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Synthesis of Hexahydroindenones through a Diels–Alder Cycloaddition and Nazarov Cyclization Sequence of Triene Alcohols

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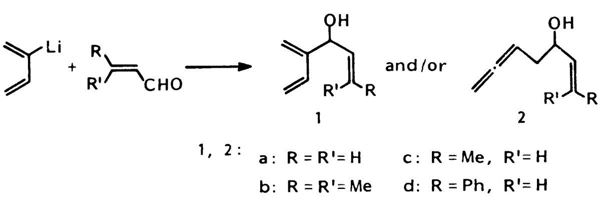
The Diels–Alder cycloaddition of 4-methylene-1,5-hexadien-3-ols with olefinic dienophiles such as dimethyl maleate, fumarate, and *N*-methylmaleimide produces 1-(1-cyclohexenyl)-2-propen-1-ols. These diene alcohols are oxidized with activated manganese(IV) oxide to give dienones, which are then treated with acid catalysts to undergo ready electrocyclization leading to hexahydroindenones with functional groups. Stereoselectivity at the electrocyclization step is found to depend upon the stereostructures of cyclohexene skeleton of the dienones as well as the reaction conditions.

2-Lithio-1,3-butadiene serves as a reagent which introduces a 1-methylene-2-propenyl unit into carbonyls by a regioselective nucleophilic addition.[1] In the preceding paper, we have already demonstrated that 1-aryl-2-methylene-3-buten-1-ols thus prepared undergo a sequence of Diels–Alder cycloaddition with electron-deficient olefins and acid-catalyzed cyclization leading to tetrahydrofluorene skeletons.[2] This sequence belongs to a new [6.5] annelation method to a benzene ring, while [6.6] annelation processes to acyclic and cyclic ketones have been established through stepwise sequence of two Diels–Alder reactions on 1-methylene-2-propenyl carbinols.[3]

The present article presents a new version of [6.5] annelation method by a sequence of two ring-forming reactions: The Diels–Alder cycloaddition of 4-methylene-1,5-hexadien-3-ols with olefins, oxidation of the diene alcohols as cycloadducts into dienones, and subsequent Nazarov cyclization. Although Nazarov reaction has been long utilized as a key reaction for natural product synthesis,[4] there are only limited examples known for the cyclization of dienones which are carrying several carbonyl functionalities.[5]

Results and Discussion

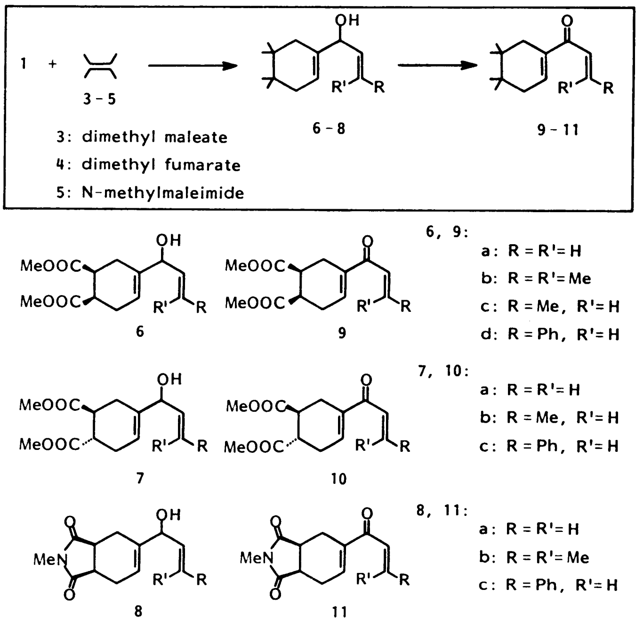
4-Methylene-1,5-hexadien-3-ols (**1**) as starting materials in the present work can be readily prepared from the regioselective reactions of 2-lithio-1,3-butadiene with 2-alkenals (Scheme 1).[1] Although some of the triene alcohols **1** were contaminated by a small amount of their isomers, 1,5,6-heptatrien-3-ols (**2**), these mixtures were able to be used for the following Diels–Alder cycloadditions without serious trouble. After the cycloaddition was over, the allene alcohols **2** were recovered unchanged and easily separated from the cycloadducts by column chromatography over silica gel.



Scheme 1.

The triene alcohols **1a—d** were employed in the Diels–Alder reactions with dienophiles such as dimethyl maleate (**3**), dimethyl fumarate (**4**), and *N*-methylmaleimide (**5**). The reactions took place smoothly under reflux in benzene to give excellent yields of cycloadducts **6—8** as mixtures of two diastereomers (Scheme 2 and Table 1).

The oxidation of 1,4-pentadien-3-ols into pentadienones is not a well-studied transformation[6] and this oxidation should be done with care because pentadienones as products are, in general, labile compounds. We used activated manganese(IV) oxide for this purpose since its versatility in the oxidation of allyl alcohol has been well-achieved.[7] Thus, the diene



Scheme 2.

alcohols **6**—**8** were successfully oxidized with activated manganese(IV) oxide in dichloromethane at room temperature to give satisfactory yields of dienones **9**—**11** as unstable compounds (Scheme 2 and Table 2).

Although details will be discussed later, electrocyclization of the dienones **9**—**11** afforded two types of enones (tetrasubstituted endo olefins **12**, **14**, and trisubstituted exo olefins **13**, **15**) as cyclized products depending upon the reaction conditions as well as the structure of starting dienones **9**—**11** (Scheme 3). In all cases, no trace of the other cyclopentenones, double-bond isomers of **12** and **14**, was even detected. This is consistent with the reported examples for the electrocyclizations of dienones including cyclohexene moiety as an olefin part.[5,8,9)]

Table 1. Diels-Alder Cycloaddition of Triene Alcohols **1**[a)]

Triene alcohol	Dienophile (equiv)	Time h	Cycloadduct	Yield[b)] %
1a[c)]	3 (2.3)	48	**6a**	88
1b	3 (2.2)	48	**6b**	86
1c	3 (1.8)	48	**6c**	94
1d[d)]	3 (3.4)	48	**6d**	83
1a[c)]	4 (2.9)	48	**7a**	88
1c	4 (2.0)	48	**7b**	90
1d[e)]	4 (1.6)	24	**7c**	87
1a	5 (1.0)	15	**8a**	83
1b	5 (1.1)	16	**8b**	90
1d[f)]	5 (1.0)	12	**8c**	99

a) All reactions were carried out under reflux in dry benzene under nitrogen. b) Isolated yields. c—f) Contaminated by the corresponding allene alcohols: c) **1a**:**2a**=10:1; d) **1d**:**2d**=19:1; e) **1d**:**2d**=10:1; f) **1d**:**2d**=7:9.

Table 2. Oxidation of Diene Alcohols **6**—**8** with Manganese(IV) Oxide[a)]

Diene alcohol	MnO_2/DA[b)]	Temp °C	Time h	Product	Yield[c)] %
6a	23	rt	2.5	**9a**	80
6b	27	rt	17	**9b**	72
6c	22	rt	5	**9c**	79
6d	30	rt	0.5	**9d**	56
7a	25	0	1	**10a**	84
7b	22	rt	5	**10b**	79
7c	28	rt	2.5	**10c**	78
8a	5	rt	20	**11a**	46[d)]
8b	24	rt	2	**11b**	52
8c	18	rt	20	**11c**	53

a) All reactions were carried out in dichloromethane. b) Molar ratio (DA: diene alcohols **6**—**8**). c) Isolated yield. d) The starting material **8a** was recovered in 16% yield.

A wide variety of acid catalysts including both Brønsted and Lewis acids have served in the electrocyclization of dienones and their equivalents.[5)] We hoped to avoid the use of aqueous acids since the dienones **9**—**11** are all bearing some substituents sensitive to hydrolysis and since aqueous acids sometimes cause abnormal cyclization.[10)] In addition, a cyclization procedure under mild conditions was desired, under which stereoselective cyclization would be achieved and acid-catalyzed epimerization of the cyclized products would be suppressed.

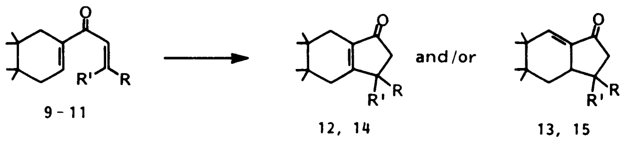
First we tested the electrocyclization of the dienone **9a** in the presence of *p*-toluenesulfonic acid (*p*-TsOH). This reaction gave 55% of expected product **12a** when heated under reflux in benzene for 4.5 h, but the reaction temperature and time are both unacceptable. So, some Lewis acid catalysts were examined in dichloromethane (Table 3); gallium(III) chloride was found much more effective than some other Lewis acids such as titanium(IV) chloride, aluminum(III) chloride, tin(IV) chloride, boron trifluoride, and trimethylsilyl trifluoromethanesulfonate. For example, the cyclization was completed within 30 min below 0 °C to give 73% of **12a** when two equimolar amounts of gallium(III) chloride were employed.

