Anal. Calcd for $C_{24}H_{22}O_6N_2S$: C, 61.80; H, 4.75; N, 6.01. Found: C, 61.65; H, 4.67; N, 5.95.

1-(2,6-Dideoxy-β-D-*arabino*-hexopyranosyl)cytosine (3). A solution of 175 mg (0.38 mmol) of thionucleoside **10** in anhydrous methanol (25 ml) was placed in a glass sealing tube (50 ml) an which after saturation with ammonia at 0° was sealed and heated at 110–120° for 20 h. The tube was cooled and opened and its contents were evaporated to dryness. The residue, already homogeneous by TLC in A and C, was purified by PLC on cellulose plates (Machery and Nagel 300–50 with 0.5-mm coatings) with 2-propanol–concentrated ammonia–water (7:1:2). Elution of the main zone (R_f 0.71) with water, evaporation of the eluate to dryness, and trituration with methanol–acetone afforded 51 mg (53%) of **3** as fine crystals of mp 135–140° after softening from 120° on and $[\alpha]^{25}D$ −4.3° (*c* 0.55, H_2O) [reported[7] mp 137–140° and $[\alpha]^{25}D$ −4° (*c* 0.38, H_2O)]; CD (H_2O) θ +1200 (240 nm), +1300 (278), cf. Figure 1. The uv data in 0.1 N HCl and 0.1 N NaOH were identical, i.e. ϵ_{max} (pH 13)/ϵ_{max} (pH 1) 0.68; the NMR spectrum in D_2O was superimposable on that reported[7] for oxamicetin derived **3**.

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Registry No.—**3**, 52598-18-2; **4**, 6067-28-3; **5**, 6027-64-1; **6**, 57459-51-5; **7**, 5139-56-0; **8**, 57459-52-6; **9**, 57459-53-7; **10**, 57459-54-8; **11**, 57459-55-9; **12**, 57459-56-0; acetic acid, 108-24-7; methanesulfonyl chloride, 124-63-0; benzoyl chloride, 98-88-4.

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Regiospecificity of the 1,4 Cycloaddition of 2-Methyl-1-penten-3-one to Methyl Crotonate and to Methyl Methacrylate

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The thermal cycloaddition of 2-methyl-1-penten-3-one (**6**) to methyl methacrylate (**2**) gave 3,6-dimethyl-2-ethyl-1-oxacyclohex-2-ene-6-carboxylic acid methyl ester (**12**), and subsequent reduction of the ester group and acid-catalyzed cyclization gave 1,4-dimethyl-5-ethyl-6,8-dioxabicyclo[3.2.1]octane (**14**). In contrast to this result, the addition of **6** to methyl crotonate (**7**) gave 3,6-dimethyl-2-ethyl-1-oxacyclohex-2-ene-5-carboxylic acid methyl ester (**10**), and reduction and cyclization gave 3,7-dimethyl-1-ethyl-2,6-dioxabicyclo[2.2.2]octane (**11**). A dimer of **6**, 3,6-dimethyl-2-ethyl-6-propanoyl-1-oxacyclohex-2-ene (**16**), was formed in both thermal addition reactions, and the dimerization of **2** to yield 2-methyl-5-methylene-1,6-hexanedioic acid dimethyl ester (**18**) co-occurred with the addition of **6** to **2**.

Brevicomin (**5**),[1] frontalin (**4**),[2] and multistriatin (**9**)[3] are related bicyclic ketal structures that are components of the aggregation pheromones of three bark beetle species, *Dendroctonus brevicomis, Dendroctonus frontalis,* and *Scolytus multistriatus.* The aggregation pheromones of these insects are potentially useful agents for survey and control of insect populations. These compounds have been synthesized by different routes,[4–6] one of which utilized the cycloaddition of an α,β-unsaturated ketone to an α,β-unsaturated ester.[7]

Mundy and coworkers synthesized **4** via the cycloaddition of methyl vinyl ketone (**1**) to methyl methacrylate (**2**).[7] The cycloaddition product (**3**) was subsequently reduced and cyclized to yield **4.** One critical feature of this synthetic approach is the regiospecificity of the 1,4-cycloaddition reaction. Mundy's synthesis was based on earlier work of Smith and coworkers,[8] and in both studies addition proceeded via path a and not b. Furthermore, cycloadditions with dienophiles such as α,β-unsaturated nitriles, al-

