A reactive lactonic dienophile – 3-carbethoxy-5,5-dimethyl-2(5*H*)-furanone. Application to the synthesis of a monoterpenoid lactone

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In contrast to the low dienophilicity generally observed for α,β-unsaturated lactones, the title compound **2** is shown to be a reactive dienophile. Under stannic chloride catalysis, it undergoes Diels–Alder reaction regio- and stereoselectively with a variety of dienes at room temperature. The synthesis of (±)-*o*-mentha-1,3-dien-1→8-olide (**20**) has been achieved by a two-step sequence using lactone ester **2**. Addition of **2** to 1-acetoxy-1,3-butadiene afforded epimeric acetoxy lactones **12** and **13** which were converted to the monoterpenoid lactone **20** by treatment with lithium iodide dihydrate in collidine.

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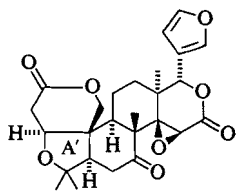
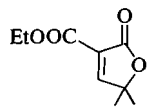
Alors que les lactones, α,β-non saturées ne sont généralement pas de bons dièmophiles, le composé **2** est un dièmophile réactif. Sous l'effet de la catalyse acide du chlorure stanneux, il subit, à la température ambiante, une réaction de Diels–Alder régio- et stéréo-sélective avec divers dièmes. On a réalisé la synthèse du (±)-*o*-menthadiène-1,3 olide-1→8 (**20**) en deux étapes à partir de la lactone ester **2**. L'addition de **2** à l'acétoxy-1 butadiène-1,3 fournit les acétoxy lactones épimères **12** et **13** qui peuvent être transformées dans la lactone **20** par traitement avec le dihydrate de l'iodure de lithium dans la collidine.

[Traduit par le journal]

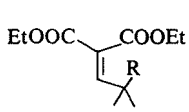
Although α,β-unsaturated esters and carboxylic acids have long been characterized as reactive dienophiles and have been widely used as such in organic synthesis (1), the Diels–Alder reaction of the corresponding lactones has not been extensively studied in spite of its potential utility as a more direct approach to useful intermediates. Possibly this is due to the expectation of a low level of reactivity for such compounds. In one known example (2), addition of 2,3-dimethyl-1,3-butadiene to coumarin was effected in only 22% yield under severe conditions while butadiene and isoprene failed to react. Fortunately, the reactivity of an α,β-unsaturated lactone should be enhanced, as predicted by the Alder rule (3), by introduction of an additional electron-withdrawing substituent to the potentially dienophilic double bond. For instance, γ,γ-dimethylaconic acid has been shown to be a useful dienophile which reacts efficiently with isoprene at high temperature (4). In our experience as well (5–7), the addition of a carbalkoxy substituent can produce a substantial increase in reactivity relative to the unsubstituted parent system. Our interest in lactonic dienophiles stems from a projected synthesis of the citrus bitter principal limonin (**1**) (8, 9). Carbethoxy activated lactone **2** would be a useful synthon for the introduction of the A′ ring. A close examination of the Diels–Alder characteristics of **2** (reactivity, orientation, and stereochemistry of adducts) is warranted prior to proceeding toward the ultimate objective of employing **2** in a Diels–Alder approach to limonin.



1



2



3 R = H
4 R = Br

Lactone ester **2**[1] was prepared in 67% yield from the known diester **3** (11) by bromination with *N*-bromosuccinimide followed by the cyclization of the resulting bromide **4** using silver oxide in aqueous tetrahydrofuran. Interestingly, a more economical procedure proved to be the pyrolytic cyclization of bromide **4** to give lactone ester **2** in 51% overall yield. In general, lactone ester **2** was found to react efficiently with a variety of dienes under stannic chloride catalysis.[2] The reaction occurred readily in ether at room temperature to give adducts in good yield (Table 1) with the exception of furan which produced only addition product **14**. With unsymmetrically substituted dienes (Entries 2 and 4–6), the adducts were found to be those predicted on the basis of the normal rules

[1]After the completion of this work, the preparation of the corresponding methyl ester was described using similar procedures (10).

