after recrystallization from hexane gave mp 195–197 °C; $[\alpha]^{32}_D$ +17.5° (*c* 0.78, $CHCl_3$); IR (KBr) 2998, 2920, 2830, 1693, 1588, 1423, 1407, 1316, 1141, 1092, 1068, 899, 863, 789, 713 cm^{-1}; NMR ($CDCl_3$) τ 3.58 (s, 4 H), 4.03 (s, 2 H), 6.50–7.97 (m, 16 H), 8.10–8.85 (m, 4 H).

Anal. Calcd for $C_{24}H_{26}O_2$: C, 83.20; H, 7.56. Found: C, 83.57; H, 7.46.

(+)-[8]-Bridged [2.2]Paracyclophane (19) (from 24). The bis(ethanedithiol) **24b** was prepared by the method described for the preparation of **13**, utilizing **24a** (100 mg, 0.29 mmol), acetic acid (15 mL), ethanedithiol (3 mL), and 47% borontrifluoride (1 mL). To a solution of crude **24b** (0.14 g) in ethyl acetate (15 mL) was added W-5 Raney nickel (0.5 g). Refluxing followed by removal of the Raney nickel and concentration gave a solid which was subjected to alumina column chromatography. Elution with hexane–benzene gave **19**: mp 135–136 °C; $[\alpha]^{20}_D$ +33.2° (*c* 0.84, $CHCl_3$).

Anal. Calcd for $C_{24}H_{30}$: C, 90.50; H, 9.50. Found: C, 90.44; H, 8.54.

Registry No.—(*S*)-(+)-**4**, 54059-74-4; (*R*)-(−)-**5**, 36757-10-5; (±)-**6b**, 63534-00-9; (+)-**6b**, 63534-01-0; (±)-**6c**, 63534-02-1; (±)-**6c** DNP, 63534-03-2; (±)-**6d**, 63534-04-3; (*S*)-(+)-**6d**, 63597-46-6; (*S*)-(+)-**6d** (+)-α-(β-naphthylethylamine), 63597-47-7; (+)-**6e**, 63534-05-4; (−)-**6f**, 63534-06-5; (+)-**6g**, 63534-07-6; (±)-**7a**, 63534-08-7; (−)-**7b**, 63534-09-8; **8a**, 1197-60-0; **8b**, 32543-06-9; (±)-**9**, 63534-10-1; (−)-**10**, 63597-48-8; (±)-**11**, 5088-46-0; (+)-**12**, 63534-11-2; (±)-**13**, 63534-12-3; (±)-**14a**, 36659-11-7; (−)-**14a**, 63534-13-4; (±)-**14b**, 36659-12-8; (±)-**14b** DNP, 63534-14-5; (±)-**14c**, 63534-15-6; (−)-**14c**, 36659-13-9; (−)-**14c** brucine, 63534-16-7; (−)-**14d**, 36757-09-2; (+)-**14e**, 36659-14-0; (+)-**14f**, 36659-16-2; (±)-**14g**, 63534-17-8; *R*-(−)-**14h**, 63534-18-9; (−)-**15**, 36659-18-4; (+)-**16**, 63597-49-9; (−)-**17**, 36659-19-5; (−)-**18**, 36659-20-8; (+)-**19**, 63534-19-0; (*S*)-(+)-**21a**, 63534-20-3; (+)-**22**, 63534-21-4; (*S,S*)-(+)-**23**, 36659-04-8; (+)-**24a**, 63534-22-5; (+)-**24b**, 63534-23-6; (+)-α-(β-naphthyl)ethylamine, 3906-16-9; brucine, 357-57-3; *p*-xylyltrimethylammonium bromide, 16814-21-4.

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Synthesis of Methyl *dl*-Jasmonate and Its Related Compounds from Methyl (*E*)- and (*Z*)-4,4-Dimethoxy-2-butenoates

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A synthesis of methyl *dl*-jasmonate (**1b**) and its dehydro derivatives **2b** and **3b** from methyl (*E*)- and (*Z*)-4,4-dimethoxy-2-butenoates (**4**) is described. Dimethyl 2-acetyl-3-dimethoxymethylglutarate (**5**) could be obtained by Michael addition of **4** with methyl acetoacetate in excellent yields. Deacetalization of dimethyl 2-acetyl-3-dimethoxymethyl-2-(2-pentynyl)glutarate (**7a**) followed by cyclization with base after alkylation of **5** (R′ = Me) with 2-pentynyl bromide afforded 5-methoxycarbonyl-4-methoxycarbonylmethyl-5-(2-pentynyl)-2-cyclopentenone (**10a**). Reduction of **10** (R′ = Me) with $NaBH_4$ in MeOH giving 2-methoxycarbonyl-3-methoxycarbonylmethyl-2-(2-pentynyl)cyclopentanol (**13a**) and subsequent oxidation of **13** with chromic acid gave 2-methoxycarbonyl-3-methoxycarbonylmethyl-2-(2-pentynyl)cyclopentanone (**14a**), a precursor of **1b**. Cis hydrogenation of **7a** → **7b**, **10a** → **10b**, **13a** → **13b**, and **14a** → **14b** using Lindlar catalyst proceeded in quantitative yields. Direct demethoxycarbonylation of **10b** (R = 2-*cis*-pentenyl) with Me_2SO–H_2O–NaCl in a sealed tube afforded a mixture of **2b** and **3b**. However, acid-catalyzed de-*tert*-butoxycarbonylation of **10b** (R′ = *t*-Bu), prepared from **5** (R′ = *t*-Bu) by alkylation followed with cyclization, under reflux in benzene gave **2b** as a sole product. Hydrogenation of **10a** with palladium on charcoal afforded **14c** (R = pentyl). The products **2b** and **3b** could be converted into **1b** smoothly.

