the mixture is stirred for 1 h at 0 °C. Workup with saturated ammonium chloride solution and CH_2Cl_2, followed by flash chromatography (cyclohexane/CH_2Cl_2, 4:6), affords the pure products **2a,b** and **5a,b**.

(4*R*,5*S*)-1,5-Dimethyl-4-phenyl-3-(3'-methyl-2'-butenoyl)imidazolidin-2-one (2a). Reaction from **1a** and 3-methyl-2-butenoyl chloride affords 12.8 g (94%) of **2a** as white crystals: mp 158 °C; IR (Nujol) 1715, 1660, 1630 cm^{-1}; ^1H NMR δ 0.8 (d, 3 H, J = 6 Hz), 1.95 (s, 3 H), 2.09 (s, 3 H), 2.85 (s, 3 H), 3.9 (dq, 1 H, J = 6, 7 Hz), 5.35 (d, 1 H, J = 7 Hz), 7.1–7.4 (m, 6 H, vinyl + Ar H); ^{13}C NMR δ 15.0, 21.1, 27.9, 28.2, 54.0, 59.3, 117.3, 127.0, 127.9, 128.5, 137.1, 155.8; $[\alpha]_D$ -105.4° (*c* 1.2, CH_2Cl_2); MS, *m/e* 272 (M^+), 189, 176, 108, 57. Anal. Calcd for $C_{16}H_{20}N_2O_2$: C, 70.56; H, 7.40; N, 10.29. Found: C, 70.44; H, 7.39; N, 10.31.

(4*S*,5*R*)-1,5-Dimethyl-4-phenyl-3-(3'-methyl-2'-butenoyl)imidazolidin-2-one (2b). Reaction from **1b** and 3-methyl-2-butenoyl chloride affords 12.5 g (92%) of **2b** as white crystals: mp 159 °C; $[\alpha]_D$ +106.1° (*c* 0.9, MeOH). Anal. Calcd for $C_{16}H_{20}N_2O_2$: C, 70.56; H, 7.40; N, 10.29. Found: C, 70.49; H, 7.41; N, 10.26.

(4*R*,5*S*)-1,5-Dimethyl-4-phenyl-3-propanoylimidazolidin-2-one (5a). Reaction from **1a** and propanoyl chloride affords 11.3 g (92%) of **5a** as white crystals: mp 90 °C; IR (Nujol) 1765, 1740 cm^{-1}; ^1H NMR δ 0.8 (d, 3 H, J = 6 Hz), 1.1 (t, 3 H, J = 5 Hz), 2.85 (s, 3 H), 3.0 (q, 2 H, J = 5 Hz), 3.9 (dq, 1 H, J = 6, 7 Hz), 5.3 (d, 1 H, J = 7 Hz), 7.0–7.4 (m, 5 Ar H); ^{13}C NMR δ 8.6, 14.9, 28.1, 29.3, 54.0, 59.3, 127.0, 128.0, 128.5, 136.9, 173.5; $[\alpha]_D$ -54.7° (*c* 1, CH_2Cl_2); MS, *m/e* 246 (M^+), 217, 189, 94. Anal. Calcd for $C_{14}H_{18}N_2O_2$: C, 68.27; H, 7.37; N, 11.37. Found: C, 68.19; H, 7.35; N, 11.40.

(4*S*,5*R*)-1,5-Dimethyl-4-phenyl-3-propanoylimidazolidin-2-one (5b). Reaction from **1b** and propanoyl chloride affords 11.4 g (93%) of **5b** as white crystals: mp 91 °C; $[\alpha]_D$ +54.2° (*c* 1, CH_2Cl_2). Anal. Calcd for $C_{14}H_{18}N_2O_2$: C, 68.27; H, 7.37; N, 11.37. Found: C, 68.23; H, 7.36; N, 11.39.

General Procedure for Alkylation of 3-Acylimidazolidin-2-ones 2a,b and 5a,b. To a solution of the 3-acylimidazolidin-2-one **2a,b** or **5a,b** (30 mmol) in THF (40 mL) at -78 °C is added 30 mmol of lithium diisopropylamide (LDA) in THF (20 mL). After 1 h, a solution of the appropriate alkyl halide (30 mmol) in THF (20 mL) is slowly dropped and the mixture is allowed to warm to 0 °C in 12 h. Workup with 2 M HCl and CH_2Cl_2, followed by flash chromatography on silica gel (cyclohexane/CH_2Cl_2, 6:4), yields the products **3a,b** or **6** and **8** as diastereomeric mixtures, the ratios of which are determined on the basis of the ^{13}C NMR spectra.

(4*R*,5*S*,2'*R*)-1,5-Dimethyl-4-phenyl-3-[2'-(1-propen-2-yl)-5'-methyl-4'-hexenoyl]imidazolidin-2-one (3a). Reaction from **2a** and 1-bromo-3-methyl-2-butene affords 8.5 g (83%) of **3a** as white crystals: diastereomeric ratio 96:4; mp 71 °C; IR (Nujol) 1740, 1670, 900 cm^{-1}; ^1H NMR δ 0.75 (d, 3 H, J = 6 Hz), 1.45 (s, 3 H), 1.6 (s, 3 H), 1.8 (s, 3 H), 2.0–2.6 (m, 3 H), 2.8 (s, 3 H), 3.8 (dq, 1 H, J = 6, 7 Hz), 4.5–5.1 (m, 3 H), 5.25 (d, 1 H, J = 7 Hz), 7.2 (m, 5 Ar H); ^{13}C NMR δ 15.0, 17.6, 21.2, 25.7, 28.2, 30.1, 50.3, 53.5, 59.7, 112.8, 121.8, 127.0, 128.3, 133.0, 137.0, 144.0, 172.9; $[\alpha]_D$ -88.8° (*c* 1, CH_2Cl_2); MS, *m/e* 340 (M^+), 272, 189, 108, 71. Anal. Calcd for $C_{21}H_{28}N_2O_2$: C, 74.08; H, 8.29; N, 8.23. Found: C, 74.18; H, 8.27; N, 8.21.