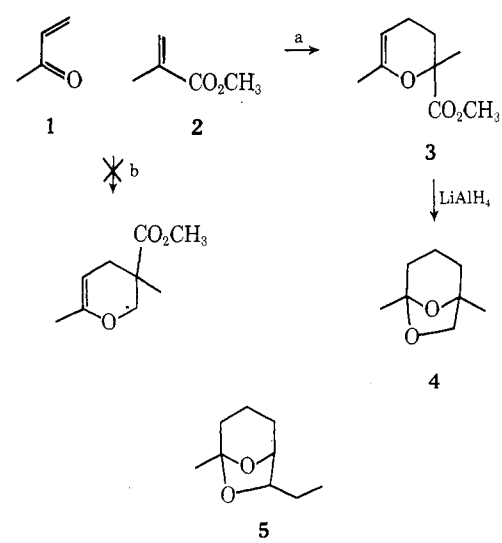


Table I
NMR Data for the 2-Oxacyclohexene Derivatives

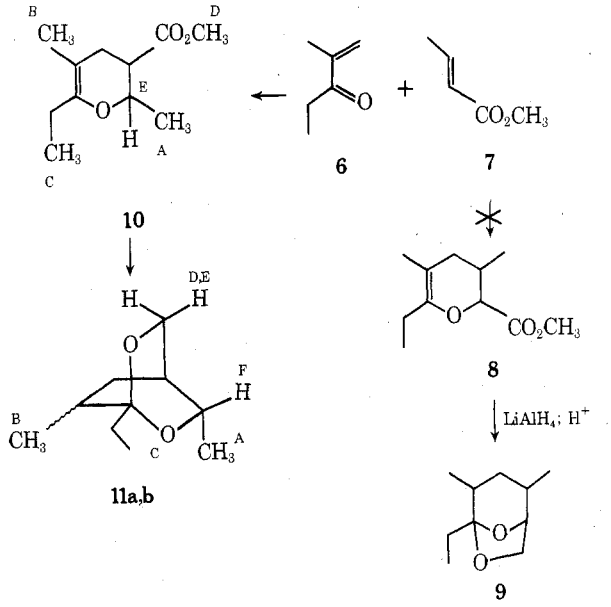
Compd	Chemical shifts,[a] δ, ppm				
	Protons				
	A	B	C	D	E
10	1.27 (3 H, d, J = 6.0)	1.62 (3 H, s)	1.02 (3 H, t, J = 7.5)	3.72 (3 H, s)	3.84 (1 H, m)
12	1.45 (3 H, s)	1.56 (3 H, s)	1.05 (3 H, t, J = 7.3)	3.70 (3 H, s)	
16	1.28 (3 H, s)	1.57 (3 H, s)	1.02 (3 H, t, J = 7.5)	1.09 (3 H, t, J = 6.5)	

[a] s = singlet, d = doublet, t = triplet, m = multiplet; J (observed splittings) in hertz.

dehydes, ketones, alcohols, and vinyl ethers, enamines, vinyl carbamates, and vinyl ureas have been reported; and in each case the 6-substituted 2-oxacyclohexene derivative was formed.[9,10]

Results and Discussion

We explored an analogous reaction pathway for the synthesis of **9.** This reaction sequence involved the addition of 2-methyl-1-penten-3-one (**6**) to methyl crotonate (**7**), which yielded a carbomethoxy 2-oxacyclohexene intermediate. In principle, intermediates **8** or **10** could result from the cycloaddition reaction. The reduction and cyclization of **8** would yield the desired ketal **9;** however, **10** would lead to 3,7-dimethyl-1-ethyl-2,6-dioxabicyclo[2.2.2]octane (**11**).