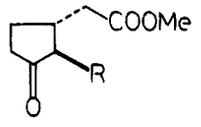
Our continuing interest in the jasmonoid syntheses[1] has led to discovering an economically significant method in obtaining methyl *dl*-jasmonate (**1b**)[2] and methyl dehydrojasmonates (**2b** and **3b**) without using troublesome reagents. In the course of our efforts to investigate the electrolysis of 2-substituted furans, we have found an effective, one-step preparative way of methyl (*E*)- and (*Z*)-4,4-dimethoxy-2-butenoates (**4**).[3] It should be noted that the butenoates **4** are expected to be a powerful Michael acceptor and they are indeed smoothly obtained in good yield by the simple electrolyses of furfuryl alcohol, furfural, and 2-furoic acid. We now report a straightforword synthesis of the jasmonates **1b**, **2b**, and **3b** from **4** via the intermediates **5**, **7**, **10**, **13**, and **14**.

When the butenoates **4** were allowed to react with methyl acetoacetate using alkali metal carbonates in methanol (Table I, runs 1, 2, and 3), the yield of **5** (R′ = Me) was in the ranges of 0–35% yields along with the formation of **6** (6–11% yields). A successful Michael addition of methyl acetoacetate to **4** was

Table I. Constituents of the Michael Adducts of 4 with Methyl Acetoacetate

Run	Substrate	Base	Time (h)	Yield of products, % 5 (R′ = Me)	6	4[a]
1	4(Z)	Li_2CO_3	20	35	6	29
2	4(Z)	Na_2CO_3	5	22	9	18
3	4(Z)	K_2CO_3	16		11	
4	4(Z)	KF	72	97		
5	4(E)	KF	72	98		

[a] The recovered substrates 4.



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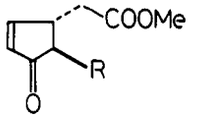

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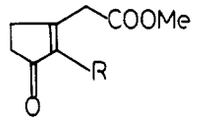

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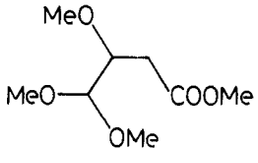
a: R = $-CH_2C{\equiv}CEt$
b: R = $-CH_2CH{=}^{cis}CHEt$
c: R = $-(CH_2)_4Me$



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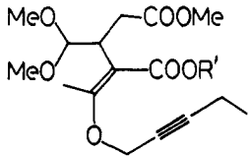

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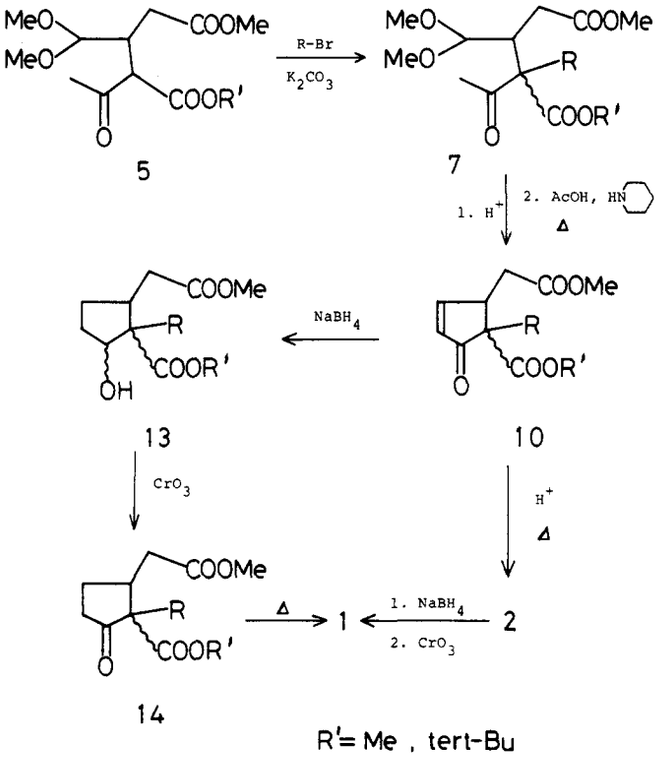
accomplished in 97–98% yields by using potassium fluoride in methanol as shown in Table I (runs 4 and 5). In contrast to our results, an earlier report demonstrates that fluoride ion is considered to be a strong base in aprotic solvents because of lack of hydrogen bonding.[4]

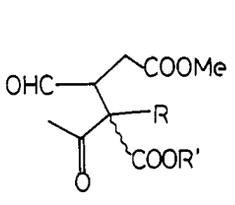
Alkylation of **5** (R′ = Me) with pentynyl bromide using potassium carbonate in acetone afforded the desired C-alkylated **7a** (R′ = Me, 72% yield) together with the O-alkylated **8a** (R′ = Me, 27% yield), whereas the yield of **7a** (R′ = Me) increased to 81% by addition of a catalytic amount of potassium iodide. The products **7a** and **8a** could be separated by column chromatography.

An aqueous THF solution of **7** (R′ = Me) was hydrolyzed with 1% perchloric acid at 26–28 °C, giving **9** (R′ = Me), and subsequent base-catalyzed cyclization with piperidine–acetic acid in benzene afforded **10** (R′ = Me) in 52–56% yield (based on **7**) after removal of water azeotropically. However, the prolonged heating of the aqueous THF solution of **7a** (R′ = Me) with 3–4% perchloric acid over 33 °C provided the lactone derivative **11a** preferentially. Cis hydrogenation of **7a → 7b, 10a → 10b, 13a → 13b,** and **14a → 14b** in a mixed solvent of hexane and acetone using Lindlar catalyst[5] proceeded in quantitative yields.

