 1.94 g (24.6 mmol) of pyridine, successively. The dark brown suspension was stirred for 2 days at room temperature. The resulting mixture was diluted with 30 mL of water and the organic layer was extracted with ether, washed with water, and dried over $MgSO_4$. The solvent was evaporated under vacuum and the residual oil was separated by column chromatography on silica gel (hexane–ether, 5:1) to give 1.81 g of the ester **7b**: yield 73%; IR (neat) 1727, 1656, 1606, 1584, 719 cm^{-1}; ^1H NMR (CCl_4) δ 0.6–2.2 (m, 9 H, C_4H_9), 1.28 (t, 3 H, J = 7 Hz, ester CH_3), 1.31 (t, 3 H, J = 7 Hz, ester CH_3), 4.17 (q, 2 H, J = 7 Hz, ester CH_2), 4.21 (q, 2 H, J = 7 Hz, ester CH_2), 5.79 (m, 1 H, C_4 H), 6.80 (d, 1 H, J = 8 Hz, C_3 H), 7.3–8.1 (m, 5 H, C_6H_5); ^{13}C NMR ($CDCl_3$) 13.8 (q), 14.0 (q), 22.4 (t), 27.1 (t), 33.5 (t), 61.6 (t), 71.5 (d), 128.4 (d, ortho), 128.9 (s), 129.7 (d, meta), 133.2 (s, C_2), 133.6 (d, para), 145.6 (d, C_3), 163.5 (s), 164.5 (s), 165.5 ppm (s). Anal. Calcd for $C_{20}H_{26}O_6$: C, 66.28; H, 7.23. Found: C, 66.17; H, 6.99.

Ethyl 4-(Benzoyloxy)-2-(ethoxycarbonyl)-2-decenoate (7c). The $TiCl_4$/py-catalyzed condensation of **5c** (0.008 33 mol) with ethyl malonate (0.009 71 mol) gave 2.62 g of **7c** after one purification with column chromatography on silica gel: yield 73%; IR (neat) 1725, 1655, 1601, 1585, 716 cm^{-1}; ^1H NMR (CCl_4) δ 0.6–2.5 (m, 17 H, C_5H_{11} and ester 2 CH_3), 4.14 (q, 2 H, J = 7 Hz, ester CH_2), 4.18 (q, 2 H, J = 7 Hz, ester CH_2), 5.77 (m, 1 H, C_4 H), 6.80 (d, 1 H, J = 8 Hz, C_3 H), 7.3–8.1 (m, 5 H, C_6H_5). Anal. Calcd for $C_{22}H_{30}O_6$: C, 67.67; H, 7.74. Found: C, 67.54; H, 7.82.

Ethyl (2*E*)-2-Acetyl-4-(benzoyloxy)-2-octenoate (10) and the 2*Z* Isomer. The $TiCl_4$/py-catalyzed condensation of **5b** (0.0092 mol) with ethyl acetoacetate (0.0101 mol) gave 2.04 g of a 46:54 (^1H NMR spectra) mixture of (2*E*)-**10** and (2*Z*)-**10**, yield 67%. Each component was isolated by column chromatography on silica gel (hexane–ether, 5:1).

Compound (2*E*)-**10**:[29] IR (neat) 1725, 1645, 1604, 1588 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.6–2.1 (m, 9 H, C_4H_9), 1.28 (t, 3 H, J = 7 Hz, ester CH_3), 2.32 (s, 3 H, $C(O)CH_3$), 4.17 (q, 2 H, J = 7 Hz, ester CH_2), 5.78 (m, 1 H, C_4 H), 6.71 (d, 1 H, J = 8 Hz, C_3 H), 7.15–8.13 (m, 5 H, C_6H_5); ^{13}C NMR ($CDCl_3$) 13.9 (q), 14.2 (q), 22.5 (t), 27.6 (t), 30.7 (q), 33.6 (t), 61.6 (t), 71.9 (d), 128.5 (d, ortho), 129.7 (d, meta), 130.2 (s), 133.3 (d, para), 136.5 (s), 145.3 (d, C_3), 166.1 (s), 164.1 (s), 195.1 ppm (s). Anal. Calcd for $C_{19}H_{24}O_5$: C, 68.66; H, 7.28. Found: C, 68.76; H, 7.26.