The ir and MS spectra provided evidence that a carbomethoxy 2-oxacyclohexene derivative (**10**) was formed from the thermal addition of **6** and **7.** The ir spectrum contained a strong carbonyl absorption at 1737 cm^{-1} and a vinyl ether absorption at 1686 cm^{-1}. The mass spectrum gave a molecular ion at *m/e* 198 and an M − CO_2CH_3 at 139. The NMR signals are assigned in Table I, and these data show that 3,6-dimethyl-2-ethyl-1-oxacyclohex-2-ene-5-carboxylic acid methyl ester (**10**), not the 6-carbomethoxy 2-oxacyclohexene derivative (**8**), was the reaction product. The NMR signals provided evidence for an ethyl group, a vinyl methyl group, a methyl group on a carbon atom α to an ether oxygen atom, and a methine proton α to an ether oxygen atom. The chemical shifts of the methyl group doublet at 1.27 ppm and the methine proton multiplet at 3.8 ppm are inconsistent with structure **8.** The methyl group at C-5 in **8** is on the carbon atom β to the ether oxygen atom and the carbomethoxy group, and the predicted chemical shift for this methyl group would be upfield from the observed value of 1.27 ppm. Also, the methine proton at C-6 in **8** is α to both the ether oxygen atom and the carbomethoxy group, and the signal should appear as a doublet at lower field than 3.8 ppm.

Reduction of **10** with lithium aluminum hydride and acid treatment yielded a mixture of two compounds (**11a** and **11b,** ~50:50) which were separated by GLC. As shown in Table II, the NMR, ir, and MS spectra of **11a** and **11b** were similar and indicated that both structures were 3,7-dimethyl-1-ethyl-2,6-dioxabicyclo[2.2.2]octanes. The mass spectra contained a molecular ion at *m/e* 170, and characteristic absorptions associated with CH, CC, and CO stretching and bending frequencies were observed in the ir spectra. Although some similarities were noted, the spectra of **11a** and **11b** were not identical with those recorded for any of the isomers of **9.**[11] Products **11a** and **11b** were stable in dilute CCl_4 and $CDCl_3$ solutions; however, neat samples appeared to be unstable. A related bicyclic acetal, 2,6-dioxabicyclo[2.2.2]octane, was previously described as "... hygroscopic and unstable toward oligomerization under ordinary conditions ...".[12]

The combined NMR, ir, and MS data and their mode of formation indicated that **11a** and **11b** were epimeric at C-7.[13] One of the characteristic differences between the isomers of **11** and the isomers of **9** was the presence of a doublet near 1.3 ppm in **11a** and **11b.** The methyl groups in **9** are on carbon atoms β to an oxygen atom, and the corresponding signals in the NMR occur at higher field than 1.3 ppm. The C-3 methyl group in **11** is on the carbon atom α to an oxygen atom, and a chemical shift of 1.3 ppm is consistent with that predicted.

The cycloaddition characteristics of the enone **6** were tested by the addition of **6** to a commonly used dienophile, methyl methacrylate (**2**). The addition occurred in the manner previously reported for the addition of acrolein[8] or methyl vinyl ketone[7] to **2.** 3,6-Dimethyl-2-ethyl-1-oxacyclohex-2-ene-6-carboxylic acid methyl ester (**12**) was identi-