The hydride reduction of 2-cyclopenten-1-ones[6] has been well investigated; however, selective 1,4 reduction of the enones has not yet been reported, in contrast to the cases of 2-cyclohexen-1-ones.[7] The reduction of the mixed products **2b** and **3b** (5:1) to the diol **12** with 14 equiv of metal lithium in liquid ammonia and subsequent oxidation and esterification, giving **1b,** has been discussed by Ducos and Rouessac.[8] In an effort to ascertain how the double bond in the ring of **10** could



R′= Me , tert-Bu



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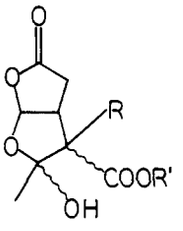

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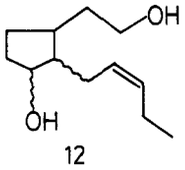

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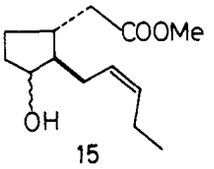

15

be selectively reduced, the following several examinations were attempted. Thus, reduction of **10b** (R′ = Me) with 4 equiv of lithium tri-*tert*-butoxyaluminumhydride[6a] in THF at 5 °C for 18 h afforded a mixture of **13b** (R′ = Me, 51%) and **14b** (R′ = Me, 26%) (Table II, run 1). Similarly, reduction of **10b** (R′ = Me) with 2 equiv of sodium borohydride in methanol and/or in dioxane under reflux for 1 h afforded the alcohol **13b** (R′ = Me, 80 and 41% yields) (Table II, runs 2 and 3). On the other hand, catalytic hydrogenation of **10b** (R′ = Me) with palladium on charcoal or palladium on barium sulfate in methanol at 24 °C for 30 min gave **14c** (R′ = Me) in 88–97% yields (runs 4 and 5).

The Jones oxidation of both **13a** (R′ = Me), derived from **10a** (R′ = Me), and **13b** (R′ = Me) with chromic acid–sulfuric acid in methylene chloride gave the corresponding cyclopentanones **14a** and **14b** in 71–84% yields, and subsequent demethoxycarbonylation in aqueous dimethylsulfoxide (Me_2SO) containing a small amount of sodium chloride (NaCl)[2d] in a sealed tube led to the jasmonates **1a–b,** smoothly.

Methyl dehydrojasmonate (**2b**), isolated from jasmine absolutes of Italian[9] and Spanish[10] jasmines (*Jasminum grandiflorum L.*), has received considerable attention as new odorous stuff.[1a] However, in a synthetical sense, it is lacking

Table II. Reduction of 10b (R′ = Me) with Various Reducing Reagents

Run	Reagent	Solvent	Temp, °C	Time, h	Yield of products, % 13b	14b	14c
1	$Li(t\text{-}BuO)_3AlH$	THF	5	18	51	26	
2	$NaBH_4$	Dioxane	102	1	41		
3	$NaBH_4$	MeOH	65	1		80	
4	Pd/C	MeOH	20	0.8			97
5	$Pd/BaSO_4$	MeOH	24	0.5			88

in the literature in obtaining **2b** except for the paper regarding the simultaneous formation of **2a** and **3a** in the retro-Diels–Alder reaction of 3-oxo-4-(2-pentynyl)-5-methoxycarbonylmethyl-*endo*-tricyclo[5.2.1.$0^{2,6}$]-8-decene.[8] In our experiment, demethoxycarbonylation of **10b** (R′ = Me) in aqueous Me_2SO-NaCl in a sealed tube at 170–175 °C for 4 h afforded a mixture of **2b** and **3b** (2:1)[11] in 46% yield, whereas the cyclopentenone **10b** (R′ = *t*-Bu), prepared by alkylation of the Michael adduct **5** (R′ = *t*-Bu) followed by cyclization, underwent acid-catalyzed decomposition under reflux in benzene for 20 min, to give pure **2b** in 83% yield. This reaction condition[12] may provide thermodynamically stable trans-isomer **2b**. Supporting evidence for the configuration of **2b** comes from the results of the ^{13}C NMR spectra of **2b** and **1b**, showing homogeneous peaks in very fine detail, and from the following conversion of **2b** to **1b**.[13] Conversion of **2b** and/or the mixture **2b** and **3b** into **1b** via **15** was carried out by reduction with sodium borohydride in methanol followed with Jones oxidation. An alternative route to **1b** from **10b** (R′ = *t*-Bu) via **13b** (R′ = *t*-Bu) and **14b** (R′ = *t*-Bu) was also examined in a similar manner to that described for **10b** (R′ = Me).

Experimental Section

Boiling points are uncorrected. ^1H NMR spectra were determined at 60 MHz with a Hitachi R-24 spectrometer and the chemical-shift values are expressed in δ value (ppm) relative to a Me_4Si internal standard. ^{13}C NMR spectra were taken at 25.05 MHz in the Fourier mode using a JEOL FX-100 spectrometer. Samples were dissolved in $CDCl_3$ containing Me_4Si as an internal standard. IR spectra were determined with a Japan Spectroscopic Co. Ltd., IRA-I, infrared recording spectrophotometer fitted with a grating. The mass spectra were obtained with a JEOL Model JMS-OIBM-2, ionizing voltage 75 eV.

Dimethyl 2-Acetyl-3-dimethoxymethylglutarate (5, R′ = Me). A mixture of **4**(*Z*) (2.22 g, 13.8 mmol), KF (2.5 g, 43.0 mmol), and $AcCH_2CO_2Me$ (2.7 g, 23.2 mmol) in MeOH (5 mL) was vigorously stirred for 3 days under reflux. The mixture was allowed to cool to room temperature and the solvent was evaporated in vacuo. The residue was poured into brine and extracted with AcOEt. The extracts were dried (Na_2SO_4) and concentrated. After removal of the solvents, the residue was chromatographed (SiO_2, benzene–AcOEt, 10/1) to give **5** (R′ = Me, 3.69 g, 97%): bp 88–91 °C (1.9 mm); ^1H NMR ($CDCl_3$) δ 2.24 (s, 3, CH_3CO), 2.41–2.64 (m, 2, CH_2CO), 2.77–3.22 (m, 1, CH), 3.31, 3.35 (2, s, 6, CH_3O), 3.66 (s, 3, CH_3O), 3.72 (s, 3, CH_3O), 3.79 (d, 1, *J* = 6 Hz, CHCO), 4.38 (t, 1, *J* = 6 Hz, OCHO); IR (neat) 1735 (C=O), 1715 cm^{-1} (C=O).

Anal. Calcd for $C_{12}H_{20}O_7$: C, 52.17; H, 7.30. Found: C, 52.32; H, 7.40.

Similarly, upon heating to reflux a mixture of **4**(*E*) and $AcCH_2CO_2Me$ in the presence of KF in MeOH afforded **5** (R′ = Me) in 98% yield.