(4*S*,5*R*,2'*S*)-1,5-Dimethyl-4-phenyl-3-[2'-(1-propen-2-yl)-5'-methyl-4'-hexenoyl]imidazolidin-2-one (3b). Reaction from **2b** and 1-bromo-3-methyl-2-butene affords 8.2 g (80%) of **3b** as white crystals: diastereomeric ratio 97:3; mp 73 °C; $[\alpha]_D$ +90.1° (*c* 1.02, CH_2Cl_2). Anal. Calcd for $C_{21}H_{28}N_2O_2$: C, 74.08; H, 8.29; N, 8.23. Found: C, 74.13; H, 8.28; N, 8.24.

(4*R*,5*S*,2'*S*)-1,5-Dimethyl-4-phenyl-3-(2'-methyldecanoyl)imidazolidin-2-one (6). Reaction from **5a** and 1-iodooctane affords 8.4 g (79%) of **6** as a low-melting solid: diastereomeric ratio 97:3; IR (Nujol) 1730, 1680 cm^{-1}; ^1H NMR δ 0.8 (d, 3 H, J = 6 Hz), 0.85 (t, 3 H, J = 4 Hz), 1.1 (d, 3 H, J = 6 Hz), 1.2 (m, 14 H), 1.4–1.8 (m, 1 H), 2.8 (s, 3 H), 3.9 (dq, 1 H, J = 6, 7 Hz), 5.3 (d, 1 H, J = 7 Hz), 7.3 (m, 5 Ar H); ^{13}C NMR δ 14.1, 15.0, 16.8, 22.7, 28.3, 29.3, 29.6, 31.9, 34.2, 37.5, 53.8, 59.4, 127.1, 128.0, 128.4, 137.0, 173.5; $[\alpha]_D$ -15.0° (*c* 1, CH_2Cl_2); MS, *m/e* 358 (M^+), 261, 248, 242, 189, 87, 85. Anal. Calcd for $C_{22}H_{34}N_2O_2$: C, 73.70; H, 9.56; N, 7.81. Found: C, 73.57; H, 9.57; N, 7.78.

(4*S*,5*R*,2'*R*)-1,5-Dimethyl-4-phenyl-3-(2'-methyl-3'-phenylpropanoyl)imidazolidin-2-one (8). Reaction from **5b** and benzyl bromide affords 8.7 g (86%) of **8** as white crystals: diastereomeric mixture 96:4; mp 88 °C; IR (Nujol) 1730, 1685 cm^{-1}; ^1H NMR δ 0.75 (d, 3 H, J = 6 Hz), 1.05 (d, 3 H, J = 6 Hz), 2.4 (dd, 1 H, J = 9, 14 Hz), 2.8 (s, 3 H), 3.4 (dd, 1 H, J = 6, 14 Hz), 3.8 (dq, 1 H, J = 6, 7 Hz), 4.35 (m, 1 H, J = 6, 9 Hz), 5.35 (d, 1 H, J = 7 Hz), 6.9–7.4 (m, 5 Ar H); ^{13}C NMR δ 15.0, 16.3, 28.2, 39.5, 39.8, 53.7, 59.4, 125.9, 126.9, 127.8, 128.2, 128.4, 129.3, 136.7, 139.7, 176.0; $[\alpha]_D$ +11.7° (*c* 1, CH_2Cl_2); MS, *m/e* 336 (M^+), 223, 189, 94, 85. Anal. Calcd for $C_{21}H_{24}N_2O_2$: C, 74.97; H, 7.19; N, 8.33. Found: C, 74.87; H, 7.18; N, 8.35.

General Procedure for Reductive Cleavage of 3-Acylimidazolidin-2-ones 3a,b, 6, and 8. A solution of the imidazolidin-2-one **3a,b**, **6**, or **8** (20 mmol) in THF (40 mL) is slowly added at 0 °C under inert atmosphere to a stirred suspension of 1.6 g (40 mmol) of LAH in THF (30 mL), and the mixture is stirred at 0 °C for 1 h. After the reaction is quenched by cautious addition of MeOH (3 mL), workup with 2 M HCl and ethyl acetate, followed by flash chromatography on silica gel (cyclohexane/ethyl acetate, 8:2), provides the alcohols **4a,b**, **7**, and **9**. Further elution with ethyl acetate gives the imidazolidin-2-ones **1a** or **1b** in 90–93% yield.

(*R*)-2-(1-Propen-2-yl)-5-methyl-4-hexen-1-ol (Lavandulol) (4a). Reductive cleavage of **3a** gives 2.8 g (92%) of **4a** as an oil: IR (neat) 3360, 895 cm^{-1}; ^1H NMR δ 1.65 (s, 3 H), 1.8 (s, 6 H), 1.9–2.4 (m, 3 H), 2.1 (br s, 1 H, OH), 3.45 (d, 2 H, J = 4 Hz), 4.75 (s, 1 H), 4.85 (s, 1 H), 5.1 (t, 1 H, J = 5 Hz); ^{13}C NMR δ 17.8, 19.6, 25.7, 28.5, 50.0, 63.8, 112.9, 122.2, 132.7, 145.6; $[\alpha]_D$ -10.04° (*c* 1, MeOH) (lit.[9a] $[\alpha]_D$ for *S* isomer +10.8° (*c* 0.94, MeOH)). Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.97; H, 11.78.