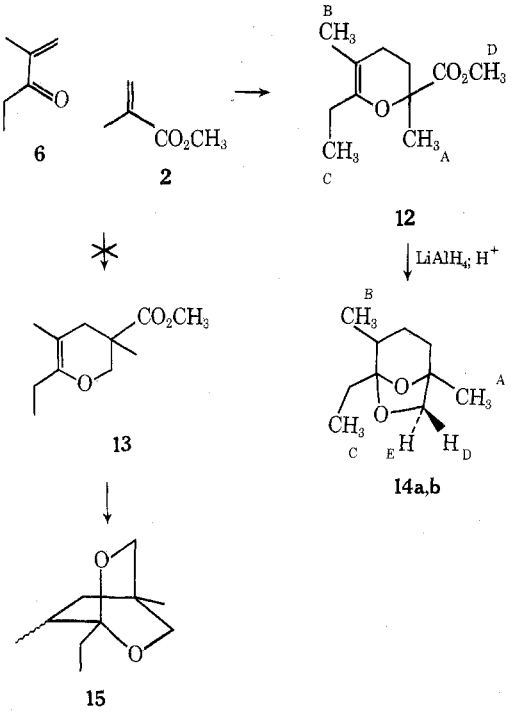


Table II
NMR Data for the Dioxabicyclooctanes

Compd	Chemical shifts,[a] δ, ppm					
	Protons					
	A	B	C	D	E	F
11a	1.27 (3 H, d, J = 6.5)	0.96 (3 H, d, J = 6.5)	0.89 (3 H, t, J = 7.5)	3.99 (2 H, m)		4.17 (1 H, m)
11b	1.26 (3 H, d, J = 6.5)	0.98 (3 H, d, J = 6.5)	0.88 (3 H, t, J = 8.0)	3.99 (2 H, m)		4.17 (1 H, m)
14a	1.31 (3 H, s)	0.83 (3 H, d, J = 6.2)	0.93 (3 H, t, J = 7.3)	3.41 (1 H, dd, J_1 = 6.8, J_2 = 1.0)	3.86 (1 H, d J = 6.6)	
14b	1.31 (3 H, s)	0.99 (3 H, d, J = 7.2)	0.92 (3 H, t, J = 7.3)	3.38 (1 H, dd, J_1 = 6.5, J_2 = 1.8)	3.88 (1 H, d, J = 6.7)	

[a] dd = doublet of doublets; J (observed splittings) in hertz.

fied as a reaction product, but the 5-carbomethoxy-2-oxacyclohexene derivative **13** was not found.

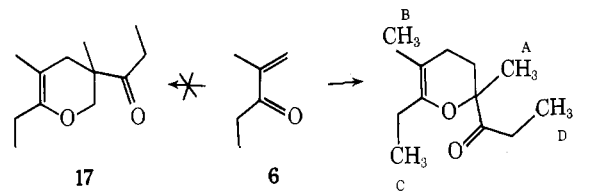
The structure of **12** is based on the NMR, ir, and MS spectra. The ir spectrum has characteristic absorptions for the vinyl ether and the ester group, and the mass spectrum has a molecular ion at m/e 198 and an M − CO_2CH_3 at 139. The NMR spectrum supports structure **12** but not **13.** The singlets at 1.56 and 1.45 ppm are assigned to the methyl groups at C-3 and C-6, respectively. The predicted high-field signals (1.2–1.3 ppm) for a C-5 methyl group and low-field signals (3.0–3.5 ppm) for C-6 methylene protons for **13** were not observed.

The $LiAlH_4$ reduction of **12** and subsequent acid-catalyzed cyclization yielded 1,4-dimethyl-5-ethyl-6,8-dioxabicyclo[3.2.1]octane diastereomers **14a** and **14b,** which were separated by GLC. Their MS and ir spectral characteristics and those of the isomeric bicyclic ketal **9** were similar;[11] the mass spectrum gave a molecular ion at m/e 170. The presence of the C-1 methyl group in **14a** and **14b** is clearly demonstrated by the presence of a singlet at 1.31 ppm in the NMR spectrum.

The relative stereochemistry at C-4 was assigned according to the relative chemical shifts observed for endo and exo methyl groups in the isomers **9**[11] in which the chemical shifts for the endo methyl groups were always upfield of the shifts for the exo methyl groups. Since the C-4 methyl group in **14a** is 0.09 ppm upfield of the corresponding methyl group in **14b,** the methyl group at C-4 is assigned the endo configuration in **14a** and the exo configuration in **14b.**

The NMR spectra precluded the possibility that structure **15** was formed and thereby supported the conclusion that **12** and not **13** was formed from the cycloaddition of **6** and **2.** The bicyclic ketal structure **15** contains four methylene protons α to oxygen atoms, but only two downfield methylene proton signals were observed in the NMR spectrum. Also, the bridgehead methyl group in **15** is on the carbon atom β to the oxygen atoms, and the predicted chemical shift for these protons would be upfield from the observed methyl group at 1.31 ppm.

In the thermal addition reactions, where **6** was added to **2** and to **7,** the dimerization of **6** yielded an additional cycloaddition product, 3,6-dimethyl-2-ethyl-6-propanoyl-1-oxacyclohex-2-ene (**16**).[14] At lower temperature (210°) and with shorter heating periods (2 hr), **16** was the major product in the GLC chromatogram. A sample of **16** was isolated and purified by preparative GLC, and the identity of the