Dimethyl 2-Acetyl-3-dimethoxymethyl-2-(2-pentynyl)-glutarate (7a, R′ = Me). A mixture of K_2CO_3 (2.08 g, 15.1 mmol), **5** (R′ = Me, 553 mg, 2.0 mmol), pentynyl bromide (320 mg, 2.18 mmol), and KI (444 mg, 2.67 mmol) in acetone (30 mL) was stirred at room temperature for 1 h and then refluxed for an additional 12 h. The mixture was allowed to stand to room temperature. The insoluble material was separated by centrifugation and the organic layer was concentrated. The residue was chromatographed (SiO_2, benzene–AcOEt, 8/1) to give **7a** (R′ = Me, 558 mg, 81%) and **8a** (R′ - Me, 88 mg, 13%).

The C-alkylation product **7a** boiled at 97–101 °C (0.08 mm): ^1H NMR (CCl_4) δ 1.11 (t, 3, *J* = 7 Hz, CH_3), 1.81–2.26 (m, 5, $CH_2C{\equiv}C$, CH_3CO), 2.26–2.55 (m, 2, CH_2CO), 2.55–2.85 (m, 2, $CH_2C{\equiv}C$), 2.98–3.48 (m, 7, CH_3O, CH), 3.61 (s, 3, CH_3O), 3.65 (s, 3, CH_3O), 4.15–4.34 (m, 1, OCHO); IR (neat) 2837 (CH_3O), 1729 (C=O), 1710 cm^{-1} (C=O); MS *m/e* (rel intensity) 342 (M^+, 0.8), 311 (19), 279 (5), 267 (37), 221 (16), 219 (17), 207 (13), 191 (8), 181 (5), 161 (10), 160 (24), 130 (19), 101 (20), 91 (7), 75 (100).

Anal. Calcd for $C_{17}H_{26}O_7$: C, 59.64; H, 7.65. Found: C, 59.67; H, 7.76.

The O-alkylation product **8a** (R′ = Me) boiled at 85–89 °C (0.005 mm): ^1H NMR (CCl_4) δ 1.13 (t, 3, CH_3), 1.87–2.60 (m, 4, $CH_2C{\equiv}C$, CH_2CO), 2.29 (s, 3, CH_3CO), 3.12, 3.25 (2 s, 6, CH_3O), 3.11–3.78 (m, 1, $CHC{=}C$), 3.55, 3.66 (2 s, 6, CH_3OCO), 4.41–4.66 (m, 3, $OCH_2C{\equiv}C$, OCHO); IR (neat) 2832 (CH_3O), 1737 (C=O), 1708 (C=O), 1619 cm^{-1} (C=C).

Anal. Calcd for $C_{17}H_{26}O_7$: C, 59.64; H, 7.65. Found: C, 59.42; H, 7.44.

Dimethyl 2-Acetyl-3-dimethoxymethyl-2-(*cis*-2-pentenyl)-glutarate (7b, R′ = Me). A mixture of Lindlar catalyst (208 mg) and **7a** (R′ = Me, 194 mg, 0.57 mmol) in hexane (1 mL) and acetone (1 mL) was stirred under 1 atm of hydrogen at room temperature. After 40 min, hydrogen uptake stopped and the mixture was filtered free from the catalyst and concentrated in vacuo. Column chromatography of the residue (SiO_2, benzene–AcOEt, 5/1) gave **7b** (R′ = Me, 195 mg, 100%), bp 82–87 °C (0.14 mm): ^1H NMR (CCl_4) δ 0.95 (t, 3, CH_3), 1.76–2.32 (m, 5, CH_3CO, $CH_2C{=}C$), 2.37–2.86 (m, 4, $CH_2C{=}C$, CH_2CO), 2.95–3.50 (m, 7, CH_3O, CH), 3.66, 3.71 (2 s, 6, CH_3O), 4.27 (m, 1, OCHO), 4.82–5.77 (m, 2, HC=CH); IR (neat) 2835 (CH_3O), 1733 (C=O), 1708 cm^{-1} (C=O); MS *m/e* (rel intensity) 344 (M^+, 0.33), 313 (27), 312 (12), 270 (14), 269 (48), 253 (24), 242 (28), 238 (11), 237 (30), 221 (15), 209 (14), 207 (11), 183 (35), 181 (14), 160 (13), 153 (29), 130 (50), 101 (18), 75 (100).

Anal. Calcd for $C_{17}H_{28}O_7$: C, 59.29; H, 8.19. Found: C, 59.14; H, 8.44.

5-Methoxycarbonyl-4-methoxycarbonylmethyl-5-(2-pentynyl)-2-cyclopentenone (10a, R′ = Me). A solution of **7a** (R′ = Me, 53 mg, 0.15 mmol) in THF (2 mL) and aqueous 1% $HClO_4$ (2 mL) was stirred for 12 h at 26–28 °C. The solution was neutralized with aqueous $NaHCO_3$ and concentrated to ca. 2 mL of total volume under reduced pressure. The residue was poured into brine and extracted with AcOEt. The extracts were dried (Na_2SO_4) and evaporated in vacuo to give the crude aldehyde **9a** (R′ = Me, 50 mg): ^1H NMR (CCl_4) δ 9.65 (CHO); IR (neat) 2841 (CHO), 1733, 1716 cm^{-1} (C=O). Without further purification, the oily product was subjected to the following cyclization reaction. A stirred mixture of **9a** (50 mg) in a mixed solution of AcOH (0.1 mL), piperidine (0.1 mL), and benzene (25 mL) was refluxed for 6 h. After cooling to room temperature most of the solvent was removed by a rotary evaporator. The residue was diluted with AcOEt (20 mL), washed with 10% HCl, aqueous $NaHCO_3$, and brine, dried (Na_2SO_4), and concentrated. Column chromatography of the residue (SiO_2, benzene–AcOEt, 12/1) gave **10a** (R′ = Me, 24 mg, 56%). From the next running fraction, **7a** (R′ = Me, 4 mg) was recovered. The cyclopentenone **10a** (R′ = Me) boiled at 110–115 °C (0.15 mm): ^1H NMR (CCl_4) δ 1.05 (t, 3, CH_3), 1.80–2.30 (m, 2, $CH_2C{=}C$), 2.34–2.86 (m, 4, $CH_2C{=}C$, CH_2CO), 2.86–3.50 (m, 1, CH), 3.61, 3.67 (2 s, 6, CH_3O), 6.14 (dd, 1, *J* = 6 Hz, *J* = 2 Hz, C=CHCO), 7.59 (dd, 1, *J* = 6 Hz, *J* = 2 Hz, HC=CCO); IR (neat) 1732, 1710 (C=O), 1595 cm^{-1} (C=C); MS *m/e* (rel intensity) 279 ($M^+ + 1$, 29), 278 (M^+, 100), 247 (60), 246 (44), 219 (97), 215 (23), 205 (77), 189 (19), 187 (39), 179 (33), 159 (66), 147 (24), 145 (26), 131 (36), 117 (23), 115 (23), 91 (26).