Other maleate cycloadducts **9b**—**d** underwent smooth cyclization in the presence of gallium(III) chloride to give tetrasubstituted olefins **12b**—**d** and/or trisubstituted olefins **13b**—**d**, both with high stereoselectivities (Scheme 4 and Table 4). In each case, the crude reaction mixture was found to be consisting of two major products by TLC and ^{1}H NMR spectrum, one of which was identical with **12**. When this

Table 3. Electrocyclization of Dienone **9a** in the Presence of Various Lewis Acid Leading to **12a**[a)]

Lewis acid (equiv)	Temperature °C	Time h	Yield % of **12a**[b)]
$TiCl_4$ (1.0)	rt	1	22
$AlCl_3$ (2.0)	rt	2	25
$BF_3\cdot OEt_2$ (2.0)	rt	7 d	26
Me_3SiOTf (1.0)	rt	5	47
$SnCl_4$ (0.5)	−8 to rt	20	39
$SnCl_4$ (0.5)	rt	4	52
$GaCl_3$ (1.0)	rt	0.5	63
$GaCl_3$ (2.0)	−20 to 0	0.5	73

a) All reactions were carried out in dry dichloromethane under nitrogen. b) Isolated yield.

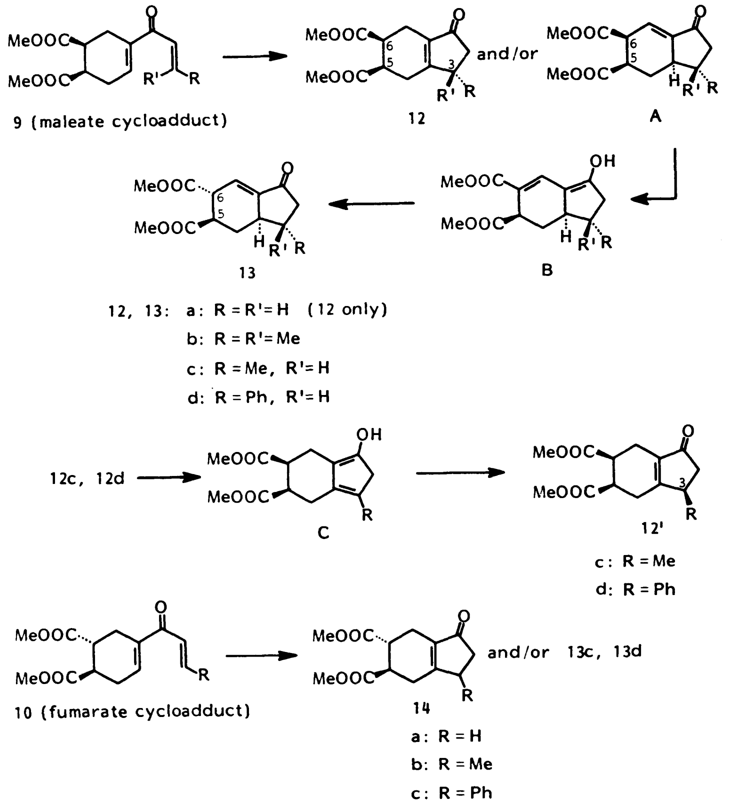


Scheme 3.

mixture was subjected to column chromatography over silica gel, the other product **A** completely isomerized into **13** which was also obtained from the electrocyclization of fumarate cycloadducts **10** as will be mentioned below. It is thus clear that the unstable primary products **A** and **13** are carrying cis and trans two adjacent ester groups, respectively.

Fumarate cycloadducts **10a**—**c** were similarly treated with gallium(III) chloride under the conditions listed in Table 4 to give tetrasubstituted olefins **14** together with aforementioned trisubstituted olefins **13c** and **13d**.

Structures of **12**, **13**, and **14** were determined mainly on the basis of spectral data except that the stereochemistry at the 3-positions of **12** and **13** could not be assigned only on their spectroscopic basis. Therefore, mechanistic consideration was taken into account. In the preceding paper,[2] we found that



Scheme 4.

Table 4. Acid-Catalyzed Electrocyclization of Dienones 9—11

Dienone	Acid (equiv)	Solvent[a]	Temperature °C	Time h	Product (yield)[b] %
9a	$GaCl_3$ (1.0)	DCM	−20 to 0	0.5	**12a** (73)
	p-TsOH (0.5)	BZ	reflux	4.5	**12a** (55)
9b	$GaCl_3$ (1.0)	DCM	rt	5 d	**12b** (68), **13b** (29)
	p-TsOH (1.0)	T	reflux	24	**12b** (57)
9c	$GaCl_3$ (1.0)	DCM	rt	24	**12c** (40), **13c** (49)
	p-TsOH (0.5)	BZ	reflux	6.5	**12c**+**12c'** (1:1, 59)
9d	$GaCl_3$ (1.0)	DCM	rt	5	**12d** (81), **13d** (5)
	p-TsOH (0.5)	T	reflux	12	**12d**+**12d'** (1:1, 63), **13d** (33)
10a	$GaCl_3$ (1.0)	DCM	rt	3	**14a** (90)
10b	$GaCl_3$ (1.0)	DCM	rt	3	**14b** (62),[c] **13c** (26)
10c	$GaCl_3$ (2.0)	DCM	rt	18	**14c** (80), **13d** (4)
11a	$GaCl_3$ (1.0)	DCM	rt	6	**15a** (17)
11b	$GaCl_3$ (2.0)	DCM	rt	6 d	**15b**+**15b'** (1:1, 90)
11c	$GaCl_3$ (1.0)	DCM	rt	2 d	**15c**+**15c'** (1:2, 46)

a) DCM: dichloromethane; BZ: benzene; T: toluene. b) Isolated yield. The isomer ratios were determined by ^{1}H NMR. c) A 1:1 mixture of stereoisomers.

dimethyl 4-(α-hydroxybenzyl)-4-cyclohexene-1,2-dicarboxylates underwent highly stereoselective electrocyclization leading to dimethyl 3,4a-*cis*-1*H*-2,3,4,4a-tetrahydrofluorene-2,3-dicarboxylate. The high stereoselectivity observed above in the Nazarov cyclization of maleate cycloadducts **9** presumably resulted in the same manner (Fig. 1): Pentadienyl cation **D** as an intermediate cyclizes through one of two possible conrotatory rotations to form allyl anion **E** which is sterically less hindered than the isomeric anion derived by the other rotation. Deprotonation of **E** at the 3a- or 7-position leads to **12** or **A**, respectively. Thus, the substituent R in **9** becomes cis to 5-H.

Small couplings of J_{5-6} (3.6 Hz) indicates the validity of 5,6-cis geometry of tetrasubstituted olefins **12** derived from **9**. On the other hand, trans configuration of epimerized products **13** is confirmed by relatively large couplings of J_{5-6} (10.0 Hz). One of 4-methylene hydrogens of **13b** couples with two adjacent methine hydrogens (3a-H and 5-H) with 12.0 Hz of diaxial couplings, indicating 3a,5-cis structure (Fig. 2). The stereostructures of tetrasubstituted olefins **14b** and **14c** derived from fumarate cycloadducts **10b** and **10c** could not be assigned by spectral data.

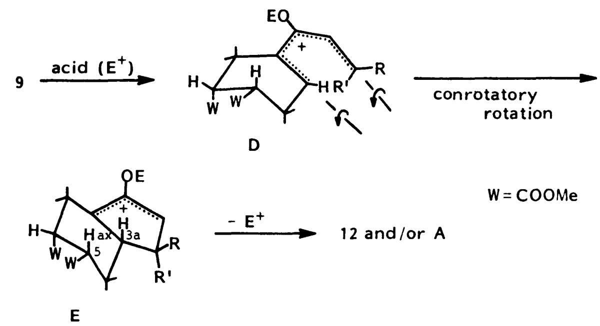
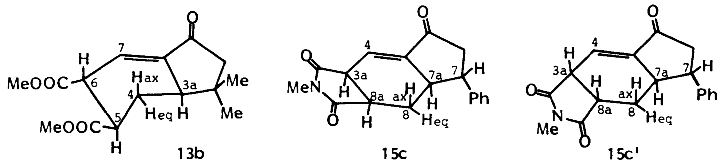


Fig. 1. Stereoselective cyclization of maleate cycloadducts **9** through conrotatory rotation of pentadienyl cation **D**.

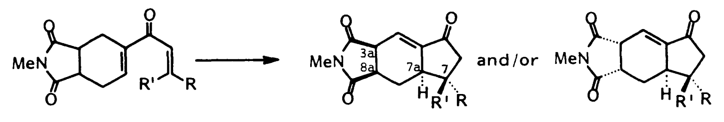
The aforementioned ready epimerization at the 6-position of a trisubstituted olefin **A** probably took place through an acid-catalyzed dienolization (via **B**, Scheme 4). Contrary to the highly stereoselective electrocyclization of **9** in the presence of gallium(III) chloride, similar cyclizations with *p*-TsOH occurred in a nonstereoselective fashion. For example, a mixture of two stereoisomers **12c**+**12c′** (1:1) or **12d**+**12d′** (1:1) was obtained when the cyclization of **9c** or **9d** was carried out under reflux in benzene or toluene with *p*-TsOH, respectively (Table 4). As **12d** was found to isomerize into **12d′** in the presence of *p*-TsOH under comparable conditions, it is easily understood that **12d** undergoes a similar acid-catalyzed epimerization via dienol **C** (Scheme 4).