[2]Under similar conditions, two other Lewis acids were briefly examined as potential catalysts. Boron trifluoride etherate gave virtually no reaction while reactions catalyzed by ferric chloride proved to be very slow relative to those catalyzed by stannic chloride.

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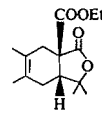
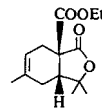
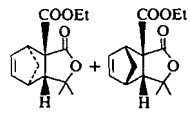
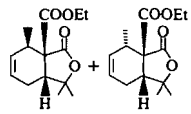
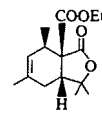
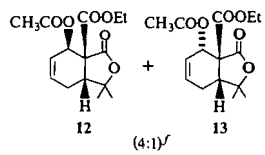
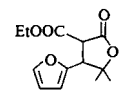
TABLE 1. Diels–Alder reactions of lactone ester **2**

Entry	Diene[a]	Time(h)[b]	Adduct(s) (ratio)	% Yield
1		6	 **5**	91
2		3	 **6**	86
3		0.25	 **7** + **8** (20:1)[d]	100
4		24	 **9** + **10** (7:3)[e]	75
5		22	 **11**	93
6		24[c]	 **12** + **13** (4:1)[f]	60
7		19	 **14**[g]	89

[a]In each case 20 equiv. of diene was used except for that of 1-acetoxyl-1,3-butadiene in which 10 equiv. was used.
[b]Unless otherwise specified, reactions were performed in ether at ambient temperature using stannic chloride (0.5 equiv.) as a catalyst.
[c]This reaction was carried out at 0°C using 1 equiv. of stannic chloride.
[d]Separation was effected by column chromatography on silica gel.
[e]Separation was effected by flash chromatograph (12).
[f]Inseparable mixture was obtained. The ratio was based on the ^{1}Hmr spectrum of the mixture.
[g]A single product was obtained, the stereochemistry of which could not be readily assigned.

(*ortho* and *para*) governing the orientation of Diels–Alder addition (1). In cases where differing secondary orbital overlap (13) would affect the stereochemistry of the adducts (Entries 3–6), experimental results showed a strong preference of the diene to overlap with one carbonyl over the other.

Several aspects of the structural assignments should be discussed. With respect to the orientation of the adducts derived from unsymmetrical dienes, assignments in cases of **9–13** were easily made since in each case the signal which was readily assigned to the ring junction proton appeared as a doublet of doublets in the ^{1}Hmr indicating the presence of two protons on the adjacent carbon. Assignment of the regiochemistry of adduct **6** was concluded after comparison of the ^{13}Cmr spectrum with those of the structurally related compounds **15** and **16**, the structures of which have been rigorously established (7). The adduct **6** showed two triplets at δ 28.1 and 27.1 for the two carbocyclic methylene carbons similar to the cor-

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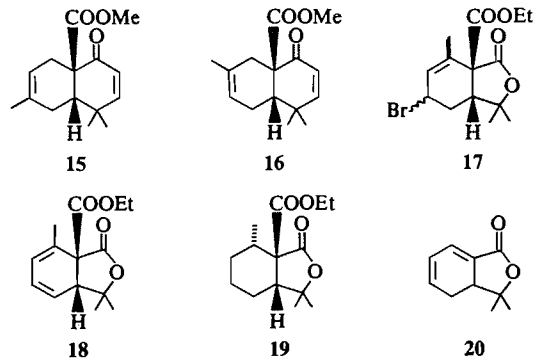
responding carbons (δ 29.0 and 28.7) in compound **15** and in marked contrast to the signals at δ 33.1 and 24.2 observed in isomer **16**.