Anal. Calcd for $C_{15}H_{18}O_5$: C, 64.74; H, 6.52. Found: C, 64.64; H, 6.30.

5-Methoxycarbonyl-4-methoxycarbonylmethyl-5-(*cis*-2-pentenyl)-2-cyclopentenone (10b, R′ = Me). Method A. A solution of **7b** (R′ = Me, 250 mg, 0.73 mmol) in THF (3 mL) and aqueous 1.5% $HClO_4$ (2 mL) was stirred for 12 h at 26–28 °C. The mixture was neutralized with aqueous $NaHCO_3$ and concentrated to ca. 2 mL of total volume under reduced pressure. The workup of the residue was similar to that employed for the preparation of **10a** (R′ = Me) described above, giving **9b** (R′ = Me, 248 mg): ^1H NMR (CCl_4) δ 9.56, 9.65 (CHO); IR (neat) 1735, 1717 cm^{-1} (C=O). Without further purification, the oily product was subjected to the following cyclization reaction. A mixture of **9b** (R′ = Me, 248 mg) in a mixed solution of AcOH (0.1 mL) and piperidine (0.1 mL) in benzene (30 mL) was refluxed for 6 h under stirring. After workup in the usual manner as described above there was obtained **10b** (R′ = Me, 105 mg, 52%) after

chromatography (SiO_2, benzene–AcOEt, 12/1). From the next running fraction, **7b** (R′ = Me, 5.4 mg) was recovered. The cyclopentenone **10b** (R′ = Me) boiled at 81–85 °C (0.005 mm): ^1H NMR (CCl_4) δ 0.97 (t, 3, CH_3), 2.05 (q, 2, J = 7 Hz, $CH_2C{=}C$), 2.27–3.51 (m, 5, $CH_2C{=}C$, CH_2CO, CH), 3.62, 3.66 (2 s, 6, CH_3O), 4.76–5.75 (m, 2, HC=CH), 6.09 (dd, 1, J = 5 Hz, J = 2 Hz, C=CHCO), 7.47 (dd, 1, J = 5 Hz, J = 2 Hz, HC=CCO); IR (neat) 1736, 1710 (C=O), 1597 cm^{-1} (C=C).

Anal. Calcd for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19. Found: C, 64.07; H, 7.35.

Method B. The cyclopentenone **10b** (R′ = Me) was prepared by hydrogenation of **10a** (R′ = Me, 45 mg, 0.16 mmol) in hexane (1 mL) and acetone (0.1 mL) using Lindlar catalyst (68 mg). Column chromatography (SiO_2, benzene–AcOEt, 5/1) of the product gave **10b** (R′ = Me, 43 mg, 95%), whose spectral data were identical with those of the specimen obtained in the preceding experiment.

2-Methoxycarbonyl-3-methoxycarbonylmethyl-2-(*cis*-2-pentenyl)cyclopentanol (13b, R′ = Me) from 10b (R′ = Me). A solution of **10b** (R′ = Me, 11 mg, 0.039 mmol) and $NaBH_4$ (3.0 mg, 0.079 mmol) in MeOH (2 mL) was refluxed at ca. 80 °C for 1 h. The solution was allowed to cool to room temperature and then 4 drops of AcOH was added. After stirring for an additional 30 min, the solution was concentrated in vacuo and the residue was passed through a short silica gel column (2 × 0.9 cm, benzene–AcOEt, 2/1, 15 mL). Evaporation of the solvents followed by column chromatography (SiO_2, benzene–AcOEt, 5/1) gave **13b** (R′ = Me, 8.9 mg, 80%): bp 74–78 °C (0.01 mm); ^1H NMR (CCl_4) δ 0.93 (t, 3, CH_3), 1.40–2.90 (m, 12), 3.59, 3.66 (2 s, 6, CH_3O), 3.85–4.12 (m, 1, CHO), 4.95–5.75 (m, 2, HC=CH); IR (neat) 3506 (OH), 1727 cm^{-1} (C=O).

Anal. Calcd for $C_{15}H_{24}O_5$: C, 63.36; H, 8.51. Found: C, 63.47; H, 8.78.

2-Methoxycarbonyl-3-methoxycarbonylmethyl-2-(2-pentynyl)cyclopentanol (13a, R′ = Me). A solution of **10a** (R′ = Me, 20.0 mg, 0.072 mmol) and $NaBH_4$ (5.4 mg, 0.143 mmol) in MeOH (2 mL) was refluxed at 80 °C for 1 h under N_2. After the usual workup, there was obtained **13a** (R′ = Me, 17.5 mg, 86.3%): bp 70–75 °C (0.005 mm); ^1H NMR (CCl_4) δ 1.11 (t, 3, CH_3), 1.38–2.95 (m, 12), 3.60, 3.68 (2 s, 6, CH_3O), 3.90–4.45 (m, 1, HCO); IR (neat) 3433 (OH), 1725 cm^{-1} (C=O).

Anal. Calcd for $C_{15}H_{22}O_5$: C, 63.81; H, 7.85. Found: C, 63.90; H, 8.02.