Compound (2*Z*)-**10**:[29] IR (neat) 1715, 1640, 1600, 1585 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.6–2.1 (m, 9 H, C_4H_9), 1.31 (t, 3 H, J = 7 Hz, ester CH_3), 2.46 (s, 3 H, $C(O)CH_3$), 4.17 (q, 2 H, J = 7 Hz, ester CH_2), 5.49 (m, 1 H, C_4 H), 6.68 (d, 1 H, J = 9 Hz, C_3 H), 7.15–8.13 (m, 5 H, C_6H_5); ^{13}C NMR ($CDCl_3$) 13.9 (q), 14.2 (q), 22.5 (t), 27.2 (t), 30.7 (q), 33.5 (t), 61.6 (t), 71.9 (d), 128.5 (d, ortho), 129.7 (d, meta), 129.9 (s), 133.3 (d, para), 136.4 (s, C_2), 144.8 (d, C_3), 164.1 (s), 165.9 (s), 200.4 ppm (s). Anal. Calcd for $C_{19}H_{24}O_5$: C, 68.66; H, 7.28. Found: C, 68.81; H, 7.64.

(3*E*)-5-(Benzoyloxy)-3-nonen-2-one (12). A solution of 1.91 g (6.0 mmol) of $Ph_3P{=}CHC(O)CH_3$[15] and 1.02 g of (4.61 mmol) of 2-(benzoyloxy)hexanal (**5b**) in 12 mL of benzene was refluxed for 14 h with stirring. To this solution was added 10 mL of petroleum ether and the resulting precipitate was removed by filtration. The filtrate was concentrated under vacuum and the residual oil was purified by column chromatography on silica gel (hexane–acetone, 10:1) to give 0.595 g of **12**: yield 55%; IR (neat) 1722, 1680, 1636, 1604, 1586 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (br t, 3 H, J = 6 Hz, CH_3), 1.1–2.1 (m, 6 H, 3 CH_2), 2.15 (s, 3 H, CH_3), 5.57 (m, 1 H, C_5 H), 6.07 (dd, 1 H, J = 16, 1.7 Hz, C_3 H), 6.65 (dd, 1 H, J = 16, 5 Hz, C_4 H), 7.1–8.1 (m, 5 H, C_6H_5). Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.75; H, 7.76.

Ethyl (2*E*)-4-(benzoyloxy)-2-octenoate (13b) was obtained by the reaction of **5b** (6.23 mmol) with $Ph_3P{=}CHCO_2Et$[16] (8.10 mmol) in the manner similar to the foregoing experiment: yield 0.93 g (52%); IR (neat) 1722, 1656, 1603, 1585 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92 (br t, 3 H, J = 6 Hz, CH_3), 1.24 (t, 3 H, J = 7 Hz, ester CH_3), 1.2–2.1 (m, 6 H, $3CH_2$), 4.09 (q, 2 H, J = 7 Hz, ester CH_2), 5.59 (m, 1 H, C_4 H), 5.88 (dd, 1 H, J = 15.8, 1.6 Hz, C_2 H), 6.85 (dd, 1 H, J = 15.8, 5.2 Hz, C_3 H), 7.2–8.2 (m, 5 H, C_6H_5); ^{13}C NMR ($CDCl_3$) 13.8 (q), 14.1 (q), 22.3 (t), 27.0 (t), 33.5 (t), 60.4 (t), 72.8 (d), 121.5 (d, C_2), 128.4 (d, ortho), 129.5 (d, meta), 129.9 (s), 133.0 (d, para), 145.4 (d, C_3), 165.4 (s), 165.9 ppm (s). Anal. Calcd for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 70.41; H, 7.81.

Ethyl (2*E*)-4-(benzoyloxy)-2-decenoate (13c) was obtained by the reaction of **5c** (0.011 mol) with $Ph_3P{=}CHCO_2Et$[16] (0.0143 mol) in the manner similar to the foregoing experiment: yield 1.82 g (52%); IR (neat) 1720, 1656, 1600, 1582 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (br t, 3 H, J = 6 Hz, CH_3), 1.0–2.1 (m, 10 H, 5 CH_2), 1.27 (t, 3 H, J = 7 Hz, ester CH_3), 4.20 (q, 2 H, J = 7 Hz, ester CH_2), 5.69 (m, 1 H, C_4 H), 6.03 (dd, 1 H, J = 15, 1.7 Hz, C_2 H), 6.99 (dd, 1 H, J = 15, 5 Hz, C_3 H), 7.25–8.25 (m, 5 H, C_6H_5). Anal. Calcd for $C_{19}H_{26}O_4$: C, 71.67; H, 8.23. Found: C, 71.60; H, 8.33.