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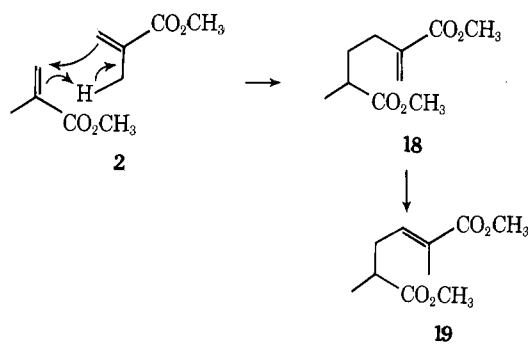
compound was established by spectrometric methods. The MS and ir spectra of **16** were related to those of **10** and **12.** The mass spectrum gave a molecular ion at m/e 196 and an M − CH_3CH_2CO peak at 139, and the ir spectrum contained carbonyl (1720 cm^{-1}) and vinyl ether (1685 cm^{-1}) peaks. The chemical shift assignments are consistent with structure **16.** Structure **17** would be expected to show a downfield absorption for the CH_2O group; these are not present in the spectrum.

In the reaction mixture of **6** and **2,** the tail-to-tail dimerization of **2** yielded 2-methyl-5-methylene-1,6-hexanedioic acid dimethyl ester (**18**). This structure was consistent with



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the recorded spectral data. The mass spectrum gave a molecular ion (m/e 200) and M − CO_2CH_3 (141) and M − HCO_2CH_3 (140) peaks. The ir absorptions corresponded to ester groups (1735 and 1725 cm^{-1}) and to a terminal double bond (1628 and 945 cm^{-1}). In the NMR spectrum, signals were observed for the C-2 methyl group (1.17 ppm), the carbomethoxy groups (3.67 and 3.74 ppm), and the terminal olefinic protons (5.55 and 6.16 ppm).

The terminal dimerization of **2** in the absence of radical, cationic, or anionic catalysts has been investigated, and **19** and **18** were reported as major and minor products, respectively.[15] In the absence of catalysts the dimerization can proceed via the ene mechanism with one molecule of **2** acting as the ene component and a second acting as the eno-

phile. The initial product, **18**, was the only product isolated under our conditions; however, the isomerization of **18** to **19** could occur with other reaction conditions.

Conclusions

Colonge and Descotes reviewed the 1,4-cycloaddition reactions of α,β-unsaturated carbonyl compounds with substituted olefins.[9] They observed that with terminally unsubstituted dienophiles the electronic nature of the functional group on th dienophile did not affect the direction of addition, but that high electron density on the dienophile did facilitate the addition. The dimerization of acrolein to yield 2-oxacyclohexene-6-carboxaldehyde is a typical example of this type of cycloaddition, and theoretical treatments have been provided by Devaquet and Salem[16] and by Alston and Shillady.[17]

Our observations that the addition of **6** and **2** yielded **12** and that the dimerization of **6** gave **16** are consistent with reported thermal cycloaddition reactions where enones such as acrolein and methyl vinyl ketone were added to isobutylene,[8,18] methyl acrylate,[8] and **2**.[7,8] Since in each case the 6-substituted 2-oxacyclohexene derivative was the only reported product, the methyl group and the carbomethoxy group apparently have the same net effect in controlling the regiospecificity of the reaction.

In the cycloaddition of **6** and **2**, the effects of the methyl group and the carbomethoxy group were in the same direction; however, the cycloaddition of **6** and **7** provided a novel situation where the directing effects of the methyl group were in opposition to those of the carbomethoxy group. In the latter case, the 5-carbomethoxy-2-oxacyclohexene derivative (**10**) was formed.

The cycloaddition of α,β-unsaturated aldehydes and ketones to substituted olefins represents a potential direct route to intermediates, which can be converted into dioxabicyclo[3.2.1]octanes; however, some characteristics of this reaction should be considered. The cycloaddition reaction may yield dimers such as **16** and **18** which complicate the purification scheme and reduce the yield of the substituted dihydropyran derivative. Furthermore, dienophile substituent effects can lead to 5-carbomethoxy-2-oxacyclohexene-intermediates, which give dioxabicyclo[2.2.2]octanes on reduction and cyclization.

Experimental Section

Mass spectra were recorded on an Hitachi RMU-6E; the ir spectra in carbon tetrachloride solution on a Perkin-Elmer 621; and the Fourier transform ^{1}H NMR spectra in deuteriochloroform solution on a Varian XL-100 as δ values with tetramethylsilane as an internal reference. Preparative GLC was performed with a Varian Aerograph Series 2700, and quantitative determinations were based on peak areas relative to an internal standard.