The Cyclopentanol 13b (R′ = Me) from 13a (R′ = Me). A mixture of **13a** (R′ = Me, 28 mg, 0.01 mmol) and Lindlar catalyst (44 mg) in hexane (1 mL) and acetone (0.1 mL) was stirred under 1 atm of hydrogen at room temperature. After 1 h, the hydrogen uptake stopped and the mixture was filtered free from the catalyst and concentrated in vacuo. Column chromatography of the residue (SiO_2, benzene–AcOEt, 5/1) gave **13b** (R′ = Me, 21.5 mg, 77%), bp 74–78 °C (0.01 mm), which was identical in all respects with those of the product obtained in the preceding experiment.

2-Methoxycarbonyl-3-methoxycarbonylmethyl-2-(*cis*-2-pentenyl)cyclopentanone (14b, R′ = Me). To a solution of **13b** (R′ = Me, 6.8 mg, 0.024 mmol) in CH_2Cl_2 (2 mL), 100 mg of aqueous 2 M chromic acid was added dropwise. The mixture was stirred at room temperature for 12 h under a heterogeneous system. The yellow-orange solution was taken up in AcOEt and washed with brine, aqueous $NaHCO_3$, and brine. The AcOEt layer was dried (Na_2SO_4) and concentrated. Column chromatography (SiO_2, benzene–AcOEt, 10/1) of the residue gave **14b** (R′ = Me, 5.7 mg, 84%), bp 73–77 °C (0.007 mm) [lit.[2d] bp 84.0–85.0 °C (0.0 15 mm)], whose spectral data were identical with those of an authentic sample.

Methyl *dl*-Jasmonate (1b) from 14b (R′ = Me). Demethoxycarbonylation of **14b** (R′ = Me, 130 mg, 2.2 mmol) in aqueous Me_2SO–NaCl at 176 °C for 4 h gave **1b** (69 mg, 86%), whose spectral data (IR, ^1H NMR, and MS) were identical with those of an authentic sample.

2-Methoxycarbonyl-3-methoxycarbonylmethyl-2-(2-pentynyl)cyclopentanone (14a, R′ = Me). To a solution of **13a** (R′ = Me, 17 mg, 0.06 mmol) in CH_2Cl_2 (2 mL), aqueous 2 M chromic acid (ca. 0.2 mL) was added dropwise and the mixture was stirred at room temperature for 12 h. After the usual workup, there was obtained **14a** (R′ = Me, 12 mg, 71%), bp 78–82 °C (0.008 mm) [lit.[2d] bp 78–80 °C (0.02 mm)], whose IR and ^1H NMR spectra were identical with those of an authentic sample.

2-Methoxycarbonyl-3-methoxycarbonylmethyl-2-pentylcyclopentan-1-one (14c, R′ = Me). A mixture of **10b** (R′ = Me, 32 mg, 0.11 mmol) and palladium on charcoal (60 mg) in MeOH (2 mL) was stirred under 1 atm of hydrogen at room temperature. After 50 min, hydrogen uptake stopped and the mixture was filtered free from catalyst and concentrated. Column chromatography of the residue (SiO_2, benzene–AcOEt, 5/1) gave **14c** (31 mg, 97%), whose IR and ^1H NMR spectra were identical with those of an authentic sample.[2d]

Methyl 4-*tert*-Butoxycarbonyl-3-dimethoxymethyl-5-oxohexanoate (5, R′ = *t*-Bu). A mixture of **4**(*Z*) (1.66 g, 10.4 mmol), KF (2.0 g, 34.4 mmol), and $AcCH_2CO_2$-*t*-Bu (1.81 g, 11.5 mmol) in *t*-BuOH (2 mL) was vigorously stirred for 2 days under reflux. After the same workup as described for **5** (R′ = Me), there was obtained **5** (R′ = *t*-Bu, 2.86 g, 86%): bp 72–76 °C (0.014 mm); ^1H NMR (CCl_4) δ 1.43 (br s, 9, CH_3), 2.17 (s, 3, CH_3CO), 2.30–2.60 (m, 2, CH_2CO), 2.60–3.19 (m, 1, AcCHCO), 3.19–3.38 (m, 6, CH_3O), 3.58–3.72 (m, 3, CH_3OCO), 3.19–3.72 (m, 1, CH), 4.31 (t, 1, J = 5 Hz, OCHO); IR (neat) 1736 (C=O), 1715 cm^{-1} (shoulder, C=O).

Anal. Calcd for $C_{15}H_{26}O_7$: C, 56.59; H, 8.23. Found: C, 56.65; H, 8.13.

5-*tert*-Butoxycarbonyl-4-methoxycarbonylmethyl-5-(2-pentynyl)-2-cyclopentenone (10a, R′ = *t*-Bu) from 5 (R′ = *t*-Bu) via 7a. A mixture of K_2CO_3 (1.38 g, 9.99 mmol), **5** (R′ = *t*-Bu, 450 mg, 1.42 mmol), pentynyl bromide (270 mg, 1.84 mmol), and KI (308 mg, 1.86 mmol) in acetone (30 mL) was refluxed for 12 h. After the usual workup as described above, there was obtained 478 mg of an oily product, whose ^1H NMR spectrum indicated that the product consisted of **7a** (R′ = *t*-Bu, 75%) and **8a** (R′ = *t*-Bu, 13%). Without further purification, the mixture was subjected to the following cyclization reaction. A solution of the mixture **7a** and **8a** (60 mg, 0.16 mmol) in THF (3 mL) and aqueous 1.5% $HClO_4$ (2.5 mL) was stirred for 12 h at 28–29 °C. The workup of the reaction mixture was similar to that employed for the preparation of **10a** (R′ = Me), giving an oily material (79 mg), which was subjected to reflux in a mixed solution of AcOH (0.1 mL), piperidine (0.1 mL), and benzene (5 mL) for 4 h. Upon evaporation of the solvent, the residue was worked up in the usual manner as described above. After chromatography (SiO_2, benzene–hexane–AcOEt, 6/3/1), there was obtained 22 mg (48% based on **7a**, R′ = *t*-Bu) of **10a** (R′ = *t*-Bu): bp 82–86 °C (0.006 mm); ^1H NMR (CCl_4) δ 1.02 (t, 3, CH_3), 1.37 (br s, 9, CH_3), 1.76–2.73 (m, 6, $CH_2C{=}C$, CH_2CO), 3.33–3.58 (m, 1, CH), 3.66 (s, 3, CH_3O), 6.10 (dd, 1, J = 5, 2 Hz, C=CHCO), 7.50 (dd, 1, J = 5, 2 Hz, HC=CCO); IR (neat) 1734, 1711 (C=O), 1595 cm^{-1} (C=C).