(*S*)-2-(1-Propen-2-yl)-5-methyl-4-hexen-1-ol (Lavandulol) (4b). Reductive cleavage of **3b** gives 2.75 g (90%) of **4b** as an oil: $[\alpha]_D$ +9.94° (*c* 1, MeOH) (lit.[9a] $[\alpha]_D$ +10.8° (*c* 0.94, MeOH)). Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.97; H, 11.77.

(*S*)-2-Methyldecan-1-ol (7). Reductive cleavage of **6** gives 2.8 g (82%) of **7** as an oil: IR (neat) 3400, 1460 cm^{-1}; ^1H NMR δ 0.95 (m, 6 H), 1.3 (m, 14 H), 2.3 (br s, 1 H, OH), 3.4 (m, 2 H); ^{13}C NMR δ 14.1, 16.6, 22.7, 27.0, 29.5, 29.6, 30.0, 31.9, 33.2, 35.7, 68.4; $[\alpha]_D$ -9.4° (*c* 1, CH_2Cl_2) (lit.[13,14] -10.0° (*c* 4.2, CH_2Cl_2)). Anal. Calcd for $C_{11}H_{24}O$: C, 76.68; H, 14.04. Found: C, 76.52; H, 14.06.

(*R*)-2-Methyl-3-phenylpropan-1-ol (9). Reductive cleavage of **8** gives 2.5 g (83%) of **9** as an oil: IR (neat) 3350 cm^{-1}; ^1H NMR δ 0.88 (d, 3 H, J = 6 Hz), 1.55 (br s, 1 H, OH), 1.95 (m, 1 H), 2.45 (dd, 1 H, J = 6, 13 Hz), 2.80 (dd, 1 H, J = 5, 13 Hz), 3.5 (d, 2 H, J = 5 Hz), 7.2 (m, 5 Ar H); ^{13}C NMR δ 16.5, 37.8, 39.7, 67.6, 125.9, 128.3, 129.2, 140.2; $[\alpha]_D$ +10.3° (*c* 1; C_6H_6) (lit.[13,16] $[\alpha]_D$ +11.0° (*c* 1, C_6H_6). Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.87; H, 9.40.

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Registry No. **1a**, 92841-65-1; **1b**, 112791-04-5; **2a**, 112712-53-5; **2b**, 112791-05-6; **3a**, 112712-54-6; **3b**, 112791-06-7; **4a**, 498-16-8; **4b**, 50373-53-0; **5a**, 112712-55-7; **5b**, 112791-07-8; **6**, 112712-56-8; **7**, 79847-79-3; **8**, 112712-57-9; **9**, 77943-96-5; 3-methyl-2-butenoyl chloride, 3350-78-5; propanoyl chloride, 79-03-8; 1-bromo-3-methyl-2-butene, 870-63-3; 1-iodooctane, 629-27-6; benzyl bromide, 100-39-0.

Type II Intramolecular [2 + 2] Cycloadditions of Alkenes with Alkylvinylketenes. Synthesis of Methyl Jasmonate

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The cycloaddition of ketenes to alkenes provides an attractive route to cyclobutanones and a general method for functionalization of alkenes. We have recently initiated a program to develop the intramolecular version of this

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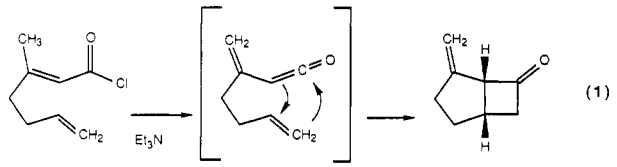
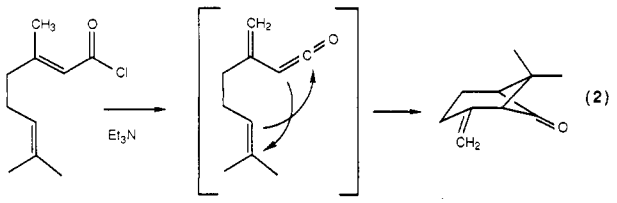
reaction into a general synthetic method.[1,2] Excellent results have been obtained with vinyl ketenes.[1b,c,g,h,2b,c,e,g] The alkene-containing side chain can be attached to the α,β-unsaturated ketene at the ketene carbon (type I), the α-carbon (type II), or β-carbon (type III).[1d] Type II vinylketenes can be prepared by treatment of β,β-disubstituted α,β-unsaturated acid chlorides with triethylamine in benzene or toluene at reflux (eq 1 and 2).[1g,h] We have



(1)



(2)

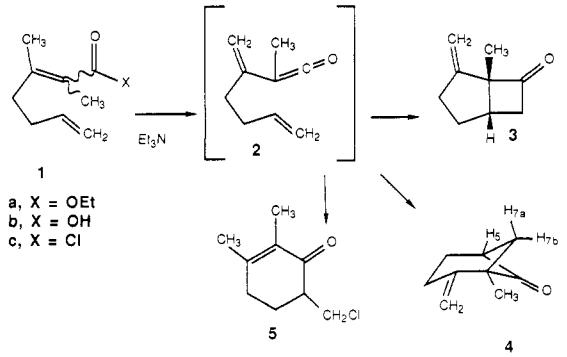
shown that deprotonation occurs largely on the less-substituted γ-carbon ($CH_3 > CH_2 > CH$).[1h] The stereochemistry of the α,β-unsaturated acid chloride has no effect on the mixture of vinylketenes formed. The regiochemistry of the cycloaddition is controlled by the electronic effects of substituents on the double bond. Alkenes in which the internal end of the double bond is more substituted give bicyclo[3.2.0]heptanones (eq 1) while those in which the terminal end of the double bond is more substituted give bicyclo[3.1.1]heptanones (eq 2).