Addition of 2-Methyl-1-penten-3-one (6) to Methyl Crotonate (7). A solution of **6**[13] (0.98 g, 10 mmol), **7** (1.00 g, 10 mmol), and toluene (1% hydroquinone, 0.5 ml) was heated for 4 hr at 210°. The thermal additions were performed at autogenous pressure in glass tubes (6 mm × 60 cm, filled to ⅓ capacity), which were sealed under nitrogen and rocked continuously during the reaction. One product, 3,6-dimethyl-2-ethyl-6-propanoyl-1-oxacyclohex-2-ene (**16**), was isolated by GLC fractionation with a SE-30 column (5% on 60–80 AW DMCS Chromosorb G: silylated glass, 10 mm × 3.6 m; He, 100 ml/min; 190°) in 38% yield (by GLC peak area). A single peak with retention time (t_R) 10.0 min was collected for NMR, ir, MS, and elemental analysis. The GLC analysis indicated that **16** was the major product and that 3,6-dimethyl-2-ethyl-1-oxacyclohex-2-ene-5-carboxylic acid methyl ester (**10**) was not formed.

Infrared spectrum (CCl_4) 2995, 2930, 2890, 1720, 1685, 1450, 1370, 1160, 1138, 1100, 1063, 905 cm^{-1}; mass spectrum *m/e* (rel intensity) 27 (6), 29 (16), 41 (15), 43 (100), 57 (14), 69 (11), 81 (7), 95 (11), 121 (7), 139 (49), 196 (M^+, 11).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.46; H, 10.20. Found: C, 73.26; H, 10.35.

The reaction was repeated with **6** (1.96 g, 20 mmol) and **7** (10.0 g, 100 mmol), and toluene (1% hydroquinone, 10 ml) at 260–280°. The reaction mixture was fractionated by short-path distillation, and the volatile material was collected in two fractions: A, 37–42° (49 mm), and B, 79–85° (0.2 mm). Both fractions were analyzed by GLC, and A contained toluene and unreacted starting material. The SE-30 fractionation of B gave **10**, with t_R 10.8 min (90% of fraction B, 13% overall yield). The fraction collected from the SE-30 column gave a single peak, t_R 17.4 min, when rechromatographed on a Carbowax 20M column (5% on AW DMCS 60–80 Chromosorb G; silylated glass, 6 mm × 6 m; He, 60 ml/min; 160°), and samples were collected for NMR, ir, MS, and elemental analyses. A minor peak (<2%) with retention time corresponding to **16** was observed in the GLC chromatogram of B.

Infrared spectrum (CCl_4) 2985, 2960, 2945, 1737, 1686, 1435, 1385, 1367, 1112, 1088, 1062, 1030, 902 cm^{-1}; mass spectrum *m/e* (rel intensity) 27 (17), 29 (37), 39 (16), 41 (41), 43 (23), 57 (40), 69 (100), 99 (10), 100 (10), 109 (11), 123 (15), 139 (34), 198 (M^+, 19).

Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.66; H, 9.09. Found: C, 66.46, H, 9.17.

Addition of 2-Methyl-1-penten-3-one (6) to Methyl Methacrylate (2). A solution of **6** (1.96 g, 20 mmol) and **2** (10 g, 100 mmol) and toluene (1% hydroquinone, 10 ml) was heated at 260–280° for 4.5 hr. The resulting mixture was fractionated by short-path distillation, and the solvent and unreacted starting material were removed as fraction A at 32–35° (49 mm). Fraction B was collected at 75–84° (0.2 mm) and redistilled to yield two fractions: B1, 75–79° (0.2 mm), 0.45 g; B2, 79–83° (0.2 mm), 1.9 g. GLC analysis of B1 indicated that this fraction contained 65% 3,6-dimethyl-2-ethyl-1-oxacyclohex-2-ene-6-carboxylic acid methyl ester (**12**). B2 contained 90% 2-methyl-5-methylene 1,6-hexanedioic acid dimethyl ester (**18**). The overall yields of **12** and **18** were 8 and 18.5%, respectively. Both products **12** and **18** were purified by GLC chromatography; **12** and **18** had t_R 8.4 and 10.8 min, respectively, on the SE-30 column, and **12** had t_R 12.9 min on the Carbowax 20M column.