Ethyl 6-(Benzoyloxy)-2,4-dodecadienoate (27). To a solution of 1.85 g (4.07 mmol) of [(2*E*)-3-(ethoxycarbonyl)allyl]triphenylphosphonium bromide[8b] in 11 mL of dimethylformamide was added dropwise 7.5 mL of 0.57 N ethanolic NaOEt (4.26 mmol). After the mixture was stirred for 5 min at room temperature, 1.0 g (4.03 mmol) of 2-(benzoyloxy)octanal (**6c**) was added and the mixture was stirred for an additional 16 h. The solvent was removed under vacuum and the residual oil was extracted with hexane–ether (1:1). The extract, after evaporation of the solvent under vacuum, was separated by column chromatography on silica gel (hexane–acetone, 10:1) to give 0.552 g (40%) of **17** (2*E*,4*E*/2*E*,4*Z* mixture). HPLC analysis (Yanaco SA-I, 4 mm × 25 cm, hexane–ether (5:1), 0.56 mL/min) of this product showed two peaks (38:62)[17,30] at the retention times of 8.7 and 8.9 min. Compound **17** (2*E*,4*E*/2*E*,4*Z* mixture): IR (neat) 1718, 1638, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.5–2.1 (m, 16 H, C_6H_{13} and ester CH_3), 4.16 (q, 0.8 H, J = 7 Hz, ester CH_2), 4.19 (q, 1.2 H, J = 7 Hz, ester CH_2), 5.6–6.5 (m, 3 H, C_2 H, C_4 H, and C_5 H), 7.2–8.2 (m, 6 H, C_3 H and C_6H_5); mass spectrum, m/e (relative intensity) 344 (M^+, 78), 298 (21), 105 ($C_6H_5C{=}O$, 100), 77 (C_6H_5, 26); ^{13}C NMR ($CDCl_3$) (figure enclosed in brackets is a minor peak due to the 2*E*,4*E* isomer) 14.0 (q), 14.3 (q), 22.6 (t), 25.0 (t), 29.0 (t), 31.7 (t), 34.8 (t), [34.4 (t)], 60.5 (t), [60.4 (t)], 71.2 (d), [74.1 (d)], 124.1 (d, C_2), [122.4 (d)], 128.4 (d, ortho), 129.6 (d, meta), 130.3 (s), 133.0 (d, para and C_4), [133.1 (d)], 137.1 (d, C_5), [138.4 (d)], 140.0 (d, C_3), [143.3 (d)], 165.8 (s), 166.8 ppm (s), [166.6 (s)]. Anal. Calcd for $C_{21}H_{28}O_4$: C, 73.23; H, 8.19. Found: C, 73.11; H, 8.35.

Pd(0)-Catalyzed Elimination of Benzoic Acid. The following experiment with compound **9b** is typical of the Pd(0)-catalyzed elimination of benzoic acid from γ-benzoyloxy-α,β-unsaturated compounds **7b**, **7c**, **10**, **12**, **13b**, **13c**, **17**, and **20**. See also table III.

Ethyl (4*E*)-2-(Ethoxycarbonyl)-2,4-octadienoate (9b). A suspension of 1.09 g (3 mmol) of ethyl 4-(benzoyloxy)-2-(ethoxycarbonyl)-2-octenoate (**7b**) and 0.180 g (0.15 mmol) of $(Ph_3P)_4Pd$ in 60 mL of THF was refluxed with stirring for 6 h under nitrogen atmosphere. The resulting mixture was filtered to remove solid material and the filtrate was diluted with ether. The ethereal solution was washed with aqueous $NaHCO_3$, dried over $MgSO_4$, and concentrated under vacuum. The residual oil was separated by column chromatography on silica gel (hexane–ether, 10:1) to give 0.454 g of **9b**: yield 63%; IR (neat) 1721, 1635, 1604 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.93 (br t, 3 H, J = 7 Hz,

(29) On standing at room temperature, each isomer gradually underwent a partial transformation to the other isomer to give a mixture of the 2*E* and 2*Z* isomers.

(30) Due to the 2*E*,4*E* and 2*E*,4*Z* isomers.