Anal. Calcd for $C_{18}H_{24}O_5$: C, 67.48; H, 7.55. Found: C, 67.36; H, 7.70.

5-*tert*-Butoxycarbonyl-4-methoxycarbonylmethyl-5-(*cis*-2-pentenyl)-2-cyclopentenone (10b, R′ = *t*-Bu). Hydrogenation of **10a** (R′ = *t*-Bu, 69 mg, 0.22 mmol) in hexane (0.5 mL) and acetone (0.5 mL) in the presence of Lindlar catalyst (320 mg) afforded **10b** (R′ = *t*-Bu, 70 mg, 100%): bp 81–84 °C (0.005 mm); ^1H NMR (CCl_4) δ 0.97 (t, 3, CH_3), 1.42 (s, 9, CH_3), 2.05 (q, J = 7 Hz, 2, $CH_2C{=}C$), 2.34–2.71 (m, 4, $CH_2C{=}C$, CH_2CO_2), 3.26 (m, 1, CH), 3.66 (s, 3, CH_3O), 4.79–5.69 (m, 2, HC=CH), 6.09 (dd, 1, J = 5 Hz, J = 2 Hz, C=CHCO), 7.50 (dd, 1, J = 5 Hz, J = 2 Hz, HC=CCO); IR (neat) 1734, 1712 (C=O), 1596 cm^{-1} (C=C).

Anal. Calcd for $C_{18}H_{26}O_5$: C, 67.06; H, 8.13. Found: C, 66.91; H, 8.36.

Methyl Dehydrojasmonate (2b). A mixture of **10b** (R′ = *t*-Bu, 54 mg, 0.17 mmol) and a catalytic amount of anhydrous *p*-toluenesulfonic acid in benzene (2 mL) was refluxed for 20 min. The mixture was quenched with $NaHCO_3$ (powder, 10 mg). After removal of the solvent under reduced pressure, the residue was chromatographed (SiO_2, benzene–AcOEt, 10/1) to give **2b** (31 mg, 83%): bp 88–92 °C (2.5 mm); ^1H NMR ($CDCl_3$) δ 0.95 (t, 3, CH_3), 1.88–3.18 (m, 8), 3.70 (s, 3, CH_3O), 4.95–5.75 (m, 2, HC=CH), 6.15 (dd, 1, J = 6, 1.6 Hz, C=CHCO), 7.60 (dd, J = 6, 2 Hz, HC=CCO); ^{13}C NMR (multiplicity, carbon no.) δ 14.1 (q, 12), 20.5 (t, 11), 27.7 (t, 8), 38.1 (t, 2), 43.2 (d, 3), 51.0 (d, 7), 51.8 (q, 13), 124.4 (d, 9), 133.7 (d, 5 or 10), 134.4 (d, 10 or 5), 165.3 (d, 4), 171.7 (s, 1), 210.0 (s, 6); IR (neat) 1736, 1706 (C=O), 1599 cm^{-1}.

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.06; H, 8.19.

3-Methoxycarbonylmethyl-2-(*cis*-2-pentenyl)cyclopentanol (15) from 2b. A solution of **2b** (18 mg, 0.08 mmol) and $NaBH_4$ (9 mg, 0.2 mmol) in MeOH (2 mL) was refluxed at 80 °C for 1 h. After the usual workup, there was obtained **15** (16 mg, 87%) after chromatography (SiO_2 benzene–AcOEt, 5/1): bp 63–67 °C (0.01 mm); ^1H NMR (CCl_4) δ 0.99 (t, 3, CH_3), 1.22–2.88 (m, 13), 3.61 (s, 3, CH_3O), 3.67–4.22 (m, 1, CHO), 5.20–5.52 (m, 2, HC=CH); IR (neat) 3400 (OH), 1735 (C=O), 1722 cm^{-1} (shoulder).

Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 69.00; H, 9.75.

Methyl *dl*-Jasmonate (1b) from 15. To a solution of **15** (15 mg, 0.066 mmol) in CH_2Cl_2 (1 mL) aqueous 2 M chromic acid (0.2 mL) was added dropwise. The mixture was stirred at 18–20 °C for 12 h and then worked up in the usual manner as described for the Jones oxidation of **13** to give **1b** (10 mg, 68%) after chromatography (SiO_2, benzene–

hexane–THF, 11/5/1): bp 92–96 °C (2.7 mm) [lit.[2d] bp 110–112 °C (5 mm)].

2-*tert*-Butoxycarbonyl-3-methoxycarbonylmethyl-2-(*cis*-2-pentenyl)cyclopentanol (13b, R′ = *t*-Bu). A solution of **10b** (R′ = *t*-Bu, 37 mg, 0.11 mmol) and $NaBH_4$ (6 mg, 0.16 mmol) in MeOH (1.5 mL) was refluxed for 1 h. The mixture was quenched with AcOH (0.1 mL) and concentrated in vacuo. Column chromatography (SiO_2, benzene–AcOEt, 5/1) of the residue gave **13b** (R′ = *t*-Bu, 36 mg, 96%): bp 75–79 °C (0.005 mm); ^1H NMR (CCl_4) δ 0.98 (t, 3, CH_3), 1.20–2.69 (m, 21), 3.60 (s, 3, CH_3O), 3.96 (m, 1, CHO), 5.21–5.54 (m, 2, HC=CH); IR (neat) 3509 (OH), 1721 cm^{-1} (C=O).