12: infrared spectrum (CCl_4) 2995, 2975, 2960, 2940, 1757, 1735, 1686, 1145, 1372, 1295, 1158, 1114 cm^{-1}; mass spectrum *m/e* (rel intensity) 27 (12), 29 (29), 39 (15), 41 (42), 42 (100), 53 (9), 55 (14), 57 (68), 59 (9), 67 (8), 69 (95), 70 (8), 79 (8), 81 (18), 83 (6), 85 (8), 88 (6), 95 (18), 96 (6), 97 (6), 98 (8), 99 (14), 100 (5), 101 (5), 109 (46), 110 (42), 111 (11), 121 (14), 123 (17), 127 (9), 137 (14), 138 (15), 139 (57), 140 (8), 141 (34), 142 (6), 166 (17), 169 (7), 198 (M^+, 46), 199 (6).

Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.66; H, 9.09. Found: C, 66.81; H, 9.16.

18: infrared (CCl_4) 3030, 2985, 2960, 2885, 1735, 1725, 1628, 1460, 1435, 1195, 1170, 1150, 1065, 945 cm^{-1}; mass spectrum *m/e* (rel intensity) 27 (25), 29 (16), 39 (29), 40 (22), 41 (44), 53 (26), 55 (25), 56 (30), 57 (30), 59 (45), 69 (28), 81 (78), 88 (100), 109 (35), 113 (27), 125 (26), 126 (58), 140 (44), 141 (25), 168 (33), 169 (30), 200 (M^+, 3); NMR spectrum δ 1.17 (3 H, d, J = 7.0 Hz), 3.67 (3 H, s), 3.74 (3 H, s), 6.16 (1 H, m), 5.55 (1 H, d, J = 1.3 Hz).

Anal. Calcd for $C_{10}H_{16}O_4$; C, 60.00; H, 8.00. Found: C, 60.21; H, 8.11.

3,7-Dimethyl-1-ethyl-2,6-dioxabicyclo[2.2.2]octane (11a,b). A GLC purified sample of **10** (11.3 mg, 0.057 mmol) in 1 ml of tetrahydrofuran (THF) was dried over 4Å sieves for 24 hr and stirred with lithium aluminum hydride (2.5 ml of a 0.029 *M* THF solution, 0.071 mmol) at 25° for 30 min. A sulfuric acid solution (1 *M*) was added dropwise until the solution was acidic to pH paper (about 150 μl), and the mixture was allowed to stand for 14 hr. The THF solution was separated from the gray precipitate and placed over anhydrous sodium carbonate for 6 hr, and the resulting neutral solution was dried over 4-Å sieves for 14 hr. GLC chromatography on the SE-30 column at 150° showed one peak (37% yield by peak area), t_R 20.0 min; however, fractionation with a Carbowax 20M column at 125° gave two peaks at approximately equal size with t_R 23.4 and 24.3 min. The two peaks were collected and designated **11a** and **11b**, respectively. Neat samples of **11a,b** were unstable and formed two phases on standing at room temperature.

11a: infrared spectrum (CCl_4) 2975, 2935, 2875, 1465, 1373, 1204, 1152, 1128, 1063, 937, 925 cm^{-1}; mass spectrum *m/e* (rel intensity) 27(10), 29 (18), 43 (15), 54 (8), 55 (26), 57 (100), 71 (10), 72 (3), 81 (5), 86 (6), 95 (10), 99 (4), 128 (9), 170 (M^+, 9).

11b: infrared spectrum (CCl_4) 2980, 2945, 2880, 1465, 1375, 1205, 1165, 1130, 1064, 927 cm^{-1}; mass spectrum *m/e* (rel intensity) 27 (10), 29 (28), 41 (16), 43 (11), 54 (13), 55 (20), 57 (100), 71 (12), 72 (4), 81 (6), 86 (8), 95 (4), 99 (7), 128 (10), 170 (M^+, 10).

1,4-Dimethyl-5-ethyl-6,8-dioxabicyclo[3.2.1]octane (14a,b).

A GLC purified sample of **12** (14.0 mg, 0.071 mmol) was reduced with $LiAlH_4$ (0.071 mmol) and worked up as in the preceding experiment. The SE-30 fractionation yielded one peak (49% yield), t_R 14.0 min, and the elemental analysis was obtained for this material. Chromatography with Carbowax 20M gave two peaks of approximately equal size, t_R 12.7 and 13.5 min, which were designated **14a** and **14b**, respectively.