Even in the presence of gallium(III) chloride, maleimide cycloadducts **11** experienced nonstereoselective cyclization giving trisubstituted olefins **15** and/or **15′** (Scheme 5 and Table 4). This selectivity looks the same to that previously observed on the related cyclization.[2] No formation of tetrasubstituted olefins may be due to the serious steric hindrance anticipated to exist in the folded conformation of cyclohexene ring. The structures of **15** and **15′** were confirmed mainly on the basis of ^{1}H NMR data which were already shown in Fig. 2. The axial hydrogen (8-H$_{ax}$) of **15c** couples with both 7a-H and 8a-H with



$J_{4ax-3a}=12.0$	$J_{5-6}=10.0$	$J_{8ax-7a}=10.0$	$J_{8ax-7a}=10.5$
$J_{4ax-5}=12.0$		$J_{8ax-8a}=12.5$	$J_{8ax-8a}=6.0$
$J_{4ax-4eq}=12.0$		$J_{8ax-8eq}=11.0$	$J_{8ax-8eq}=12.5$
$J_{4eq-3a}=5.0$		$J_{8eq-8a}=6.0$	$J_{8eq-8a}=2.0$
$J_{4eq-5}=3.0$		$J_{8a-3a}=8.5$	$J_{8a-3a}=8.0$

Fig. 2. Stereostructures and coupling constants (Hz) of **13b**, **15c**, and **15c′**.



11 (maleimide cycloadduct) 15 15'

15, 15′: a: R=R′=H (15 only)
b: R=R′=Me
c: R=Ph, R′=H

Scheme 5.

large coupling (10.0 and 12.5 Hz), whereas 8-H_{ax} of **15c′** shows a small coupling constant toward 8a-H (6.0 Hz).

Experimental

General. Melting points were determined on a Yanagimoto melting point apparatus and are uncorrected. IR spectra were taken with a JASCO IRA-1 or a JASCO A-702 spectrometer. ^{1}H NMR spectra were recorded on a Hitachi R-40 (90 Hz), a JEOL FX-100 instrument (100 MHz), or Bruker AM 360 (360 MHz), and ^{13}C NMR on a JEOL FX-100 spectrometer at 25.05 MHz. Chemical shifts are expressed in parts per million downfield from tetramethylsilane as an internal standard. Mass spectra were measured with a JEOL-01SG-2 spectrometer at 70 eV of ionization energy. GC-Mass spectra as well as high resolution mass spectra (HRMS) were also obtained on the same instrument. Elemental analyses were performed on a Hitachi 026 CHN analyzer. Thin-layer chromatography (TLC) was accomplished on 0.2 mm precoated plates of silica gel 60 F-254 (Merck) or of aluminum oxide 60 F-254 type-E (Merck); visualization was with ultraviolet light (254 and 365 nm), iodine, molybdophosphoric acid (5% in ethanol), or *p*-anisaldehyde (5% in ethanol containing 5% of sulfuric acid). For preparative column chromatography, Wakogel C-200, C-300 (Wako), and Silicagel 60 (Merck) were employed. Flash chromatography was carried out on an EYELA EF-10 apparatus using a column (20×180 mm) packed with Silicagel 60 (Merck, size: 0.04—0.063 mm). Preparative high-performance liquid chromatography (HPLC) was performed on a Kusano KHLC-201 apparatus with a UV-detector Uvilog-III using a column (22×300 mm) packed with silica gel (Wakogel LC-50H). Gas liquid chromatography (GLC) was accomplished on a Yanaco G-2800 gas chromatograph (Yanagimoto) with a flame ionization detector using a glass column (SE-30, 3×2000 mm) or a glass capillary column (Silicone GE, SE-30, 0.25×5000 mm). Micro vacuum distillation was carried out on a Sibata GTO-250R Kugelrohr distilling apparatus. Solvents were evaporated with a Tokyo Rikakikai rotary evaporator type-V at about 50 °C unless otherwise stated.

Materials and Solvents. 4-Methylene-1,5-hexadien-3-ol (**1a**), 6-methyl-3-methylene-1,5-heptadien-4-ol (**1b**), *trans*-3-methylene-1,5-heptadien-4-ol (**1c**), and *trans*-4-methylene-1-phenyl-1,5-hexadien-3-ol (**1d**) were prepared from 2-lithio-1,3-butadiene and the corresponding aldehydes according to the reported method.[1] Although some of these triene alcohols **1** were often contaminated by the corresponding allene alcohols **2**, the mixtures were used for the following Diels-Alder reactions without purification. Gallium(III) chloride was prepared from metal gallium and dry hydrogen chloride and purified by distillation.

General Procedure for the Diels-Alder Reactions of Triene Alcohols 1 with Olefinic Dienophiles 3—5 Leading to Cycloadducts 6—8. Triene alcohols **1a—d** were heated under reflux in dry benzene with a slightly excess amount of dimethyl maleate (**3**), dimethyl fumarate (**4**), or *N*-methylmaleimide (**5**) under the reaction conditions listed in Table 1. The benzene was evaporated in vacuo and the residue was chromatographed over silica gel with hexane-ethyl acetate (4:1 to 1:3 v/v) or hexane-diethyl ether (1:1 v/v) to give cycloadducts **6—8** which were all mixtures of two diastereomers. The results are summarized in Table 1.

6a: Colorless liquid; IR (neat) 3400 and 1750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.2—3.2 (7H, m, CH_2, CH, and OH), 3.66 (6H, s, COOMe), 4.48 (1H, br d, *J*=5.5 Hz, C$\underline{\mathrm{H}}$OH), 5.10 (1H, dt, *J*=10.0, 1.5, and 1.5 Hz, =CH_2 (cis)), 5.25 (1H, dt, *J*=17.5, 1.5, and 1.5 Hz, =CH_2 (trans)), 5.70 (1H, br s, 2-H), and 5.82 (1H, ddd, *J*=17.5, 10.0, and 5.5 Hz, CH=); ^{13}C NMR ($CDCl_3$) δ=24.83, 25.01, 25.48, 25.60 (each t, 3- and 6-C), 39.75, 39.86, 39.98 (each d, 4- and 5-C), 51.84 (q, COOMe), 76.09, 76.27 (each d, -CHOH-), 115.25 (t, =CH_2), 120.71, 120.88 (each d), 137.09, 137.20 (each s, 1-C), 138.61, 138.79 (each d), and 173.55 (s, COOMe); MS *m/z* (rel intensity, %) 236 (M^+−18, 9), 176 (52), 117 (100), and 79 (20).

Found: C, 61.45; H, 7.13%. Calcd for $C_{13}H_{18}O_5$: C, 61.40; H, 7.13%.

6b: Unstable colorless liquid; IR (neat) 3500 and 1725 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.1—3.2 (7H, m, CH_2, CH, and OH), 2.69, 2.73 (each 3H, d, *J*=1.0 Hz, =CMe_2), 3.65, 3.68 (6H, each s, COOMe), 4.70 (1H, d, *J*=9.0 Hz, C$\underline{\mathrm{H}}$OH), 5.18 (1H, br d, *J*=9.0 Hz, CH=), and 5.66 (1H, br s, 2-H); ^{13}C NMR ($CDCl_3$) δ=18.30, 18.53 (each q, =CMe_2), 25.12, 25.35, 25.71, 25.88 (each t, 3- and 6-C), 40.09, 40.12 (each d, 4- and 5-C), 51.95 (q, COOMe), 71.89, 72.01 (each d, CHOH), 119.19, 119.60 (each t, =CH_2), 125.89, 126.24 (each d), 133.65, 135.19, 135.83, 138.48 (each s), 173.77, and 173.95 (each s, COOMe); MS *m/z* (rel intensity, %) 282 (M^+, 2), 264 (19), 204 (26), 145 (100), 91 (30), 83 (27), 79 (29), and 77 (23).

6c: Colorless liquid; IR (neat) 3500 and 1725 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.70 (3H, d, *J*=6.0 Hz, =CHMe), 2.3—2.6 (5H, m, CH_2 and OH), 2.9—3.2 (2H, m, CH), 3.65 (6H, s, COOMe), 4.40 (1H, br d, *J*=5.5 Hz, C$\underline{\mathrm{H}}$OH), and 5.3—5.8 (3H, m, CH=); ^{13}C NMR ($CDCl_3$) δ=17.69 (q, =CHMe), 25.14, 25.48, 25.63 (each t, 3- and 6-C), 39.81, 40.06 (each d, 4- and 5-C), 51.80 (q, COOMe), 75.92 (d, CHOH), 119.83, 120.11, 127.28, 131.77, 131.96 (each d), 137.81 (s, 1-C), and 173.57 (s, COOMe); MS *m/z* (rel intensity, %) 268 (M^+, 1), 250 (22), 191 (20), 190 (44), 131 (100), and 69 (20).