CH_3), 1.28 (t, 3 H, J = 7 Hz, ester CH_3), 1.31 (t, 3 H, J = 7 Hz, ester CH_3), 1.2–2.7 (m, 4 H, 2 CH_2), 4.17 (q, 2 H, J = 7 Hz, ester CH_2), 4.24 (q, 2 H, J = 7 Hz, ester CH_2), 5.98–6.75 (m, 2 H, C_4 H and C_5 H), 7.22 (d, 1 H, J = 11 Hz, C_3 H). Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 64.68; H, 8.11.

Ethyl (4*E*)-2-(Ethoxycarbonyl)-2,4-decadienoate (9c). The treatment of **7c** (0.5 mmol) with Pd(0) catalyst in the usual manner[31] gave 97 mg of **9c**: yield 68%; IR (neat) 1725, 1639, 1605 cm^{-1}; ^1H NMR (CCl_4) δ 0.6–2.5 (m, 11 H, C_5H_{11}), 1.28 (t, 3 H, J = 7 Hz, ester CH_3), 1.30 (t, 3 H, J = 7 Hz, ester CH_3), 4.18 (q, 2 H, J = 7 Hz, ester CH_2), 4.23 (q, 2 H, J = 7 Hz, ester CH_2), 5.78–6.76 (m, 2 H, C_4 H and C_5H), 7.20 (d, 1 H, J = 11 Hz, C_3 H). Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.14; H, 9.01. Found: C, 67.47; H, 9.08.

Ethyl (2*E*,4*E*)-2-Acetyl-2,4-octadienoate (11). The treatment of **10** (2*E*/2*Z* mixture, 0.003 mol) with Pd(0) catalyst in the usual manner[31] gave 0.78 g of **11**: yield 42%; IR (neat) 1720, 1632, 1581 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95 (br t, 3 H, J = 7 Hz, CH_3), 1.35 (t, 3 H, J = 7 Hz, ester CH_3), 1.15–2.55 (m, 4 H, 2 CH_2), 2.26 (s, 3 H, CH_3), 4.27 (q, 2 H, J = 7 Hz, ester CH_2), 6.15–6.85 (m, 2 H, C_4 H and C_5 H), 7.15 (d, 1 H, J = 11 Hz, C_3 H); mass spectrum, m/e (relative intensity) 210 (M^+, 1), 165 (M – OEt, 22), 150 (100). Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63. Found: C, 68.30; H, 8.57.

(3*E*,5*E*)-3,5-Nonadien-1-one (14).[7] The treatment of **12** (1.73 mmol) with Pd(0) catalyst in the usual manner afforded 0.41 g (89%) of the crude product.[31] GLC analysis (N_2 42 mL/min, oven temp. 140 °C) of this product showed two peaks at the retention times (component, integrated percentage) of 7.6 min (unidentified, 5%) and 8.6 min (**14**, 95%), which were separated to each component by preparative GLC. Compound **14**: IR (neat) 1688, 1665, 1634, 1598 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (br t, 3 H, J = 6 Hz, CH_3), 1.0–2.4 (m, 4 H, 2 CH_2), 2.06 [s, 3 H, $C(O)CH_3$], 5.60–6.55 (m, 3 H, C_3 H, C_5 H, and C_6 H), 6.7–7.17 (m, 1 H, C_4 H).

Ethyl (2*E*,4*E*)-2,4-Octadienoate (15b) and the 2*E*,4*Z* Isomer. The treatment of **13b** (3.1 mmol) with Pd(0) catalyst in the usual manner afforded 0.427 g (80%) of crude product.[31] GLC analysis (N_2, 42 mL/min; oven temperature 150 °C) of this product showed two peaks at the retention times (component, integrated percentage) of 6.6 min [(2*E*,4*Z*)-**15b**, 8%] and 7.4 min [(2*E*,4*E*)-**15b**, 92%], which were separated to each component by preparative GLC.