With regard to the stereochemical assignments, the ring junction stereochemistry of all the adducts follows from the *cis*-principle (1) for which no violations have been observed. The complete stereochemistry of cyclopentadiene adducts **7** and **8** was further deduced as follows. Examination of Dreiding models showed the lactone ring junction proton should be shielded by the double bond in structure **7** while in structure **8** this proton should not be affected (14). Examination of the ^{1}Hmr spectrum of the major adduct showed a signal at δ 2.37 which was assignable to the ring junction proton while the corresponding proton in the minor isomer showed a relatively normal shift of δ 2.92 (δ 2.66–3.29 for other compounds in this series). In cases of adducts **9–13** which are conformationally flexible, the complete stereochemistry could not be assigned without ambiguity by spectroscopic analysis. A number of chemical methods were attempted[3] but were not succesful. The depicted stereochemistry of these compounds was tentatively assigned based mainly on the results obtained for cyclopentadiene, which indicated that the Diels–Alder reaction proceeded with a preferential secondary overlap of the diene with the ester carbonyl rather than the lactone carbonyl.

This report enlarges the scope of application of Diels–Alder reactions to the synthesis of lactone-containing systems and further demonstrates the advantage of using an activated dienophile to prepare useful adducts from relatively less reactive dienophile systems. A simple application of this particular dienophile (**2**) to the synthesis of natural products is illustrated by the two-step synthesis of



15 **16** **17** **18** **19** **20**

o-mentha-1,3-dien-1→8-olide (**20**), a monoterpene lactone isolated from the urine of the koala bear (*Phascolarctos cinereus*) (15). The mixture of the epimeric acetoxy lactones **12** and **13**, prepared in 60% yield from **2** and 1-acetoxy-1,3-butadiene, was treated with lithium iodide dihydrate in collidine at reflux for 1 h. Racemic *o*-menthane lactone **20** was isolated in 50% yield and showed spectroscopic properties identical to those reported for the levorotatory natural compound (15).

Experimental

General

Melting points were determined on a Kofler hot stage apparatus and are uncorrected. Elemental analyses were performed by the microanalytical laboratory of this department. The ir spectra were recorded on a Nicolet 7-199 FT-IR spectrophotometer and, except where otherwise stated, were obtained on solutions in chloroform. The ^{1}Hmr spectra were recorded on a Varian HA-100, Bruker WH-200, or WH-400 spectrometer and, except where otherwise stated, were obtained on solutions in carbon tetrachloride with tetramethylsilane as internal reference. The ^{13}Cmr spectra were recorded on a Bruker WP-60/Nicolet BNC-12 system or a Bruker WH-400 spectrometer and were obtained on solutions in deuteriochloroform using tetramethylsilane as internal reference. Mass spectra (ms) were recorded using A.E.I. model MS12 or MS50 mass spectrometers. Unless stated otherwise, anhydrous magnesium sulfate was used for drying organic solutions.

Ethyl 4-bromo-2-carbethoxy-4-methyl-2-pentenoate (4)

Diester **3** (5.14 g, 24 mmol) was dissolved in carbon tetrachloride (50 mL) under an argon atmosphere and *N*-bromosuccinimide (4.7 g, 26.4 mmol) was added followed by benzoyl peroxide (100 mg, 0.41 mmol). The mixture was heated at reflux for 1 h, cooled to room temperature, filtered, and concentrated to give the crude bromo ester **4** (7.55 g). A portion of this material (1.114 g) was purified by column chromatography on silica gel. Elution with 15% ether in petroleum ether gave pure bromo ester **4** (936 mg; 91% yield); ir: 1733 (C=O) and 1643 (C=C) cm^{-1}; ^{1}Hmr δ: 6.95 (s, 1H, —CH=), 4.20, 4.18 (both q, 2H each, J = 7 Hz each, 2 × —OCH_2—), 1.91 (s, 6H, 2 × —CH_3), 1.31, and 1.29 (both t, 3H each, J = 7 Hz each, 2 × —OCH_2CH_3). *Anal.* calcd. for $C_9H_{12}O_3Br$: C 45.07, H 5.85, Br 27.26; found: C 45.06, H 5.93, Br 27.44.