Found: C, 62.71; H, 7.46%. Calcd for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51%.

6d: Pale yellow liquid; IR (neat) 3400 and 1725 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.1—3.2 (7H, m, CH_2, CH, and OH), 3.56, 3.60 (each 3H, s, COOMe), 4.02 (1H, br d, *J*=6.0 Hz, C$\underline{\mathrm{H}}$OH), 5.72 (1H, br s, 2-H), 6.14 (1H, dd, *J*=16.0 and 6.0 Hz, CH=), 6.54 (1H, dd, *J*=16.0 and 3.0 Hz, =CHPh), and 7.0—7.2 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=25.05, 25.58 (each t, 3- and 6-C), 39.72, 39.91 (each d, 4- and 5-C), 51.80 (q, COOMe), 75.87 (d, CHOH), 120.66, 126.41, 127.48, 128.45, 130.26, 130.50 (each d), 136.64, 137.32, 137.42 (each s), 173.48, and 173.57 (each s, COOMe); MS *m/z* (rel intensity, %) 330 (M^+, 8), 312 (26), 270 (35), 211 (19), 194 (25), 193 (100), 178 (21), 131 (21), 115 (65), 105 (22), 103 (26), 91 (58), 79 (25), and 77 (34).

Found: C, 68.88; H, 6.77%. Calcd for $C_{19}H_{22}O_5$: C, 69.07; H, 6.71%.

7a: Colorless liquid; IR (neat) 3450 and 1725 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.0—2.5 (5H, m, CH_2 and OH), 2.7—3.0 (2H, m, CH), 3.66 (6H, s, COOMe), 4.50 (1H, br d, *J*=5.5 Hz, C$\underline{\mathrm{H}}$OH), 5.15 (1H, dt, *J*=10.0, 1.5, and 1.5 Hz, =CH_2 (cis)), 5.26 (1H, dt, *J*=17.5, 1.5, and 1.5 Hz, =CH_2 (trans)), 5.74 (1H, br s, 2-H), and 5.83 (1H, ddd, *J*=17.5, 10.0, and 5.5 Hz, CH=); ^{13}C NMR (CDCl$_3$) δ=26.76, 27.00, 27.63, 27.78 (each t, 3- and 6-C), 41.27, 41.42 (each d, 4- and 5-C), 51.90 (q, COOMe), 75.82 (d, CHOH), 115.54, 115.64 (each t, =CH$_2$), 120.27, 120.75 (each d), 136.98, 137.27 (each s, 1-C), 138.44, 138.64 (each d), and 175.09 (s, COOMe); MS *m/z* (rel intensity, %) 236 (M$^+$−18, 3), 204 (32), 177 (20), 176 (84), 117 (100), 91 (21), 79 (33), and 77 (19).

Found: C, 61.11; H, 7.08%. Calcd for C$_{13}$H$_{18}$O$_5$: C, 61.40; H, 7.13%.

7b: Colorless liquid; IR (neat) 3500 and 1725 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.70 (3H, d, *J*=6.0 Hz, =CHMe), 1.9—2.7 (5H, m, CH$_2$ and OH), 2.7—2.9 (2H, m, CH), 3.66 (6H, s, COOMe), 4.40 (1H, d, *J*=5.5 Hz, C$\underline{\text{H}}$OH), 5.3—5.9 (2H, m, C$\underline{\text{H}}$=C$\underline{\text{H}}$Me), and 5.70 (1H, br s, 2-H); ^{13}C NMR (CDCl$_3$) δ=17.71 (q, =CHMe), 27.12, 27.53, 27.88 (each t, 3- and 6-C), 41.47 (d, 4- and 5-C), 52.00 (q, COOMe), 75.88 (d, CHOH), 119.60, 120.13, 127.89, 131.89, 132.01 (each d), 137.89, 138.18 (each s, 1-C), and 175.60 (s, COOMe); MS *m/z* (rel intensity, %) 268 (M$^+$, 1), 218 (11), 190 (32), 131 (77), 91 (28), 79 (33), and 77 (30).

Found: C, 62.49; H, 7.49%. Calcd for C$_{14}$H$_{20}$O$_5$: C, 62.67; H, 7.51%.

7c: Colorless liquid; IR (neat) 3450 and 1730 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.8—3.0 (7H, m, CH$_2$ CH, and OH), 3.64, 3.66 (each 3H, s, COOMe), 4.66 (1H, br d, *J*=6.0 Hz, C$\underline{\text{H}}$OH), 5.76 (1H, br s, 2-H), 6.14 (1H, dd, *J*=16.0 and 6.0 Hz, CH=), 6.58 (1H, d, *J*=16.0 Hz, =CHPh), and 7.0—7.4 (5H, m, Ph); ^{13}C NMR (CDCl$_3$) δ=27.00, 27.30, 27.77, 27.88 (each t, 3- and 6-C), 41.36 (d, 4- and 5-C), 52.06 (q, COOMe), 75.89 (d, CHOH), 120.54, 121.07, 128.01, 128.83, 130.01, 130.13, 131.24 (each d), 136.72, 137.48, 137.78 (each s), and 175.48 (s, COOMe); MS *m/z* (rel intensity, %) 330 (M$^+$, 32), 312 (19), 280 (25), 270 (79), 253 (25), 252 (53), 211 (43), 193 (100), 179 (20), 165 (25), 131 (36), 115 (48), 105 (33), 103 (33), 91 (66), 79 (39), and 77 (22).

Found: C, 68.91; H, 6.63%. Calcd for C$_{19}$H$_{22}$O$_5$: C, 69.07; H, 6.71%.

8a: Colorless liquid; IR (neat) 3500 and 1680 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.0—2.8 (5H, m, CH$_2$ and OH), 2.88, 2.90 (each 3H, s, NMe), 3.0—3.2 (2H, m, CH), 4.47 (1H, br d, *J*=5.5 Hz, C$\underline{\text{H}}$OH), 5.0—5.3 (2H, m, =CH$_2$), and 5.5—5.9 (2H, m, CH= and 6-H); ^{13}C NMR (CDCl$_3$) δ=23.54 (t, 4- and 7-C), 24.61 (q, NMe), 39.03, 39.28 (each d, 3a- and 7a-C), 74.70, 75.38 (each d, CHOH), 115.24, 115.39 (each t, =CH$_2$), 121.19, 121.39, 137.76, 137.95 (each d), 140.54, 140.68 (each s), 179.66, and 179.91 (each s, CON); MS *m/z* (rel intensity, %) 221 (M$^+$, 100), 203 (24), 193 (34), 192 (21), 166 (38), 126 (35), 118 (77), 117 (63), 113 (46), 112 (68), 109 (22), 107 (43), 92 (29), 91 (43), 81 (60), 80 (38), 79 (78), 78 (29), and 77 (65).

Found: C, 65.82; H, 6.81; N, 6.40%. Calcd for C$_{12}$H$_{15}$NO$_3$: C, 65.14; H, 6.83; N, 6.33%.

8b: Unstable colorless liquid; IR (neat) 3500, 1770, and 1680 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.64, 1.70 (each 3H, s, =CMe$_2$), 2.0—3.0 (5H, m, CH$_2$ and OH), 2.86, 2.88 (each 3H, s, NMe), 3.0—3.2 (2H, m, CH), 4.67 (1H, br d, *J*=8.5 Hz, C$\underline{\text{H}}$OH), 5.03 (1H, m, CH=), and 5.76 (1H, br s, 6-H); ^{13}C NMR (CDCl$_3$) δ=17.93 (q, =CMe$_2$), 23.49, 23.78, 24.26 (each t, 4- and 7-C), 24.51, 25.53 (each q, NMe), 39.23, 39.42 (each d, 3a- and 7a-C), 70.41, 71.00 (each d, CHOH), 119.63, 119.92, 124.99, 125.14 (each d), 134.93, 135.22, 141.76, 141.85 (each s), 179.52, 179.86 (each s, CON); MS *m/z* (rel intensity, %) 249 (M$^+$, 10), 131 (11), and 43 (100).

8c: Pale yellow needles (diethyl ether–hexane); mp 100—102 °C; IR (KBr) 3200, 1680, and 1620 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.0—2.8 (5H, m, CH$_2$ and OH), 2.78 (3H, s, NMe), 3.0—3.2 (2H, m, CH), 4.64 (1H, br d, *J*=7.0 Hz, C$\underline{\text{H}}$OH), 5.88 (1H, m, 6-H), 6.06 (1H, dd, *J*=16.0 and 7.0 Hz, CH=), 6.52 (1H, d, *J*=16.0 Hz, =CHPh), and 7.1—7.4 (5H, m, Ph); ^{13}C NMR (CDCl$_3$) δ=23.77, 23.94 (each t, 4- and 7-C), 24.77 (q, NMe), 39.36, 39.53 (each d, 3a- and 7a-C), 74.41, 75.71 (each d, CHOH), 121.71, 126.60, 127.83, 128.65, 129.77, 130.77, 131.19, (each d), 136.66, 141.42 (each s), 180.18, and 180.36 (each s, CON); MS *m/z* (rel intensity, %) 297 (M$^+$, 95), 279 (33), 194 (23), 193 (34), 192 (55), 186 (29), 165 (23), 116 (23), 115 (59), 113 (24), 112 (35), 105 (46), 104 (25), 103 (46), 91 (75), 80 (41), 79 (100), 78 (33), and 77 (84).