14a: infrared spectrum (CCl_4) 2985, 2945, 2895, 1462, 1382, 1130, 1112, 1045, 1040, 925, 920, 900 cm^{-1}; mass spectrum *m/e* (rel intensity) 27 (11), 29 (32), 41 (11), 43 (15), 55 (14), 57 (100), 72 (31), 81 (7), 96 (4), 114 (10), 128 (6), 140 (4), 170 (M^+, 10).

14b: infrared spectrum (CCl_4) 2985, 2940, 2885, 1453, 1378, 1122, 1105, 1043, 1030, 913 cm^{-1}; mass spectrum *m/e* (rel intensity) 27 (12), 29 (26), 41 (12), 43 (16), 55 (14), 57 (100), 72 (31), 81 (7), 96 (4), 114 (11), 128 (5), 140 (4), 170 (M^+, 9).

Anal. Calcd for $C_{10}H_{18}O_2$; C, 70.66; H, 10.59. Found: C, 70.51; H, 10.78.

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Registry No.—**2**, 80-62-6; **6**, 25044-01-3; **7**, 18707-60-3; **10**, 57428-74-7; **11a**, 57428-75-8; **11b**, 57457-89-3; **12**, 57428-76-9; **14a**, 57428-77-0; **14b**, 57428-78-1; **16**, 57428-79-2; **18**, 4513-62-6.

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Mass Spectrometric Studies of the Dioxabicyclo[3.2.1]octanes Multistriatin, Frontalin, and Brevicomin

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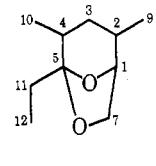
Mass spectra were recorded for three alkyl-substituted dioxabicyclo[3.2.1]octanes, 2,4-dimethyl-5-ethyl-6,8-dioxabicyclo[3.2.1]octane (multistriatin), 1,5-dimethyl-6,8-dioxabicyclo[3.2.1]octane (frontalin), and 5-methyl-7-ethyl-6,8-dioxabicyclo[3.2.1]octane (*exo*-brevicomin), and for the corresponding deuterium-labeled compounds 4,11-11-trideuteriomultistriatin, 4,4,10,10,10-pentadeuteriofrontalin, and 4,4,9,9,9-pentadeuterio-*exo*-brevicomin, and structures were assigned for the characteristic ions. Where possible the relative abundances of the observed ions were related to the alkyl group substituents, and a general fragmentation pattern was proposed.

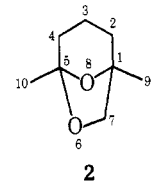
Multistriatin (**1**) was isolated and identified as one component of a three-component aggregation pheromone of the European elm bark beetle.[1] In the initial phase of the identification process, the mass spectrum exhibited several distinctive peaks, but this information did not provide definitive evidence for the bicyclic ketal ring system or the type of ring substitution.

After the structure of **1** was proved, the mass spectrum of **1** was compared with the reported spectra of known bicyclo[3.2.1]octane derivatives, including two insect pheromone components, frontalin (**2**)[2] and *exo*-brevicomin (**3**),[3] and to the known fragmentation patterns for cyclic ketals.[4] Inspection of the available data revealed that some ions were common to two or more of the bicyclic ketals. However, the identities of most of the ions were uncertain, and a fragmentation pattern for the substituted dioxabicyclo[3.2.1]octanes was not obvious.

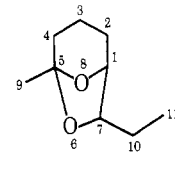
We collected three types of data for the dioxabicyclo[3.2.1]octanes **12**, and **3**: (1) unit resolution electron impact (EI) mass spectra, (2) unit resolution EI spectra of deuterium labeled compounds, (3) high-resolution EI spectra of unlabeled compounds. The objective of these experiments was to determine the characteristic fragments of these dioxabicyclo[3.2.1]octanes and the effects of alkyl substituents on the fragmentation pattern.



1



2



3

Results and Discussion

Multistriatin (**1**) exists as four diastereomers which have been synthesized and purified,[5] and the unit resolution spectrum of each isomer was recorded. Since no qualitative and only minor quantitative differences were observed in