We report here extensions of these studies to type II α,β-unsaturated ketenes bearing the unsaturated chain on the α-carbon and an alkyl group on the ketene carbon. Intramolecular cycloaddition will give a bicycloheptanone with an additional alkyl group at the ring fusion. These ketenes, e.g. **2**, are readily prepared by treatment of α,β,β-trisubstituted α,β-unsaturated acid chlorides with triethylamine in toluene at reflux.

Reaction of allylacetone with the sodium salt of triethyl phosphonopropionate[3] in DME at reflux gave **1a** in 72% yield as a mixture of stereoisomers. Hydrolysis of **1a** with aqueous barium hydroxide at reflux gave acid **1b**[4] in 75% yield, which was converted to the acid chloride **1c** by treatment with sodium hydride and oxalyl chloride in benzene at 50–60 °C.

Slow addition of a toluene solution of **1c** to a solution of triethylamine in toluene at reflux followed by heating for 3 h at reflux gave a 4% yield of **5** and a reproducible 36% yield of a difficultly separable 4:1 mixture of **3** and a minor isomer tentatively identified as **4**. As expected, there were no products derived from the isomeric unsaturated ketenes with a trisubstituted double bond. Attempts to increase the yield by modification of concentration or reaction temperature were unsuccessful.

The structure of the major product **3**, which was the expected product of the cycloaddition, was easily established by the characteristic coupling pattern of the three cyclobutyl protons in the NMR spectrum. The spectral data support the assignment of structure **4** to the minor isomer. The IR spectrum shows the presence of a cyclobutanone. The ^1H NMR spectrum is typical of a 2-methylenebicyclo[3.1.1]heptan-6-one.[1,5] The exo methylene protons absorb at δ 4.78, H_5 absorbs at δ 3.21, H_{7a} absorbs at δ 1.97 as a doublet, J = 9 Hz, and H_{7b} absorbs at δ 1.75 as a doublet of doublets, J = 9, 6.6 Hz. The isolation of **5** supports the assignment of structure **4** to the minor isomer, since **5** must be derived from addition of hydrogen chloride to **4** or an unlikely anti-Markovnikov Friedel–Crafts type addition of the acid chloride to the double bond of **1c**.



If the structure of **4** is correctly assigned this would be a rare instance where the electronic effects of substituents on the double bond do not fully control the regiochemistry of a ketene cycloaddition.[6] The loss of regiocontrol probably results from increased steric hindrance caused by the introduction of the methyl group on the ketene carbon.[6e] Similar phenomena have occasionally been observed. Reaction of methylenecyclopropane with a dialkylketene gives both regioisomers,[6b] while reaction with a chloroalkylketene gives only one regioisomer.[6d] The lack of regiocontrol in the cycloaddition of **2** suggests that this reaction is concerted since only **3** should be formed in a stepwise reaction.

The steric effects of the methyl group are clearly seen in the reactions of the ketenes derived from treatment of **6**[7] and **7** with triethylamine. No cyclobutanones were obtained in either case despite the enhanced nucleophilicity of the more highly substituted alkene. Cyclohexenone **8** was isolated in 37% yield from **6**. No cyclic products were obtained from **7**.

Vinyl cyclobutanones such as **3** are versatile synthetic intermediates, suitable for the synthesis of 2,3-disubsti-

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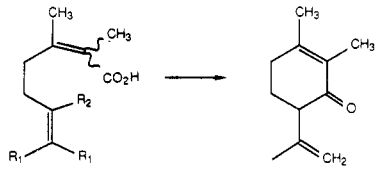
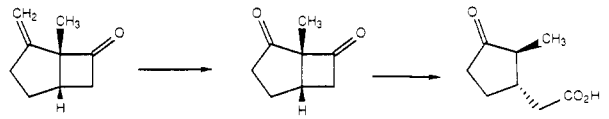


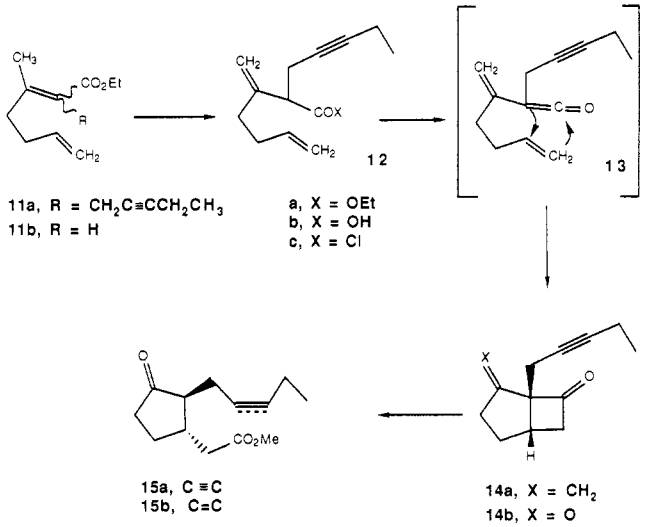
6, R_1 = CH_3, R_2 = H
7, R_1 = H, R_2 = CH_3 8

tuted cyclopentanones. Ozonolysis of the double bond of **3** gave the unstable diketone **9**[8,10c] in good yield. Chromatography on silica gel gave pure **9** in only 9% yield. Silica gel catalyzes a retro-Dieckmann condensation[8,10c] to give the keto acid **10**[9] which was isolated in 31% yield.