Found: C, 72.85; H, 6.33; N, 4.70%. Calcd for C$_{18}$H$_{19}$NO$_3$: C, 72.70; H, 6.44; N, 4.71%.

General Procedure for Oxidation of Diene Alcohols 6—8 with Activated Mangnese(IV) Oxide Leading to Dienones 9—11. Diene alcohols **6—8** and activated manganese(IV) oxide were stirred in dry dichloromethane (10—20 ml per 1 mmol of the alcohols) at room temperature under the reaction conditions listed in Table 2. The oxide was filtered off through Celite 545 and the filtrate was evaporated in vacuo. The residue was chromatographed over silica gel with hexane–ethyl acetate (1 : 1 to 2 : 1 v/v) to give **9—11**. The results are summarized in Table 2.

9a: Colorless liquid; IR (neat) 1730 and 1650 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.4—3.3 (6H, m, CH$_2$ and CH), 3.67, 3.69 (each 3H, s, COOMe), 5.72 (1H, dd, *J*=10.5 and 2.0 Hz, =CH$_2$ (cis)), 6.24 (1H, dd, *J*=17.1 and 2.0 Hz, =CH$_2$ (trans)), 6.89 (1H, m, 2-H), and 6.94 (1H, dd, *J*=17.1 and 10.5 Hz, CH=); ^{13}C NMR (CDCl$_3$) δ=24.42, 26.54 (each t, 3- and 6-C), 39.16, 39.45 (each d, 4- and 5-C), 52.02 (q, COOMe), 128.34 (t, =CH$_2$), 131.10 (d, COCH=), 137.32 (s, 1-C), 138.20 (d, 2-C), 172.92, 173.01 (each s, COOMe), and 190.16 (s, CO); MS *m/z* (rel intensity, %) 252 (M$^+$, 19), 221 (24), 220 (17), 192 (35), 133 (100), 105 (16), and 77 (29).

Found: C, 61.59; H, 6.19%. Calcd for C$_{13}$H$_{16}$O$_5$: C, 61.89; H, 6.39%.

9b: Colorless needles (diethyl ether–hexane); mp 94—97 °C; IR (KBr) 1725, 1650, and 1600 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.92, 2.08 (each 3H, d, *J*=1.3 Hz, =CMe$_2$), 2.5—3.2 (6H, m, CH$_2$ and CH), 3.64, 3.66 (each 3H, s, COOMe), 6.38 (1H, m, *J*=1.3 Hz, COCH=), and 6.78 (1H, m, 2-H); ^{13}C NMR (CDCl$_3$) δ=20.85 (q, =CMe$_2$), 24.46, 26.37 (each t, 3- and 6-C), 27.68 (q, =CMe$_2$), 39.31, 39.65 (each d, 4- and 5-C), 52.05 (q, COOMe), 120.65 (d, COCH=), 136.08 (d, 2-C), 138.76 (s, 1-C), 154.20 (s, =CMe$_2$) 173.38, 173.48 (each s, COOMe), and 192.04 (s, CO); MS *m/z* (rel intensity, %) 280 (M$^+$, 69), 249 (32), 220 (24), 161 (100), 160 (25), 83 (66), and 55 (36).

Found: C, 64.54; H, 7.29%. Calcd for C$_{15}$H$_{20}$O$_5$: C, 64.27; H, 7.19%.

9c: Colorless needles (diethyl ether–hexane); mp 80—83 °C; IR (KBr) 1725, 1660, and 1610 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.90 (3H, d, *J*=6.0 Hz, =CHMe), 2.3—3.2 (6H, m, CH$_2$ and CH), 3.66, 3.68 (each 3H, s, COOMe), and 6.5—7.2 (3H, m, C$\underline{\text{H}}$=C$\underline{\text{H}}$Me and 2-H); ^{13}C NMR (CDCl$_3$) δ=18.32 (q, =CHMe), 24.51, 26.46 (each t, 3- and 6-C), 39.18, 39.52 (each d, 4- and 5-C), 51.85 (q, COOMe), 126.16 (d, COCH=), 136.93 (d, 2-C), 137.42 (s, 1-C), 142.42 (d, =CHMe), 172.94, 173.09 (each s, COOMe), and 189.90 (s, CO); MS *m/z* (rel intensity, %) 266 (M$^+$, 52), 235 (28), 206 (27), 148 (100), 84 (18), and 69

(51).

Found: C, 63.19; H, 6.77%. Calcd for C$_{14}$H$_{18}$O$_5$: C, 63.15; H, 6.81%.

9d: Colorless needles (diethyl ether–hexane); mp 111—112 °C; IR (KBr) 1725, 1640, and 1595 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.2—3.3 (6H, m, CH$_2$ and CH), 3.65, 3.67 (each 3H, s, COOMe), 6.96 (1H, br s, 2-H), 7.24, 7.63 (each 1H, d, *J*=15.7 Hz, C$\underline{H}$=C$\underline{H}$Ph), and 7.3—7.6 (5H, m, Ph); ^{13}C NMR (CDCl$_3$) δ=24.60, 26.48 (each t, 3- and 6-C), 39.10, 39.45 (each d, 4- and 5-C), 51.96 (q, COOMe), 120.77, 128.11, 128.75, 130.10 (each d), 134.86 (s), 137.03 (d, 2-C), 137.91 (s, 1-C), 142.96 (d, PhCH=), 172.85, 173.01 (each s, COOMe), and 189.52 (s, CO); MS *m/z* (rel intensity, %) 328 (M$^+$, 29), 268 (18), 210 (19), 209 (100), 131 (71), 105 (21), 103 (66), and 77 (75).

Found: C, 69.27; H, 5.98%. Calcd for C$_{19}$H$_{20}$O$_5$: C, 69.50; H, 6.14%.

10a: Colorless liquid; IR (neat) 1725 and 1650 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.2—3.0 (6H, m, CH$_2$ and CH), 3.70 (6H, s, COOMe), 5.74 (1H, dd, *J*=10.5 and 2.0 Hz, =CH$_2$ (cis)), 6.26 (1H, dd, *J*=17.0 and 2.0 Hz, =CH$_2$ (trans)), 6.90 (1H, br s, 2-H), and 6.92 (1H, dd, *J*=17.0 and 10.5 Hz, COCH=); ^{13}C NMR (CDCl$_3$) δ=25.83, 28.41 (each t, 3- and 6-C), 40.28, 40.80 (each d, 4- and 5-C), 52.08 (q, COOMe), 128.63 (t, =CH$_2$), 130.86 (d, 2-C), 137.50 (s and d, 1-C and COCH=), 174.37 (s, COOMe), and 189.81 (s, CO); MS *m/z* (rel intensity, %) 253 (M$^+$+1, 2), 221 (23), 220 (54), 192 (83), 133 (100), and 55 (52).

Found: C, 62.12; H, 6.42%. Calcd for C$_{13}$H$_{16}$O$_5$: C, 61.96; H, 6.54%.

10b: Colorless prisms (diethyl ether–hexane); mp 67—69 °C; IR (KBr) 1725 and 1650 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.90 (3H, dd, *J*=6.5 and 1.0 Hz, =CHMe), 2.1—3.0 (6H, m, CH$_2$ and CH), 3.68 (6H, s, COOMe), 6.60 (1H, dd, *J*=15.0 and 1.0 Hz, COCH=), 6.7—6.9 (1H, m, 2-H), and 6.88 (1H, dq, *J*=15.0 and 6.5 Hz, =CHMe); ^{13}C NMR (CDCl$_3$) δ=18.41 (q, =CHMe), 26.12, 28.47 (each t, 3- and 6-C), 40.47, 41.00 (each d, 4- and 5-C), 52.12 (q, COOMe), 126.18 (d, COCH=), 136.54 (d, 2-C), 137.83 (s, 1-C), 143.42 (d, MeCH=), 174.84 (s, COOMe), and 189.90 (s, CO); MS *m/z* (rel intensity, %) 267 (M$^+$+1, 2), 206 (13), 147 (52), 105 (16), 91 (17), 79 (27), 78 (22), 77 (47), and 69 (100).

Found: C, 63.14; H, 6.80%. Calcd for C$_{14}$H$_{18}$O$_5$: C, 63.15; H, 6.81%.