3-Carbethoxy-5,5-dimethyl-2(5H)-furanone (*2*)

Crude bromo ester **4** (2.84 g, ~9.7 mmol) was dissolved in

[3]In one approach, both compounds **9** and **10** were converted, via bromide **17**, to diene **18** (>60% yield; ir (neat): 1768, 1742, 1729, 1640, 1600, and 1995 cm^{-1}; ^{1}Hmr ($CDCl_3$) δ: 5.84–6.18 (complex, 2H, —C=CH—CH=), 5.55 (dd, 1H, J = 8, J' = 6 Hz, =CH—CH—), 4.15 (q, 2H, J = 7 Hz, —OCH_2—), 3.38 (d, 1H, J = 6 Hz, —CH—), 1.94 (s, 3H, =C—CH_3), 1.47 (s, 3H, —CH_3), 1.21 (t, 3H, J = 7 Hz, —OCH_2CH_3), and 1.18 (s, 3H, —CH_3); ms M^+ 250.1202 (calcd. for $C_{14}H_{18}O_4$: 250.1203)) by allylic bromination (*N*-bromosuccinimide (1 equiv.) and α,α′-azodiisobutyronitrile (trace) in refluxing carbon tetrachloride; 1 h) and dehydrobromination (1,5-diazabicyclo[4.3.0]non-5-ene in refluxing benzene; 8 h). In an attempt to prepare compound **19** to compare with the dihydro-derivative of **9** or **10**, catalytic hydrogenation of **18** resulted only in the saturation of the disubstituted double bond even under severe conditions (e.g. Pt in EtOAc; H_2; 1500 psi). The transformation of **9** and **10** to the same diene **18** nevertheless serves to confirm their epimeric relationship and orientation.

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tetrahydrofuran (50 mL) and water (25 mL). Silver oxide (2.48 g, 10.67 mmol) was added. After stirring for 48 h at room temperature, the reaction mixture was filtered and tetrahydrofuran was removed under reduced pressure. The aqueous solution was extracted with methylene chloride. The extracts were washed with water, dried, and concentrated. Column chromatography on silica gel eluting with 50% ether in petroleum ether gave lactone ester **2** (1.12 g; 67% yield from diester **3**); mp 68–70°C (ether); ir: 1763 (C=O), 1714 (C=O), and 1638 (C=C) cm^{-1}; ^{1}Hmr δ: 8.06 (s, 1H, —CH=), 4.24 (q, 2H, J = 7 Hz, —OCH_2—), 1.52 (s, 6H, 2 × —CH_3), and 1.35 (t, 3H, J = 7 Hz, —OCH_2CH_3); ^{13}Cmr δ: 167.1, 160.4, 124.6, 83.5, 61.7, 25.0, and 14.1; ms M^+ 184.0744 (calcd. for $C_9H_{12}O_4$: 184.0735). *Anal.* calcd. for $C_9H_{12}O_4$: C 58.69, H 6.57; found: C 58.76, H 6.66.

A less expensive method was found to be the pyrolytic cyclization of the crude bromo ester **4**. Lactone ester **2** was produced directly on attempted distillation of **4** (70.8 g) at 1 Torr. The fraction collected at 128°C was pure lactone ester **2** (15.9 g). Additional **2** (4.8 g) was obtained by column chromatography of the combined lower boiling fractions (102–120°C). The total yield was 51% from diester **3**.

Diels–Alder reactions of lactone ester 2

The reactions were carried out using the general procedure illustrated below with 2,3-dimethyl-1,3-butadiene. Temperature and time of reactions as well as quantities of dienes and stannic chloride relative to **2** are noted in Table 1.