Compound (2*E*,4*E*)-**15b**:[8f] IR (neat) 1713, 1640, 1616 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (br t, 3 H, J = 7 Hz, CH_3), 1.28 (t, 3 H, J = 7 Hz, ester CH_3), 1.3–2.3 (m, 4 H, 2 CH_2), 4.18 (q, 2 H, J = 7 Hz, ester CH_2), 5.76 (d, 1 H, 16 Hz, C_2 H), 5.92–6.35 (m, 2 H, C_4 H and C_5 H), 7.25 (ddd, 1 H, J = 4, 7, 16 Hz); ^{13}C NMR ($CDCl_3$) 13.6 (q), 14.3 (q), 21.9 (t), 35.0 (t, C_6), 60.1 (t), 119.2 (d, C_2), 128.5 (d, C_4), 144.4 (d, C_5), 145.0 (d, C_3), 167.3 ppm (s).

Compound (2*E*,4*Z*)-**15b**:[32] IR (neat) 1713, 1633, 1602 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.94 (br t, 3 H, J = 7 Hz, CH_3), 1.31 (t, 3 H, J = 7 Hz, ester CH_3), 1.32–2.50 (m, 4 H, 2 CH_2), 4.20 (q, 2 H, J = 7 Hz, ester CH_2), 5.86 (d, 1 H, J = 16 Hz, C_2 H), 5.69–6.27 (m, 2 H, C_4 H and C_5 H), 7.60 (dd, 1 H, J = 11 and 16 Hz, C_3 H); ^{13}C NMR[33] ($CDCl_3$) 13.7 (q), 14.3 (q), 22.6 (t), 30.2 (t, C_6), 60.3 (t), 121.2 (d, C_2), 126.7 (d, C_4), 139.5 (d, C_3), 141.3 (d, C_5), 167.3 ppm (s).

Ethyl (2*E*,4*E*)-2,4-Decadienoate (15c) and the 2*E*,4*Z* Isomer.[8h,i] The treatment of **13c** (3.73 mmol) with Pd(0) catalyst in the usual manner afforded 1.08 g (82%) of crude product.[31] GLC analysis (N_2, 42 mL/min; over temperature 160 °C) of this product showed two peaks at the retention times (component, integrated percentage) of 4.5 min [(2*E*,4*Z*)-**15c**, 11%] and 6.7 min [(2*E*,4*E*)-**15c**, 89%], which were separated by preparative GLC.

Compound (2*E*,4*E*)-**15c**:[34] ^{13}C NMR ($CDCl_3$) 14.0 (q), 14.3 (q), 22.5 (t), 28.4 (t), 31.4 (t), 33.0 (t, C_6), 60.2 (t), 119.2 (d, C_2), 128.4 (d, C_4), 144.8 (d, C_5), 145.1 (d, C_3), 167.3 ppm (s). Compound (2*E*,4*Z*)-**15c**:[34] ^{13}C NMR[33] ($CDCl_3$) 14.0 (q), 14.3 (q), 22.5 (t), 28.2 (t, C_6), 29.0 (t), 31.4 (t), 60.2 (t), 121.1 (d, C_2), 126.4 (d, C_4), 139.5 (d, C_3), 141.7 (d, C_5), 167.3 ppm (s).

Ethyl (2*E*,4*E*,6*E*)-2,4,6-Dodecanetrienoate (18). The treatment of **17** (1 mmol) with Pd(0) catalyst in the usual manner afforded 0.10 g (52%) of crude product.[31] HPLC analysis (Yanako SA-1, 4 mm o.d. × 25 cm, hexane–ether (5:1), 0.65 mL/min) of this product showed two peaks (component, integrated percentage) at the retention times of 5.2 min (unidentified, 8%)[35] and 5.4 min (**18**, 92%).[35] The latter component was isolated by HPLC. Compound **18**: IR (neat) 1710, 1620, 1590 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.6–2.6 (m, 14 H, C_5H_{11} and ester CH_3), 4.20 (q, 2 H, J = 7 Hz, ester CH_2), 5.6–6.7 (m, 5 H, C_2 H and C_4–C_7 4 H), 7.05–7.3 (m, 1 H, C_3 H); mass spectrum, m/e 222 (M^+); ^{13}C NMR ($CDCl_3$) 14.0 (q), 14.3 (q), 22.5 (t), 28.7 (t), 31.4 (t), 32.9 (t), 60.2 (t), 120.0 (d), 127.7 (d), 130.0 (d), 140.7 (d), 141.2 (d), 144.8 (d), 167.2 ppm (s). Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.42; H, 9.85.