10c: Colorless prisms (dichloromethane–hexane); mp 130—131 °C; IR (KBr) 1725 and 1640 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.1—3.1 (6H, m, CH$_2$ and CH), 3.70 (6H, s, COOMe), 6.92 (1H, br s, 2-H), 7.2—7.6 (5H, m, Ph), 7.22, and 7.63 (each 1H, d, *J*=15.7 Hz, C$\underline{H}$=C$\underline{H}$Ph); ^{13}C NMR (CDCl$_3$) δ=26.18, 28.47 (each t, 3- and 6-C), 40.47, 41.00 (each d, 4- and 5-C), 52.12 (q, COOMe), 120.89, 128.42, 129.07, 130.48 (each d), 135.12 (s), 136.60 (d, 2-C), 138.36 (s, 1-C), 143.54 (d, PhCH=), 174.71 (s, COOMe), and 189.54 (s, CO); MS *m/z* (rel intensity, %) 328 (M$^+$, 25), 297 (25), 296 (48), 268 (53), 209 (100), 131 (62), 105 (19), 103 (52), and 77 (38).

Found: C, 69.72; H, 6.07%. Calcd for C$_{19}$H$_{20}$O$_5$: C, 69.50; H, 6.14%.

11a: Unstable colorless liquid; IR (neat) 1690 and 1650 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.2—3.3 (6H, m, CH$_2$ and CH), 2.90 (3H, s, NMe), 6.74 (1H, dd, *J*=10.5 and 2.0 Hz, =CH$_2$ (cis)), 7.22 (1H, dd, *J*=17.0 and 2.0 Hz, =CH$_2$ (trans)), 7.88 (1H, dd, *J*=17.0 and 10.5 Hz, COCH=), and 7.90 (1H, m, 6-H); ^{13}C NMR (CDCl$_3$) δ=21.55, 24.60 (each t, 4- and 7-C), 24.76 (q, NMe), 38.16, 38.63 (each d, 3a- and 7a-C), 128.81 (t, =CH$_2$), 130.34 (d, COCH=), 138.67 (d, 6-C), 139.90 (s, 5-C), 178.59, 179.00 (each s, CON), and 188.16 (s, CO); MS *m/z* (rel intensity, %) 219 (M$^+$, 37), 134 (16), 133 (21), 108 (24), 105 (30), 80 (20), 79 (81), 78 (29), and 77 (68).

Found: C, 66.01; H, 5.79; N, 6.12%. Calcd for C$_{12}$H$_{13}$NO$_3$: C, 65.74; H, 5.98; N, 6.39%.

11b: Colorless prisms (diethyl ether–hexane); mp 111—113 °C; IR (KBr) 1680 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.92, 2.08 (each 3H, d, *J*=1.0 Hz, =CMe$_2$), 2.1—3.3 (6H, m, CH$_2$ and CH), 2.92 (3H, s, NMe), 6.37 (1H, m, *J*=1.0 Hz, COCH=), and 6.88 (1H, m, 6-H); ^{13}C NMR (CDCl$_3$) δ=20.72 (q, =CMe$_2$), 21.60, 24.54 (each t, 4- and 7-C), 24.83 (q, NMe), 27.59 (q, =CMe$_2$), 38.34, 38.87 (each d, 3a- and 7a-C), 119.42 (d, COCH=), 135.97 (d, 6-C), 141.43 (s, 5-C), 155.11 (s, =CMe$_2$), 178.77, 179.24 (each s, COOMe), and 189.28 (s, CO); MS *m/z* (rel intensity, %) 247 (M$^+$, 22), 148 (24), 135 (20), 126 (25), 122 (42), 121 (21), 105 (22), 91 (25), 83 (97), 79 (57), 78 (50), and 77 (100).

Found: C, 67.91; H, 6.95; N, 5.81%. Calcd for C$_{14}$H$_{17}$NO$_3$: C, 68.00; H, 6.93; N, 5.66%.

11c: Colorless needles (diethyl ether–hexane); mp 161—162 °C; IR (KBr) 1680 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.2—2.9 (4H, m, CH$_2$), 2.92 (3H, s, NMe), 3.0—3.3 (2H, m, CH), 7.06 (1H, m, 6-H), 7.18, 7.62 (each 1H, d, *J*=16.0 Hz, C$\underline{H}$=C$\underline{H}$Ph), and 7.2—7.6 (5H, m, Ph); ^{13}C NMR (CDCl$_3$) δ=22.08, 24.83 (each t, 4- and 7-C), 25.01 (q, NMe), 38.46, 38.92 (each d, 3a- and 7a-C), 120.18 128.16, 128.81, 130.28 (each d), 134.68 (s), 137.50 (d, 6-C), 140.96 (s, 5-C), 143.72 (d, PhCH=), 178.77, 179.18 (each s, COOMe), and 187.81 (s, CO); MS *m/z* (rel intensity, %) 295 (M$^+$, 100), 294 (40), 209 (11), 184 (20), 183 (19), 131 (73), 103 (52), and 77 (53).

Found: C, 73.15; H, 5.90; N, 4.92%. Calcd for C$_{18}$H$_{17}$NO$_3$: C, 73.20; H, 5.80; N, 4.74%.

General Procedure for Acid-Catalyzed Electrocyclic Reaction of Dienones 9—11 Leading to 12—15. Use of *p*-toluenesulfonic acid as a catalyst: To a solution of *p*-toluenesulfonic acid in dry benzene or toluene (15—20 ml per 1 mmol of substrate) was added a dienone. The mixture was heated under reflux for the reaction time listed in Table 4. After cooled to room temperature, the resulting mixture was poured into ice water and extracted with diethyl ether. The ether extract was dried over anhydrous magnesium sulfate and evaporated in vacuo. The residue was chromatographed over silica gel with hexane–ethyl acetate (4:1 to 1:2 v/v). Use of gallium(III) chloride: A dienone in dichloromethane was slowly added at −20 °C to a solution of freshly prepared gallium(III) chloride in dry dichloromethane (20—30 ml per 1 mmol of substrate). After the reaction was completed (checked on TLC), the mixture was poured into ice water. The same separation procedure as above gave the cyclized products **12—15**. All the results are listed in Table 4.

12a: Colorless liquid; IR (neat) 1730, 1690, and 1650 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.4—2.5 (2H, m), 2.5—2.6 (2H, m), 2.6—2.7 (3H, m) 2.94 (1H, dd, *J*=19.8 and 7.2 Hz, one of 4-H), 3.10 (1H, ddd, *J*=7.2, 6.3, and 3.6 Hz, 5-H), 3.21 (1H, dt, *J*=5.8, 5.8, and 3.6 Hz, 6-H), 3.65, and 3.68 (each 3H, s, COOMe); ^{13}C NMR (CDCl$_3$) δ=21.31, 28.77, 29.41 (each t, 3-, 4-, and 7-C), 34.52 (t, 2-C), 39.34, 39.98 (each d, 5- and 6-C), 51.84 (q, COOMe), 136.27 (s, 7a-C), 170.61 (s, 3a-C), 172.61, 172.72 (each s, COOMe1/2 and 207.37 (s, 1-C); MS *m/z* (rel intensity, %) 252 (M$^+$, 38), 221 (23), 193 (39), 192 (23), 133 (100), 105 (43), and 91 (36).

Found: C, 61.96; H, 6.54%. Calcd for $C_{13}H_{16}O_5$: C, 61.89; H, 6.39%.

12b: Colorless liquid; IR (neat) 1725, 1680, and 1650 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.17, 1.20 (each 3H, s, 3-Me), 2.30 (2H, br s, 2-H), 2.43 (1H, ddt, *J*=18.2, 6.0, 2.0, and 2.0 Hz, one of 4-H), 2.57 (1H, br dd, *J*=19.7 and 6.5 Hz, one of 7-H), 2.63 (1H, ddd, *J*=18.2, 6.0, and 2.0 Hz, the other of 4-H), 2.86 (1H, ddd, *J*=19.7, 6.5, and 2.0 Hz, the other of 7-H), 3.10 (1H, dt, *J*=6.5, 6.5, and 3.6 Hz, 6-H), 3.15 (1H, dt, *J*=6.0, 6.0, and 3.6 Hz, 5-H), 3.66, and 3.68 (each 3H, s, COOMe); ^{13}C NMR (CDCl$_3$) δ=21.31, 23.84 (each t, 4- and 7-C), 26.60 (q, 3-Me), 39.45, 40.39 (each d, 5- and 6-C), 40.57 (s, 3-C), 51.37 (t, 2-C), 51.96, 52.08 (each q, COOMe), 134.33 (s, 7a-C), 172.72, 172.84 (each s, COOMe), 177.54 (s, 3a-C), and 205.96 (s, 1-C); MS *m/z* (rel intensity, %) 280 (M$^+$, 30), 240 (21), 221 (40), 209 (22), 161 (58), 121 (100), 119 (30), 105 (19), and 42 (71).

Found: C, 64.13; H, 7.28%. Calcd for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19%.