Lactone ester **2** (500 mg, 2.71 mmol) was dissolved in ether (25 mL) under an argon atmosphere. The solution was chilled to 0°C and stannic chloride (354 mg, 1.36 mmol) was added. A dense white precipitate was observed immediately. After 5 min, 2,3-dimethyl-1,3-butadiene (6.13 mL, 54.3 mmol) was added and stirring was continued for 6 h at room temperature. Water (20 mL) was added and the resulting mixture was extracted with methylene chloride. The extracts were washed with water, dried, filtered, and concentrated. Column chromatography on silica gel eluting with 10–20% ether in petroleum ether gave adduct **5** (657 mg; 91% yield); ir: 1769 (C=O) and 1736 (C=O) cm^{-1}; ^{1}Hmr δ: 4.16 (q, 2H, J = 7 Hz, —OCH_2—), 2.84 (dd, 1H, J = 7, J' = 3 Hz, —CH—), 2.63, 2.22 (both d, 1H each, J = 16 Hz each, —CH_2—), 1.78–2.12 (complex, 2H, —CH_2CH—), 1.68 (s, 6H, 2 × =CCH_3), 1.43 (s, 3H, —CH_3), 1.28 (t, 3H, J = 7 Hz, —OCH_2CH_3), and 1.24 (s, 3H, —CH_3); ^{13}Cmr δ: 174.6, 171.0, 125.4, 125.1, 85.9, 62.1, 56.2, 47.3, 34.5, 30.1, 29.4, 23.9, 19.0, 18.8, and 14.0; ms M^+ 266.1516 (calcd. for $C_{15}H_{22}O_4$: 266.1518). *Anal.* calcd. for $C_{15}H_{22}O_4$: C 67.65, H 8.33; found: C 67.37, H 8.36.

The adducts **6–14** showed the following spectral data.

Compound **6**; mp 43–44°C (ether – petroleum ether); ir: 1767 (C=O) and 1736 (C=O) cm^{-1}; ^{1}Hmr δ: 5.46 (m, 1H, —CH=), 4.18 (q, 2H, J = 7 Hz, —OCH_2—), 2.98 (dd, 1H, J = 7, J' = 2 Hz, —CH—), 2.87, 2.22 (both md, 1H each, J = 14 Hz each, =CHCH_2—), 1.84–2.12 (complex, 2H, —CH_2CH—), 1.72 (s, 3H, —CH_3), 1.46 (s, 3H, —CH_3), 1.29 (t, 3H, J = 7 Hz, —OCH_2CH_3), and 1.24 (s, 3H, —CH_3); ^{13}Cmr δ: 174.6, 170.6, 133.2, 118.4, 86.0, 62.1, 53.5, 46.6, 29.8, 28.1, 27.1, 23.4, 23.2, and 14.0; ms M^+ 252.1368 (calcd. for $C_{14}H_{20}O_4$: 252.1361). *Anal.* calcd. for $C_{14}H_{20}O_4$: C 66.65, H 7.99; found: C 66.76, H 8.28.

Compound **7**; ir: 1761 (C=O) and 1726 (C=O) cm^{-1}; ^{1}Hmr δ: 6.13–6.34 (complex, 2H, —CH=CH—), 4.16 (q, 2H, J = 7 Hz, —OCH_2—), 3.38 (m, 1H, =CHCH—), 3.01 (br s, 1H, =CHCHCH—), 2.37 (s, 1H, —CH—), 1.54 (s, 3H, —CH_3), 1.51 (m, 2H, —CH_2—), 1.43 (s, 3H, —CH_3), and 1.29 (t, 3H, J = 7 Hz, —OCH_2CH_3); ms M^+ 250.1206 (calcd. for $C_{14}H_{18}O_4$: 250.1205). *Anal.* calcd. for $C_{14}H_{18}O_4$: C 67.18, H 7.25; found: C 67.18, H 7.04.

Compound **8**; ir: 1762 (C=O) and 1732 (C=O) cm^{-1}; ^{1}Hmr δ: 6.29 (ddd, 1H, J = 6, J' = 3, J'' = 1 Hz, =CH—), 6.17 (dd, 1H, J = 6, J' = 4 Hz, =CH—), 4.23 (q, 2H, J = 7 Hz, —OCH_2—), 3.38 (m, 1H, =CHCH—), 3.02 (m, 1H, =CHCH—CH—), 2.92 (d, 1H, J = 4 Hz, —CH—), 1.68 (m, 2H, —CH_2—), 1.45 (s, 3H, —CH_3), 1.34 (s, 3H, —CH_3), and 1.33 (t, 3H, J = 7 Hz, —OCH_2CH_3); ms M^+ 250.1205 (calcd. for $C_{14}H_{18}O_4$: 250.1205). *Anal.* calcd. for $C_{14}H_{18}O_4$: C 67.18, H 7.25; found: C 67.26, H 7.13.