3 9 10

Replacement of the methyl group of **3** with an unsaturated five-carbon chain will permit this approach to be used for the synthesis of methyl jasmonate (**15b**). Ozonolysis of the exo methylene double bond cannot be carried out in the presence of a double bond on the side chain. Fortunately, ozonolysis of double bonds can be carried out selectively in the presence of triple bonds.[10]



11a, R = $CH_2C{\equiv}CCH_2CH_3$
11b, R = H

a, X = OEt
b, X = OH
c, X = Cl

12 13

15a, C ≡ C
15b, C=C

14a, X = CH_2
14b, X = O

All attempts to prepare **11a** by the phosphonate modification of the Wittig reaction were unsuccessful. Alkylation of triethyl phosphonoacetate with 1-bromo-2-pentyne gave the requisite phosphono ester which could not be induced to add to allylacetone. We therefore chose to introduce the 2-pentynyl group by alkylation of **11b**. Reaction of triethyl phosphonoacetate[3] with allylacetone gave **11b**[11] as a mixture rich in the *E* isomer. Conversion of **11b** to the dienolate with LDA followed by alkylation with 1-bromo-2-pentyne[12] gave **12a** in 75% yield, contaminated with regioisomers derived from deprotonation of the methylene group. The selective formation of **12a** was anticipated since deprotonation with LDA should occur selectively on the group syn to the carbonyl group[13] and the methyl group is kinetically more acidic than the methylene group.

Although β,γ-unsaturated ester **12a** could not be isomerized to **11a**,[14] it was equally well suited for the preparation of **14a**. Saponification of **12a** with potassium ethoxide in aqueous *tert*-butyl alcohol at reflux gave an 84% yield of **12b** without concomitant conjugation of the double bond. Conversion of **12b** to the acid chloride **12c** and addition to triethylamine in toluene at reflux gave a 45% yield of a 5:1 mixture of **14a** and a compound tentatively identified as the bicyclo[3.1.1]heptane isomer. Ozonolysis of **14a** in methanol at −78 °C followed by reductive workup gave the crude diketone **14b** which was stirred with potassium carbonate in methanol for 4 h at 25 °C to give methyl dehydrojasmonate (**15a**) in 47% yield and recovered **14a** in 15% yield. This completes the synthesis since methyl dehydrojasmonate has been reduced to methyl jasmonate.[10c,15]

These results indicate that type II intramolecular cycloadditions of alkylvinylketenes occur only with unhindered monosubstituted double bonds. The synthesis of methyl jasmonate indicates the utility of 4-methylenebicyclo[3.2.0]heptan-6-ones for the synthesis of cyclopentanone derivatives.

Experimental Section

Materials and Methods. NMR spectra were recorded on a Varian XL-300 spectrometer in $CDCl_3$. Chemical shifts are reported in δ and coupling constants are reported in hertz. IR spectra were obtained on a Perkin-Elmer 683 spectrometer. All air-sensitive reactions were run under nitrogen in flame-dried glassware with magnetic stirring. Reagents were added via oven-dried syringes through septa. All solvents for air- or moisture-sensitive reactions were dried by standard procedures.

Preparation of Starting Materials. 1-Bromo-2-pentyne was prepared from 2-pentyn-1-ol by treatment with PBr_3.[12] Mixtures of unsaturated esters rich in the *E* isomer were obtained by adding the ketone to a solution of the sodium salt of triethyl phosphonoacetate (prepared from NaH) in DME at 25 °C and heating the resulting solution for 30 min at reflux.[3] The desired α,β-unsaturated esters were obtained in 60–80% yield as a mixture containing 75–85% of the *E* isomer. Hydrolysis of the ester was effected by heating at reflux an aqueous suspension of the ester with barium hydroxide for 12–24 h.

4-Methylene-5-methylbicyclo[3.2.0]heptan-6-one (3). A solution of acid **1b**[4] (754 mg, 4.49 mmol) was converted to the acid chloride as described below for the preparation of **14a**. The acid chloride **1c** in 2 mL of toluene was added via syringe to a solution of triethylamine (6.3 mL, 44.9 mmol) in 20 mL of toluene at reflux. The reaction mixture was heated at reflux for 3 h, cooled, filtered through Celite, and concentrated to afford 1.176 g of crude product containing some toluene. Flash chromatography on silica gel (25:1 hexane–EtOAc) gave 222 mg (36.4%) of a 4:1 mixture of **3** and **4** followed by 32 mg (4%) of **5**. Isomers **3** and **4** were separated by preparative GC (7 ft × $^3/_8$ in., 10% XF-1150 on Chromosorb PAW at 90 °C).

Data for **3**: ^{1}H NMR 5.01 (br s, 1), 4.89 (br s, 1), 3.21 (dd, 1, J = 18.0, 8.8), 2.75 (dd, 1, J = 18.0, 5.6), 2.50–2.69 (m, 3), 1.95 (dddd, 1, J = 14.7, 11.7, 7.6, 6.6), 1.83 (br dd, 1, J = 14.7, 7.5),

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1.30 (s, 3); ^{13}C NMR 210.4, 151.9, 107.3, 74.0, 48.8, 37.7, 32.4, 30.1, 16.8; IR (neat) 2965, 1780, 1650 cm^{-1}; t_R 50 min. Anal. Calcd for $C_9H_{12}O$: 136.0889. Found: 136.0887.

Data for **4**: ^{1}H NMR 4.78 (br s, 2), 3.21 (m, 1), 2.55–2.65 (m, 1), 2.3–2.4 (m, 1), 2.15–2.25 (m, 2), 1.97 (d, 1, J = 9, H_7), 1.75 (dd, 1, J = 9, 6.6, H_7), 1.28 (s, 3); ^{13}C NMR 152.6, 106.3, 69.4, 54.9, 30.1, 28.5, 26.0, 14.5; IR ($CDCl_3$) 1775 cm^{-1}; t_R 55 min.