12c: Colorless liquid; IR (neat) 1730, 1700, and 1650 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.15 (3H, d, *J*=7.1 Hz, 3-Me), 1.99 (1H, dd, *J*=18.5 and 2.9 Hz, one of 2-H), 2.43 (1H, ddd, *J*=18.0, 6.0, and 2.2 Hz, one of 4-H), 2.50 (1H, ddd, *J*=19.0, 6.8, and 2.0 Hz, one of 7-H), 2.64 (1H, dd *J*=18.0 and 6.0 Hz, the other of 4-H), 2.65 (1H, dd, *J*=18.5 and 6.8 Hz, the other of 2-H), 2.76 (1H, m, 3-H), 2.78 (1H, dd, *J*=19.0, and 6.8 Hz, the other of 7-H), 3.15 (1H, dt, *J*=6.0, 6.0, and 3.6 Hz, 5-H), 3.20 (1H, dt, *J*=6.8, 6.8, and 3.6 Hz, 6-H), 3.63, and 3.66 (each 3H, s, COOMe); ^{13}C NMR (CDCl$_3$) δ=18.67 (q, 3-Me), 21.49, 26.71 (each t, 4- and 7-C), 35.93 (d, 3-C), 39.51, 40.27 (each d, 5- and 6-C), 43.65 (t, 2-C), 51.96, 52.08 (each q, COOMe), 135.74 (s, 7a-C), 172.77, 174.42, 174.66 (each s, COOMe and 3a-C), and 206.60 (s, 1-C); MS *m/z* (rel intensity, %) 266 (M$^+$, 8), 207 (21), 206 (21), 148 (100), 119 (20), 105 (66), 91 (42), and 77 (31).

Found: C, 62.92; H, 6.94%. Calcd for $C_{14}H_{18}O_5$: C, 63.15; H, 6.82%.

12c′ could not be separated from the mixture with **12c**. Its formation was confirmed by the appearance of additional peaks in ^{13}C NMR (CDCl$_3$) δ=21.31 (t) and 135.86 (s, 7a-C).

12d: Colorless liquid; IR (neat) 1730, 1700, 1650, and 1600 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.35 (1H, dd, *J*=19.0 and 5.9 Hz, one of 4-H), 2.42 (1H, dd, *J*=19.0 and 2.2 Hz, one of 2-H), 2.58 (1H, ddd, *J*=17.8, 6.5, and 2.1 Hz, one of 7-H), 2.70 (1H, dd, *J*=19.0 and 5.9 Hz, the other of 4-H), 2.77 (1H, ddd, *J*=17.8, 6.5, and 2.1 Hz, the other of 7-H), 2.95 (1H, dd, *J*=19.0 and 6.9 Hz, the other of 2-H), 3.01 (1H, dt, *J*=6.5, 6.5, and 3.6 Hz, 6-H), 3.19 (1H, dt, *J*=5.9, 5.9, and 3.6 Hz, 5-H), 3.68, 3.69 (each 3H, s, COOMe), 3.85 (1H, dd, *J*=6.9 and 2.2 Hz, 3-H), and 7.1—7.4 (5H, m, Ph); ^{13}C NMR (CDCl$_3$) δ=21.55, 26.95 (each t, 4- and 7-C), 39.45, 40.28 (each d, 5- and 6-C), 45.03 (t, 2-C), 47.50 (d, 3-C), 52.08 (q, COOMe), 127.17, 129.05 (each d), 136.91, 141.14 (each s), 172.43, 172.67, 172.84 (each s, COOMe and 3a-C), and 206.66 (s, 1-C).

Found: C, 69.53; H, 6.35%. Calcd for $C_{19}H_{20}O_5$: C, 69.50; H, 6.14%.

12d′: Colorless prisms (diethyl ether–hexane); mp 86—87 °C; IR (KBr) 1730, 1700, 1650, and 1600 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.36 (1H, dd, *J*=18.9 and 2.2 Hz, one of 2-H), 2.45 (1H, dd, *J*=19.7 and 6.2 Hz, one of 4-H), 2.56 (1H, ddd, *J*=18.0, 5.9, and 2.0 Hz, one of 7-H), 2.60 (1H, dd, *J*=19.7 and 6.8 Hz, the other of 4-H), 2.84 (1H, ddt, *J*=18.0, 5.9, 2.0, and 2.0 Hz, the other of 7-H), 2.95 (1H, dd, *J*=18.9 and 6.9 Hz, the other of 2-H), 3.11 (1H, ddd, *J*=6.8, 6.2, and 3.6 Hz, 5-H), 3.20 (1H, dt, *J*=5.9, 5.9, and 3.6 Hz, 6-H), 3.63, 3.68 (each 3H, s, COOMe), 3.87 (1H, dd, *J*=6.9 and 2.2 Hz, 3-H), and 7.0—7.3 (5H, m, Ph); ^{13}C NMR (CDCl$_3$) δ=21.64, 27.24 (each t, 4- and 7-C), 39.57, 40.37 (each d, 5- and 6-C), 45.37 (t, 2-C), 47.52 (d, 3-C), 51.95 (q, COOMe), 127.23, 128.89 (each d), 137.62, 141.02 (each s), 171.87, 172.51, 172.75 (each s, COOMe and 3a-C), and 207.00 (s, 1-C); MS *m/z* (rel intensity, %) 328 (M$^+$, 86), 297 (22), 269 (49), 268 (30), 209 (100), 167 (49), 165 (28), 103 (22), 77 (22), and 59 (95).

Found: C, 69.49; H, 6.13%. Calcd for $C_{19}H_{20}O_5$: C, 69.50; H, 6.16%.

13b: Colorless prisms (diethyl ether–hexane); mp 99—101 °C; IR (KBr) 1725 and 1650 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.80, 1.23 (each 3H, s, 3-Me), 1.40 (1H, q, *J*=12.0 Hz, one of 4-H), 2.20 (2H, br s, 2-H), 2.24 (1H, ddd, *J*=12.0, 5.0, and 3.0 Hz, the other of 4-H), 2.50 (1H, ddd, *J*=12.0, 5.0, and 3.0 Hz, 3a-H), 3.05 (1H, ddd, *J*=12.0, 10.0, and 3.0 Hz, 5-H), 3.70, 3.72 (each 3H, s, COOMe), 3.80 (1H, m, 6-H), and 6.70 (1H, t, *J*=3.0 Hz, 7-H); ^{13}C NMR (CDCl$_3$) δ=22.60, 26.89 (each q, 3-Me), 26.07 (t, 4-C), 36.87 (s, 3-C), 41.80, 44.91, 47.97 (each d, 3a-, 5-, and 6-C), 52.19, 52.49 (each q, COOMe), 54.60 (t, 2-C), 127.40 (d, 7-C), 141.08 (s, 7a-C), 171.60, 174.49 (each s, COOMe), and 203.84 (1-C); MS *m/z* (rel intensity, %) 280 (M$^+$, 15), 249 (25), 248 (63), 221 (30), 220 (39), 192 (27), 165 (37), 164 (100), 161 (43), 136 (44), 119 (20), 106 (20), 105 (91), 91 (34), 78 (38), and 77 (50).

Found: C, 64.46; H, 7.29%. Calcd for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19%.

13c: Unstable colorless liquid; IR (neat) 1730 and 1660 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.22 (3H, d, *J*=6.0 Hz, 3-Me), 1.30 (1H, q, *J*=12.0 Hz, one of 4-H), 1.5—2.6 (6H, m), 3.06 (1H, ddd, *J*=12.0, 10.0, and 3.0 Hz, 5-H), 3.72, 3.74 (each 3H, s, COOMe), 3.76 (1H, m, 6-H), and 6.64 (1H, t, *J*=3.0 Hz, 7-H); ^{13}C NMR (CDCl$_3$) δ=18.03 (q, 3-Me), 30.53 (t, 4-C), 36.58 (d, 3-C), 41.74, 44.85, 45.21 (each d, 3a-, 5-, and 6-C), 46.21 (t, 2-C), 52.25, 52.54 (each q, COOMe), 126.40 (d, 7-C), 142.31 (s, 7a-C), 171.60, 174.37 (each s, COOMe), and 204.19 (s, 1-C); MS *m/z* (rel intensity, %) 266 (M$^+$, 3), 206 (13), 148 (27), 105 (59), 91 (35), 79 (19), 78 (38), 77 (47), and 59 (100).

HRMS Found: *m/z* 266.1153. Calcd for $C_{14}H_{18}O_5$: M, 266.1153.

13d: Colorless liquid; IR (neat) 1730, 1665, and 1615 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.36 (1H, q, *J*=12.0 Hz, one of 4-H), 2.32 (1H, dt, *J*=12.0, 3.5, and 3.5 Hz, the other of 4-H), 2.4—2.9 (4H, m), 3.02 (1H, ddd, *J*=12.0, 10.0, and 3.0 Hz, 5-H), 3.68, 3.74 (each 3H, s, COOMe), 3.78 (1H, m, 6-H), 6.76 (1H, t, *J*=3.0 Hz, 7-H), and 7.1—7.5 (5H, m, Ph); ^{13}C NMR (CDCl$_3$) δ=30.59 (t, 4-C), 41.63, 44.97, 45.32 (each d, 3a-, 5-, and 6-C), 46.26 (t, 2-C), 47.56 (d, 3-C), 52.13, 52.55 (each q, COOMe), 126.99, 127.17, 128.82 (each d), 140.32, 141.67 (each s), 171.37, 174.13 (each s, COOMe), and 202.84 (s, 1-C).

Found: C, 69.42; H, 6.07%. Calcd for $C_{19}H_{20}O_5$: C, 69.50; H, 6.14%.