Compound **9**: ir: 1770 (C=O) and 1728 (C=O) cm^{-1}; ^{1}Hmr δ: 5.78 (m, 1H, —CH=), 5.62 (ddd, 1H, J = 10, J' = 3, J'' = 2 Hz, —CH=), 4.16 (q, 2H, J = 7 Hz, —OCH_2—), 2.66 (dd, 1H, J = 7, J' = 5 Hz, —CH_2CH—), 2.53 (mq, 1H, J = 7 Hz, =CHCH—), 2.36, 1.92 (both md, 1H each, J = 16 Hz each, =CHCH_2—), 1.35 (s, 3H, —CH_3), 1.30 (s, 3H, —CH_3), 1.28 (t, 3H, J = 7 Hz, —OCH_2CH_3), and 1.20 (d, 3H, J = 7 Hz, —CHCH_3); ^{13}Cmr δ: 174.0, 170.0, 131.8, 125.8, 84.5, 61.7, 58.1, 48.1, 33.5, 29.8, 23.8, 22.4, 15.6, and 14.1; ms M^+ 252.1361 (calcd. for $C_{14}H_{20}O_4$: 252.1362).

Compound **10**; ir: 1768 (C=O) and 1730 (C=O) cm^{-1}; ^{1}Hmr δ: 5.88 (m, 1H, =CHCH_2—), 5.70 (ddd, 1H, J = 8, J' = 3, J'' = 2 Hz, =CH—), 4.21 (q, 2H, J = 7 Hz, —OCH_2—), 2.79 (dd, 1H, J = 8, J' = 3 Hz, —CH_2CH—), 2.69 (dq, 1H, J = 7, J' = 2 Hz, —C$H$$CH_3$), 2.33, 2.01 (both m, 1H each, —CH_2—), 1.35 (s, 3H, —CH_3), 1.30 (s, 3H, —CH_3), 1.30 (d, 3H, J = 7 Hz, —CHCH_3), and 1.30 (t, 3H, J = 7 Hz, —OCH_2CH_3); ^{13}Cmr δ: 173.0, 172.0, 135.1, 127.5, 84.4, 62.1, 61.8, 50.9, 34.9, 30.9, 25.2, 24.0, 15.0, and 14.1; ms M^+ 252.1362 (calcd. for $C_{14}H_{20}O_4$: 252.1362).

Compound **11**; ir: 1772 (C=O) and 1730 (C=O) cm^{-1}; ^{1}Hmr δ: 5.31 (m, 1H, —CH=), 4.15 (q, 2H, J = 7 Hz, —OCH_2—), 2.69 (dd, 1H, J = 7, J' = 6 Hz, —CH_2CH—), 2.53 (m, 1H, =CHCH—), 2.22 (dd, 1H, J = 16, J' = 7 Hz, —CHH—), 1.97 (dd, 1H, J = 16, J' = 6 Hz, —CHH—), 1.76 (s, 3H, —CH_3), 1.36 (s, 3H, —CH_3), 1.29 (s, 3H, —CH_3), 1.28 (t, 3H, J = 7 Hz, —OCH_2CH_3), and 1.17 (d, 3H, J = 7 Hz, —CHCH_3); ^{13}Cmr δ: 174.1, 169.9, 133.7, 125.4, 84.4, 61.5, 58.1, 48.6, 34.2, 29.8, 27.6, 23.8, 23.0, 15.9, and 14.1; ms M^+ 266.1517 (calcd. for $C_{15}H_{22}O_4$: 266.1520).