Data for **5**: ^{1}H NMR 3.96 (dd, 1, J = 10.9, 3.8), 3.68 (dd, 1, J = 10.9, 7.7), 2.57 (m, 1), 2.42 (m, 1), 2.26 (m, 1), 1.94 (s, 3), 1.85 (m, 2), 1.77 (s, 3); ^{13}C NMR 155.3, 130.7, 47.6, 44.8, 31.8, 25.7, 21.5, 10.9; IR (neat) 2920, 1660, 1638, 1378 cm^{-1}. Anal. Calcd for $C_9H_{13}ClO$: 172.0656. Found: 172.0662. The data are in agreement with those reported for 2,3-dimethyl-2-cyclohexenone.[16]

2,3-Dimethyl-6-(1-methylethenyl)-2-cyclohexen-1-one (8). Acid **6**[7] (0.1307 g, 0.72 mmol) in 4 mL of dry benzene was added dropwise into a solution of NaH (0.1053 g of 60% suspension in mineral oil, hexane washed, 2.63 mmol) in 1 mL of dry benzene. The reaction mixture was stirred at 25 °C for 15 min. The reaction was cooled to 0 °C, and oxalyl chloride (0.16 mL, 1.83 mmol) was added dropwise. The mixture was stirred at 25 °C for 2.5 h and heated at reflux for 0.5 h. The solvent and excess oxalyl chloride were removed in vacuo to give a quantitative yield of crude acid chloride. The crude acid chloride in 25 mL of dry toluene was added dropwise to a boiling solution of triethylamine (0.3 mL, 2.15 mmol) in 18 mL of dry toluene. The reaction mixture was heated at reflux for 4 h. Water (10 mL) was added and the aqueous layer was extracted with hexane (4 × 50 mL). The combined organic layer was dried ($MgSO_4$) and the solvent was removed in vacuo to give 0.1913 g of crude product. Flash chromatography on silica gel (95:5 pentane–ether) gave 0.0340 g (36.7%) of **8**: ^{1}H NMR 1.75 (br s, 3), 1.78 (br s, 3), 1.92 (br s, 3), 2.14–1.93 (m, 4), 2.97 (dd, 1 J = 5.1, 10.5), 4.70–4.71 (m, 1), 4.91–4.92 (m, 1); ^{13}C NMR 198.9, 154.1, 144.0, 131.0, 113.0, 54.0, 31.7, 27.2, 21.4, 20.7, 10.6; IR ($CDCl_3$) 3060, 2900, 2860, 1705, 1650, 1630, 1435, 1415, 1365 cm^{-1}. Anal. Calcd for $C_{11}H_{16}O$: 164.1202. Found: 164.1204.

Ozonolysis of 3. Ozonolysis of **3** (119 mg, 0.876 mmol) as described below for the preparation of **14b** gave crude unstable diketone. Flash chromatography on silica gel (4:1 hexane–EtOAc) gave 11 mg (9%) of diketone **9** followed by 42 mg (31%) of keto acid **10**.

Data for 1-methylbicyclo[3.2.0]heptane-2,7-dione (**9**): 3.47 (dd, 1, J = 18.3, 8.8), 3.08 (dd, 1, J = 18.3, 5.7), 2.96 (m, 1), 2.70 (ddd, 1, J = 18.8, 12.0, 8.9), 2.52 (ddd, 1, J = 18.8, 8.5, 1.5), 2.30 (dddd, 1, J = 13.4, 12.0, 8.5, 6.8), 2.16 (dddd, 1, J = 13.4, 8.9, 1.5, 1.5), 1.31 (s, 3); IR (neat) 3060, 2970, 1780, 1725 cm^{-1}.

Data for *trans*-3-oxo-2-methylcyclopentaneacetic acid (**10**): 11.06 (br s, 1), 2.71 (dd, 1, J = 15.4, 4.8), 2.37–2.47 (m, 2), 2.24–2.34 (m, 1), 2.08–2.21 (m, 2), 1.79–1.89 (m, 1), 1.47–1.61 (m, 1), 1.11 (d, 3, J = 6.8); ^{13}C NMR 178.1, 49.5, 40.8, 38.4, 37.1, 27.2, 12.2, the carbonyl carbon was not observed. The data are in agreement with those previously reported.[9]

Ethyl 3-Methylene-2-(2-pentynyl)-6-heptenoate (12a). *n*-Butyllithium (2.5 mL of 2.2 M in hexane, 5.5 mmol) was added to a solution of diisopropylamine (0.77 mL, 5.5 mmol) in 7 mL of dry THF at 0 °C. The solution was stirred for 1 h, treated with HMPA (0.96 mL, 5.5 mmol), stirred for 30 min, and cooled to −78 °C. Ethyl 3-methyl-2,6-heptadienoate[11] (840 mg, 5.0 mmol) in 2 mL of dry THF was added dropwise to the LDA solution at −78 °C. The resulting solution was stirred for 1 h at −78 °C and treated with 1-bromo-2-pentyne[12] (696 mg, 4.74 mmol) in 2 mL of dry THF. The reaction mixture was stirred for 2 h at −78 °C and allowed to warm slowly to room temperature. The mixture was quenched with 10 mL of water and the organic layer was separated. The aqueous layer was extracted three times with 10 mL of ether. The combined organic layers were washed with 5% hydrochloric acid and brine. It was then dried ($MgSO_4$) and concentrated in vacuo to give 1.165 g of crude product. Chromatography on silica gel (hexane–EtOAc) gave 801 mg (72%) of pure **12a**: ^{1}H NMR 5.82 (ddt, 1, J = 16.6, 10.4, 6.4), 5.03 (br d, 1, J = 16.6), 5.00 (br d, 1, J = 10.4), 4.95 (br s, 2), 4.16 (q, 2, J = 7.1), 3.17 (t, 1, J = 7.7), 2.65 (ddt, 1, J = 16.6, 8.3, 2.4), 2.42 (ddt, 1, J = 16.6, 7.1, 2.4), 2.08–2.25 (m, 6), 1.26 (t, 3, J = 7.1), 1.08 (t, 3, J = 7.6); ^{13}C NMR 172.6, 145.2, 137.9, 114.8, 112.3, 83.1, 76.6, 60.6, 51.4, 34.2, 31.6, 21.2, 14.1 (2 carbons), 12.3; IR (neat) 2980, 2935, 1735, 1642, 1448 cm^{-1}. Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.58; H, 9.40.