Anal. Calcd for $C_{18}H_{30}O_5$: C, 66.23; H, 9.26. Found: C, 66.28; H, 9.50.

2-*tert*-Butoxycarbonyl-3-methoxycarbonylmethyl-2-(*cis*-2-pentenyl)cyclopentanone (14b, R′ = *t*-Bu). To a solution of **13b** (R′ = *t*-Bu, 15 mg, 0.046 mmol) in CH_2Cl_2 (1 mL) was added dropwise 2 M chromic acid (0.1 mL). The mixture was stirred at 16–20 °C for 12 h and then diluted with AcOEt. Upon the usual workup as described for the oxidation of **15**, there was obtained **14b** (R′ = *t*-Bu, 10 mg, 67%) after column chromatography (SiO_2, benzene–hexane–AcOEt, 10/5/1): bp 79–83 °C (0.01 mm); ^1H NMR (CCl_4) δ 0.97 (t, 3, CH_3), 1.29–2.79 (m, 11), 1.45 (s, 9, CH_3), 3.64 (s, 3, CH_3O), 4.94–5.59 (m, 2, HC=CH); IR (neat) 1738 cm^{-1} (C=O).

Anal. Calcd for $C_{18}H_{28}O_5$: C, 66.64; H, 8.70. Found: C, 66.87; H, 8.94.

Methyl *dl*-Jasmonate (1b) from 14b (R′ = *t*-Bu). A solution of **14b** (R′ = *t*-Bu, 7.2 mg, 0.022 mmol) in benzene (1 mL) containing a catalytic amount of *p*-toluenesulfonic acid was refluxed for 20 min. After the usual workup, the residue was chromatographed (SiO_2, benzene–AcOEt, 10/1) to give **1b** (4.5 mg, 90%): ^{13}C NMR (multiplicity, carbon no.) δ 14.1 (q, 12), 20.6 (t, 11), 25.5 (t, 4), 27.2 (t, 8), 37.8 (t, 2 or 5), 38.0 (d, 3), 38.8 (t, 5 or 2), 51.6 (q, 13), 54.0 (d, 7), 124.9 (d, 9), 134.0 (d, 10), 172.5 (s, 1), 218.8 (s, 6); IR and ^1H NMR data were identical with those of an authentic sample.

Registry No.—**1b**, 20073-13-6; **2b**, 63569-04-0; (*E*)-**4**, 32815-00-2; (*Z*)-**4**, 75314-31-5; **5** (R′ = Me), 63528-42-7; **5** (R′ = *t*-Bu), 63528-43-8; **7a** (R′ = Me), 63528-44-9; **7a** (R′ = *t*-Bu), 63528-45-0; **7b** (R′ = Me), 63528-46-1; **8a** (R′ = Me), 63528-47-2; **8a** (R′ = *t*-Bu), 63528-48-3; **9a** (R′ = Me), 63528-49-4; **9b** (CR′ = Me), 63528-50-7; **10a** (R′ = Me), 63528-51-8; **10a** (CR′ = *t*-Bu), 63528-52-9; **10b** (R′ = Me), 63528-53-0; **10b** (R′ = *t*-Bu), 63528-54-1; **13a** (R′ = Me), 63528-55-2; **13b** (R′ = Me), 63534-37-2; **13b** (R′ = *t*-Bu), 63528-56-3; **14a** (R′ = Me), 55254-74-5; **14b** (R′ = Me), 55254-73-4; **14b** (R′ = *t*-Bu), 63528-57-4; **15**, 51388-61-5; $AcCH_2CO_2Me$, 105-45-3; pentynyl bromide, 16400-32-1; $AcCH_2CO_2$-*t*-Bu, 1694-31-1.

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Cyclodimerization of Styrene

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The cyclodimerization of styrene in the presence of sulfuric acid or Amberlyst-15 resin yields a 1:1 mixture of *cis*- and *trans*-1-methyl-3-phenylindan (**1a** and **1b**) via (*E*)-1,3-diphenyl-1-butene (**4**). 1-Methyl-3-phenylindene (**8**) and 3-methyl-1-phenylindene (**9**) were synthesized and converted to **1a** and **1b**. Base-catalyzed equilibration of **1a** and **1b** as well as **8** and **9** gave **1a**:**1b** (80:20) and **8**:**9** (30:70), respectively.

cis- and *trans*-1-methyl-3-phenylindan (**1a** and **1b**) can be obtained by cyclodimerization of styrene (**2**) with sulfuric acid,[2a–g] phosphoric acid,[3a–d] polyphosphoric acid (PPA),[3b] alumina–silica,[3a] perchloric acid,[3d] chlorosulfonic acid,[3d] or by passing styrene over hot promoted B_2O_3.[4] This reaction may proceed through the cation **3**, which can eliminate a proton to form the alkene **4**, cyclize to **1a** and **1b**, or yield polymer, as shown in Scheme I.

The low-temperature dimerization kinetics of **2** to **1a** and **1b** have been reported to be second order, whereas high-temperature kinetics are complex.[3d] Two isomeric forms of **1** have been reported[5] and identified[6] as **1a**, mp 9.5 °C, and **1b**, mp 25.5 °C. It has been reported that **1a**:**1b** as a 50:45 mixture was converted to a 62:38 ratio by stirring with 10% $AlBr_3$[7] and that **1a** is isomerized to an 82:18 ratio of **1a**:**1b** with $AlCl_3$.[5] The tertiary, twice-benzylic hydrogen of **1** is reported to be more reactive in forming a radical intermediate than the tertiary benzylic hydrogen.[8]

We sought **1a** and **1b** in order to study their stereochemistry and clarify their relative thermodynamic stability. The structure and stability of **1a** and **1b** were studied through equilibration experiments and by preparations from indenes. Sulfuric acid, ethylaluminum dichloride ($EtAlCl_2$),[9] and Amberlyst-15 (A-15),[10] an insoluble sulfonic acid resin, were tested as catalysts for the cyclodimerization reaction. Using A-15 allowed convenient monitoring of this reaction. Samples were periodically withdrawn from the A-15-catalyzed reactions and analyzed by GC.[11] The linear dimer **4** appears to be