***N*-Isobutyl-(2*E*)-4-(benzoyloxy)-2-decenamide (20).** To a solution of 0.6 mL of 2.1 N methanolic NaOMe (1.28 mmol) was added a solution of 0.61 g (1.48 mmol) of [(*N*-isobutylcarbamoyl)methyl]triphenylphosphonium chloride[21] in 3 mL of methanol at room temperature. After being stirred for 5 min, a solution of 0.30 g (1.21 mmol) of 2-(benzoyloxy)octanal (**5c**) in 2 mL of methanol was added and the resulting mixture was stirred under reflux for 2 h. After the solvent was removed under vacuum, the residual oil was separated by column chromatography on alumina (petroleum ether–ether, 4:1) to give 0.36 g of **20**: yield 86%; IR (neat) 3260, 1722, 1670, 1632, 1550 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.6–2.5 [m, 20 H, C_6H_{13} and $CH(CH_3)_2$], 3.14 (t, 2 H, J = 7 Hz, NCH_2), 5.64 (m, 1 H, C_4 H), 5.76 (br s, 1 H, NH), 6.01 (dd, 1 H, J = 15, 1.5 Hz, C_2 H), 6.84 (dd, 1 H, J = 15, 6 Hz, C_3 H), 7.2–8.2 (m, 5 H, C_6H_5). Anal. Calcd for $C_{21}H_{31}O_3N$: C, 73.01; H, 9.04. Found: C, 73.22; H, 8.75.

***N*-Isobutyl-(2*E*,4*E*)-2,4-decadienamide (Pellitorine; 21).** A suspension of 0.74 g (2.14 mmol) of amide **20** and 0.13 g (0.107 mmol) of $(Ph_3P)_4Pd$ in 50 mL of THF was refluxed with stirring for 6 h. The resulting mixture was filtered and the filtrate was diluted with ether. The ethereal solution was washed with aqueous $NaHCO_3$ and dried over $MgSO_4$. After evaporation of the solvent under vacuum, the residual oil was separated by column chromatography on alumina (petroleum ether–ether, 10:1) to give 0.334 g of **21** (70% yield) as a crystal. HPLC analysis (Yanaco Gel 5510, 4 mm × 25 cm, methanol, 0.6 mL/min) showed a single peak at the retention time of 3.5 min. One recrystallization from petroleum ether gave colorless needles, mp 89–90 °C (lit.[9b] mp 90 °C). The IR and ^1H NMR spectra were identical with those reported.[9h]

Registry No. **1a**, 24764-97-4; **1b**, 24764-98-5; **1c**, 35066-22-9; **1d**, 51157-27-8; **1e**, 28832-55-5; **1f**, 762-39-0; **1g**, 20334-54-7; **4**, 532-32-1; **5a**, 80387-13-9; **5b**, 80387-14-0; **5c**, 80387-15-1; **5d**, 80387-16-2; **6a**, 80387-17-3; **6b**, 80387-18-4; **6c**, 80387-19-5; **6d**, 80387-20-8; **7b**, 80387-21-9; **7c**, 80387-22-0; **9b**, 80387-23-1; **9c**, 80387-24-2; (2*E*)-**10**, 80387-25-3; (2*Z*)-**10**, 80387-26-4; **11**, 80387-27-5; **12**, 80387-28-6; **13b**, 80387-29-7; **13c**, 80387-30-0; **14**, 80387-31-1; (2*E*,4*E*)-**15b**, 60388-61-6; (2*E*,4*Z*)-**15b**, 39924-38-4; (2*E*,4*E*)-**15c**, 7328-34-9; (2*E*,4*Z*)-**15c**, 3025-30-7; (2*E*,4*E*)-**17**, 80387-32-2; (2*E*,4*Z*)-**17**, 80387-33-3; **18**, 80387-34-4; **20**, 80387-35-5; **21**, 18836-52-7.

Supplementary Material Available: Table IV, summarizing the ^{13}C NMR spectral data of conjugated diene derivatives (1 page). Ordering information is given on any current masthead page.

(31) Obtained after one purification by column chromatography on silica gel (hexane–acetone, 10:1).

(32) Baumann, M.; Hoffmann, W. *Synthesis* **1977**, 681.

(33) Identical with those of a sample prepared independently (Tsuboi, S.; Masuda, T.; Makino, H.; Takeda, A., 43rd Annual Meeting of the Chemical Society of Japan, Tokyo, March 1981).

(34) The IR and ^1H NMR spectra were identical with those reported (see ref 8h and 8i).

(35) Retention times were too close to be separable.