3-Methylene-2-(2-pentynyl)-6-heptenoic Acid (12b). Potassium ethoxide (998 mg, 11.9 mmol) was added to a solution of ester **12a** (546 mg, 2.33 mmol) in 10 mL of *tert*-butyl alcohol and 5 mL of water. The solution was heated at 80 °C for 1.5 h. The reaction mixture was cooled and acidified with 5% hydrochloric acid. The solution was extracted with several portions of ether, which were combined, washed with brine, dried ($MgSO_4$), and concentrated in vacuo to give 780 mg of crude product. Chromatography on silica gel (4:1 hexane–acetone) gave 403 mg (84%) of pure acid **12b**: ^{1}H NMR 5.82 (ddt, 1, J = 16.6, 10.3, 6.4), 5.03 (br d, 1, J = 16.6), 5.00 (br d, 1, J = 10.3), 4.98 (br s, 2), 3.22 (t, 1, J = 7.7), 2.66 (ddt, 1, J = 16.6, 8.0, 2.5), 2.44 (ddt, 1, J = 16.6, 7.0, 2.5), 2.08–2.26 (m, 6), 1.09 (t, 3, J = 7.4); ^{13}C NMR 179.6, 144.6, 137.7, 114.9, 112.9, 83.3, 76.2, 51.3, 34.2, 31.5, 20.9, 14.0, 12.3.

5-(2-Pentynyl)-4-methylenebicyclo[3.2.0]heptan-6-one (14a). A solution of acid **12b** (214 mg, 1.04 mmol) was added to a suspension of hexane-washed NaH (47 mg of 60% dispersion in mineral oil, 1.17 mmol) in 2 mL of dry benzene at 0 °C. The mixture was stirred for 10 min and treated with oxalyl chloride (0.45 mL, 5.16 mmol). The reaction mixture was allowed to warm to room temperature slowly and heated at 55–60 °C for 1 h. The reaction mixture was cooled and concentrated in vacuo. The resulting mixture of acid chloride **12c** and NaCl was taken up in 2 mL of toluene and added via syringe to a solution of triethylamine (1.45 mL, 10.3 mmol) in 10 mL of toluene at reflux. The reaction mixture was heated at reflux for 3 h, cooled, filtered through Celite to remove NaCl and triethylammonium chloride, and concentrated in vacuo to afford 194 mg of crude product. Flash chromatography on silica gel (25:1 hexane–EtOAc) gave 87 mg (45%) of an inseparable ≈5:1 mixture of **14a** and an unidentified minor component.

Data for **14a** as determined from the mixture: ^{1}H NMR 5.06 (br s, 1), 4.88 (br s, 1), 3.19 (dd, 1, J = 18.1, 8.9), 3.00 (m, 1), 2.74 (dd, 1, J = 18.1, 5.4), 2.71 (dt, 1, J = 16.9, 2.4), 2.51–2.66 (m, 2), 2.32 (dt, 1, J = 16.9, 2.4), 2.13 (ddt, 2, J = 15.0, 7.4, 2.4), 1.98 (m, 1), 1.81 (m, 1), 1.10 (t, 3, J = 7.4); ^{13}C NMR 208.8, 149.9, 107.8, 83.1, 76.9, 75.1, 49.6, 35.3, 33.1, 30.1, 21.0, 14.2, 12.2; IR (neat) 2950, 1775, 1645, 1435 cm^{-1}.

Partial data for the minor isomer as determined from the mixture: ^{1}H NMR 4.85 (br d, 1), 4.78 (br d, 1); ^{13}C NMR 150.5, 107.1, 54.5, 28.5, 26.4, 18.4, 14.1.

Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.56. Found: C, 82.57; H, 8.68.

Methyl Dehydrojasmonate (15a). A solution of **14a** (26.5 mg, 0.14 mmol) in 3 mL of methanol was cooled to −78 °C and treated with ≈0.25 mmol of ozone in oxygen. The reaction mixture was flushed with nitrogen for 15 min at −78 °C and dimethyl sulfide (10 mg, 0.16 mmol) in 1 mL of methanol was added to the reaction mixture. The resulting solution was stirred at −78 °C for 2 h, 0 °C for 1 h, and 25 °C for 1 h and concentrated in vacuo to give the crude unstable diketone **14b**: ^{1}H NMR 3.45 (dd, 1, J = 18.3, 9.1), 3.25 (m, 1), 3.05 (dd, 1, J = 18.3, 5.4).

The diketone **14b** was added to a solution of potassium carbonate (151 mg, 7.24 mmol) in 2 mL of methanol. The solution was stirred for 4 h at 25 °C and concentrated in vacuo. The residue was taken up in ether and washed with water and brine, dried ($MgSO_4$), and concentrated in vacuo to give 22 mg of a 3:1 mixture of **15a** and recovered **14a**. Flash chromatography on silica gel (4:1 hexane–EtOAc) gave 13 mg (47%) of **15a** and 4 mg (15%) of recovered **14a**.