Compounds **12** and **13**; ir (neat): 1769 (C=O) and 1740 (C=O) cm^{-1}; ms M^+ 296.1261 (calcd. for $C_{15}H_{20}O_6$: 296.1260). *Anal.* calcd. for $C_{15}H_{20}O_6$: C 60.81, H 6.75; found: C 60.79, H 6.88. The ^{1}Hmr ($CDCl_3$) of the inseparable mixture showed two sets of signals integrated to a ratio of 4:1; major set (**12**) δ: ~6.01–6.25 (complex, 2H, —CH=CH—), 5.98 (d, 1H, J = 4 Hz, —OCH—), 4.25 (q, 2H, J = 7 Hz, —OCH_2), 3.14 (dd, 1H, J = 9, J' = 6 Hz, —C$H$$CH_2$—), ~2.46–1.98 (complex, 2H, —CH_2—), 2.04 (s, 3H, —$COCH_3$), 1.57 (s, 3H, —CH_3), 1.45 (s, 3H, —CH_3), and 1.30 (t, 3H, J = 7 Hz, —OCH_2CH_3); minor set (**13**) δ: ~6.01–6.25 (complex, 2H, —CH=CH—), 5.81 (d, 1H, J = 5 Hz, —OCH—), 4.28 (q, 2H, J = 7 Hz, —OCH_2—), 3.29 (dd, 1H, J = 8, J' = 4 Hz, —C$H$$CH_2$—), ~2.46–1.98 (complex, 2H, —CH_2—), 2.09 (s, 3H, —$COCH_3$), 1.46 (s, 3H, —CH_3), 1.38 (s, 3H, —CH_3), and 1.30 (t, 3H, J = 7 Hz, —OCH_2CH_3).

Compound **14**; ir: 1781 (C=O) and 1737 (C=O) cm^{-1}; ^{1}Hmr δ: 7.35 (dd, 1H, $J = 2, J' < 1$ Hz, =CHO—), 6.30 (dd, 1H, $J = 4$, $J' = 2$ Hz, —C*H*=CHO—), 6.19 (dd, 1H, $J = 4$, $J' < 1$ Hz, —CH=C—), 4.21 (q, 2H, $J = 7$ Hz, —OCH_2—), 3.90 (s, 2H, —CHCH—) 1.64 (s, 3H, —CH_3), 1.31 (t, 3H, $J = 7$ Hz, —OCH_2CH_3), and 1.10 (s, 3H, —CH_3); ms M^+ 252.1002 (calcd. for $C_{13}H_{16}O_5$: 252.0998). *Anal.* calcd. for $C_{13}H_{16}O_5$: C 61.90, H 6.39; found: C 62.09, H 6.45.

(±)-o-Mentha-1,3-dien-1→8-olide (20)

Lithium iodide dihydrate – collidine reagent (1.28 *N*) was freshly prepared by the sequential addition of lithium iodide (514 mg, 3.84 mmol) and water (138 μL, 7.68 mmol) to 2,4,6-collidine (3.05 mL). A mixture of acetoxy lactones **12** and **13** (152 mg, 0.51 mmol) was dissolved in this reagent (2.3 mL) under an argon atmosphere. The resulting solution was heated at reflux with stirring for 1 h. After cooling to room temperature, the reaction mixture was acidified with ice-cold 5% aqueous hydrochloric acid and extracted with ether. The extracts were washed with ice-cold aqueous hydrochloric acid and water, dried, filtered, and concentrated. Flash chromatography (12) of the residue on silica gel eluting with 5% ether in petroleum ether gave racemic *o*-menthane lactone **20** (42 mg; 50% yield); ir (neat): 1749 (C=O), 1664, and 1570 (C=C) cm^{-1}; ^{1}Hmr ($CDCl_3$) δ: 6.89 (m, 1H, —C=CH—), 6.06–6.24 (complex, 2H, —CH=CH—), 2.98 (m, 1H, —CH—), 2.12–2.46 (complex, 2H, —CH_2—), 1.54 (s, 3H, —CH_3), and 1.36 (s, 3H, —CH_3); ms *m/e*: 164.0837 (M^+; 22.59%; calcd. for $C_{10}H_{12}O_2$: 164.0837), 106.0427 (95.21%; C_7H_6O), 105.0351 (100%; C_7H_5O), 78.0492 (43.03%; C_6H_6), and 77.0375 (20.35%; C_6H_5).

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