Data for **15a**: 3.72 (s, 3), 2.85 (dd, 1, J = 15.4, 4.3), 2.47–2.61 (m, 3), 2.34–2.44 (m, 2), 2.24–2.33 (m, 1), 2.07–2.17 (m, 3), 1.90–1.97 (m, 1), 1.45–1.59 (m, 1), 1.09 (t, 3, J = 7.6); ^{13}C NMR 217.5, 172.5, 83.6, 75.7, 52.8, 51.6, 38.5, 37.8, 37.7, 27.1, 17.4, 14.1, 12.3; IR (neat) 2960, 1740, 1735 cm^{-1}; MS, m/z 222, 207, 193, 191, 163, 149, 147, 133, 122 (100), 109, 107, 91, 79, 71, 65, 55, 43, 41. The spectral data are in agreement with those previously reported.[15]

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Registry No. **1b**, 113948-94-0; **1c**, 113948-95-1; **3**, 113948-96-2; **4**, 113975-13-6; **5**, 113948-97-3; **6**, 113975-14-7; **6** (acid chloride), 113949-06-7; **8**, 113948-98-4; **9**, 113948-99-5; **10**, 113949-00-1; **12a**, 113949-01-2; **12b**, 113949-02-3; **12c**, 113949-03-4; **14a**, 113949-04-5; **14b**, 113949-05-6; **15a**, 114029-37-7; ethyl 3-methyl-2,6-heptadienoate, 103273-76-3; 1-bromo-2-pentyne, 16400-32-1.

A Study of the Fluxional Behavior in 2,11-Dithia[3.3]orthocyclophane Using Molecular Mechanics and Dynamic NMR Analysis

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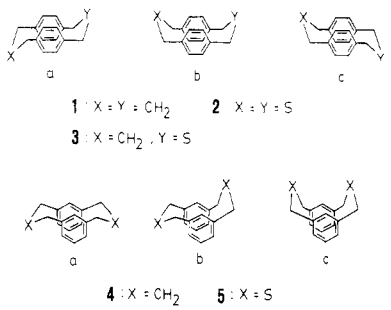
In the conformational studies of the fluxional behavior of [3.3]cyclophanes, a unique feature is the resemblance of their bridge-wobbling process to that in cyclohexane and derivatives. [3.3]Paracyclophane **1** was the first example of the series to be studied by variable-temperature ^1H NMR spectroscopy.[1] The results indicated that **1** exists as a mixture of the "chair" **1a** and "boat" **1b** conformations in a 1:2 ratio in solution. The free-energy conformational barrier was estimated[1] to be about 11.7 kcal mol^{-1}. Another independent study[2] of the same chair–boat interconversion also gave a similar energy barrier. A recent detailed structural study[3] of [3.3]metacyclophane **4** indicated that in the crystals, **4** exists as the conformer **4a**. Variable temperature NMR studies[3] also supported the existence of **4a** as the major isomer, with a barrier to isomerization to the other conformers of 11.5 kcal mol^{-1}. The conformational barriers for the $CH_2CH_2CH_2$ bridge inversion processes in **1** and **4** are thus very similar but found to be only slightly higher than that in cyclohexane (11.1 kcal mol^{-1}).[4] Conformational studies of the corresponding parent dithia[3.3]cyclophanes **2**[5] and **5**[6] were, however, less successful. In either case, the CH_2SCH_2 protons remained as an unresolved singlet even at very low temperatures.



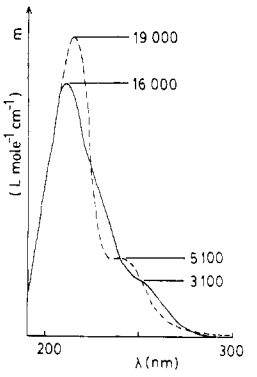
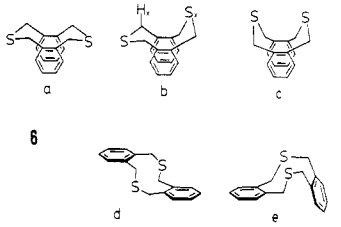


Figure 1. UV absorption spectra of **5** (—) and **6** (- - -) [30 mg/L in cyclohexane].

An obvious explanation would be due to the fast conformational interconversions with very low barriers; an alternative is the possibility that the two diastereotopic methylene protons in the "frozen" conformer have almost identical chemical shifts and are thus unresolved. The latter argument is supported by results from the conformational studies[7] of the thia[3.3]paracyclophane **3**. The energy barriers for the wobbling of the $CH_2CH_2CH_2$ (**3a** ⇄ **3b**) and CH_2SCH_2 (**3b** ⇄ **3c**) bridges were estimated at 11.5 and ca. 10 kcal mol^{-1}, respectively. The latter corresponds favorably with the conformational barrier in 1,4-dithiane (10.3 kcal mol^{-1}).[8] These data clearly show that although the longer CH_2SCH_2 bridge allows a higher flexibility, the conformational barrier for such a bridge inversion process may still be sufficiently high to be observed by ^1H NMR spectroscopy. Before this work, the fluxional behavior of the other parent dithia[3.3]cyclophane **6** was not examined. We now report the conformational studies of **6** by molecular mechanics calculations and variable-temperature ^1H NMR analysis.



2,11-Dithia[3.3]orthocyclophane **6**[9] was prepared by the coupling of 1,2-bis(bromomethyl)benzene and 1,2-bis(mercaptomethyl)benzene under high dilution conditions. Our attempts using the reported procedure[10] gave much lower and nonreproducible yields of the desired product. In order to establish whether **6** is likely to adopt the syn conformation, the UV absorption spectrum of **6** (Figure 1) was compared to that of dithia[3.3]metacyclophane **5**, which is known to exist in the syn conformation in both solution (^1H NMR spectroscopy)[6b] and in solid state (X-ray crystallography).[6] UV absorption spectroscopy has been used in some cases to illustrate the face-to-face arrangement of two benzene rings in cyclophanes which normally result in bathochromic shift and broadening of absorption bands.[11,12] A significant difference between the spectra

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