14a: Colorless needles (diethyl ether–hexane); mp 106—108 °C; IR (KBr) 1725 and 1700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.28 (1H, ddt, *J*=19.0, 5.3, 2.2, and 2.2 Hz, one of 4-H), 2.4—2.6 (6H, m), 2.72 (1H, dd, *J*=19.0 and 5.9 Hz, one of 7-H), 2.95 (1H, dt, *J*=9.2, 9.2, and 5.3 Hz, 5-H), 3.05 (1H, dt, *J*=9.2, 9.2, and 5.9 Hz, 6-H), 3.68, and 3.70 (each 3H, s, COOMe); ^{13}C NMR (CDCl$_3$) δ=22.49, 29.41, 30.24 (each t, 3-, 4-, and 7-C), 34.70 (t, 2-C), 40.63, 41.04 (each d, 5- and 6-C), 52.19 (q, COOMe), 136.56 (s, 7a-C), 169.90 (s, 3a-C), 174.02, 174.13 (each s, COOMe), and 207.06 (s, 1-C); MS *m/z* (rel intensity, %) 252 (M$^+$, 5), 220 (28), 193 (26), 192 (42), 133 (100), 105 (45), 91 (43), and 57 (20).

Found: C, 62.12; H, 6.42%. Calcd for $C_{13}H_{16}O_5$: C, 61.96; H, 6.54%.

14b (Mixture of 1 : 1 stereoisomers): Colorless liquid; IR (neat) 1730, 1700, and 1650 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.17 (3H, d, *J*=7.0 Hz, 3-Me), 2.7—3.2 (9H, m), 3.87, and 3.90 (each 3H, s, COOMe); ^{13}C NMR (CDCl$_3$) δ=18.53, 18.71 (each q, 3-Me), 22.41, 22.65, 27.65, 28.35 (each t, 4- and 7-C), 35.65, 36.13 (each d, 3-C), 40.65, 40.77, 41.24 (each d, 5- and 6-C), 43.83 (t, 2-C), 52.18 (q, COOMe), 136.01 (s, 7a-C), 174.00, 174.37, 174.48 (each s, COOMe and 3a-C), and 206.53 (s, 1-C); MS *m/z* (rel intensity, %) 266 (M$^+$, 3), 207 (17), 206 (42), 147 (100), 119 (21), 105 (64), 91 (38), 79 (19), 77 (29), and 59 (22).

HRMS Found: *m/z* 266.1164. Calcd for $C_{14}H_{18}O_5$: M, 266.1153.

14c: Colorless liquid; IR (neat) 1730 and 1700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.2—2.5 (3H, m), 2.66 (1H, br s), 2.8—3.1 (4H, m), 3.62, 3.69 (each 3H, s, COOMe), 3.87 (1H, br d, *J*=5.5 Hz, 3-H), and 7.0—7.5 (5H, m, Ph); ^{13}C NMR (CDCl$_3$) δ=22.71, 28.59 (each t, 4- and 7-C), 40.53, 41.06 (each d, 5- and 6-C), 45.18 (t, 2-C), 47.71 (d, 3-C), 52.18 (q, COOMe), 129.24 (d), 137.36, 140.89 (each s), 171.78, 174.19, 174.42 (each s, COOMe and 3a-C), and 206.48 (s, 1-C); MS *m/z* (rel intensity, %) 328 (M$^+$, 5), 268 (22), 209 (54), 167 (36), 166 (19), 165 (37), 131 (21), 115 (21), 105 (25), 104 (29), 103 (34), 91 (20), 78 (29), 77 (43), and 59 (100).

Found: C, 68.75; H, 6.15%. Calcd for $C_{19}H_{20}O_5$: C, 69.50; H, 6.14%.

15a: Colorless needles (diethyl ether–hexane); mp 170—173 °C; IR (KBr) 1710 and 1670 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.1—1.5 (2H, m), 2.2—2.5 (4H, m), 2.78 (1H, ddd, *J*=13.0, 5.0, and 2.0 Hz, one of 8-H), 2.96 (3H, s, NMe), 3.22 (1H, ddd, *J*=8.0, 5.5, and 2.0 Hz, 8a-H), 3.72 (1H, ddd, *J*=8.0, 5.2, and 2.8 Hz, 3a-H), and 6.70 (1H, dd, *J*=5.2 and 2.8 Hz, 4-H); ^{13}C NMR (CDCl$_3$) δ=25.07 (q, NMe), 27.77, 29.65 (each t, 7- and 8-C), 34.34 (d, 8a-C), 37.75 (t, 6-C), 39.86 (d, 3a-C), 42.15 (d, 7a-C), 124.82 (d, 4-C), 142.90 (s, 4a-C), 175.01, 178.24 (each s, 1- and 3-C), and 204.66 (s, 5-C); MS *m/z* (rel intensity, %); 219 (M$^+$, 15), 134 (29), 105 (35), 92 (100), 91 (59), 78 (83), 77 (47), and 51 (31).

Found: C, 65.85; H, 6.04%. Calcd for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98%.

15b+15b′: The crude reaction mixture was consisting of **15b**, **15b′**, and a small amount of **11b**. Pure **15b′** was isolated from the other two by column chromatography.

15b′: Colorless prisms (diethyl ether–hexane); mp 181—182 °C; IR (KBr) 1720, 1680, and 1650 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.82, 1.24 (each 3H, s, 7-Me), 1.50 (1H, ddd, *J*=12.8, 11.5, and 5.5 Hz, one of 8-H), 2.22 (1H, dddd, *J*=11.5, 5.0, 3.5, and 3.0 Hz, 7a-H), 2.18 (2H, br s, 6-H), 2.56 (1H, ddd, *J*=12.8, 5.0, and 2.5 Hz, the other of 8-H), 2.95 (3H, s, NMe), 3.26 (1H, ddd, *J*=8.0, 5.5, and 2.5 Hz, 8a-H), 3.70 (1H, ddd, *J*=8.0, 5.0, and 3.0 Hz, 3a-H), and 6.70 (1H, dd, *J*=5.0 and 3.5 Hz, 4-H); ^{13}C NMR (CDCl$_3$) δ=20.47 (t, 8-C) 22.59, 24.94, 26.77 (each q, NMe and 7-Me), 37.00 (s, 7-C), 39.53, 41.94, 43.77 (each d, 3a-, 7a-, and 8a-C), 54.18 (t, 6-C), 125.48 (d, 4-C), 142.60 (s, 4a-C), 175.31, 178.37 (each s, 1- and 3-C), and 203.78 (s, 5-C); MS *m/z* (rel intensity, %) 247 (M$^+$, 28), 191 (26), 163 (41), 106 (30), 105 (43), 79 (18), 78 (100), and 77 (34).

Found: C 67.92; H, 6.93; N, 5.60%. Calcd for $C_{14}H_{17}NO_3$: C, 68.00; H, 6.93; N, 5.66%.

The formation of **15b** was deduced only on the basis of ^{1}H NMR (CDCl$_3$) of the mixture with **11b**: δ=0.76, 1.24 (each 3H, s, 7-Me), 2.95 (3H, s, NMe), and 6.83 (1H, m, 4-H).

15c+15c′: Only **15c′** was separated in pure form through column chromatography of the mixture containing **15c** and **15c′**. However, **15c** was still contaminated by a small amount of **15c′**. **15c′**: Colorless prisms (dichloromethane–hexane); mp 246—248 °C; IR (KBr) 1770, 1690, and 1650 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.36 (1H, ddd, *J*=12.5, 10.5, and 6.0 Hz, one of 8-H), 2.3—2.9 (6H, m), 2.94 (3H, s, NMe), 3.19 (1H, ddd, *J*=8.0, 6.0, and 2.0 Hz, 8a-H), 3.74 (1H, ddd, *J*=8.0, 5.0, and 2.5 Hz, 3a-H), 6.78 (1H, dd, *J*=5.0 and 2.5 Hz, 4-H), and 7.28 (5H, m, Ph); MS *m/z* (rel intensity, %) 295 (M$^+$, 17), 184 (24), 163 (46), 106 (20), 105 (35), 104 (20), 77 (100), and 76 (26).

Found: C, 73.31; H, 5.91; N, 4.94%. Calcd for $C_{18}H_{17}NO_3$: C, 73.20; H, 5.80; N, 4.74%.

15c: IR (KBr) 1770, 1690, and 1650 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.04 (1H, ddd, *J*=12.5, 11.0, and 10.0 Hz, one of 8-H), 2.4—3.0 (4H, m), 2.98 (3H, s, NMe), 3.00 (1H, ddd, *J*=12.5, 8.5, and 6.0 Hz, 8a-H), 3.50 (1H, dt, *J*=8.5, 3.0, and 3.0 Hz, 3a-H), 7.00 (1H, t, *J*=3.0 Hz, 4-H), and 7.1—7.5 (5H, m, Ph).

^{13}C NMR of mixture of **15c** and **15c′** in CDCl$_3$: δ=24.77, 24.95 (each q, NMe), 25.77, 29.94 (each t, 8-C), 38.98, 39.57, 41.10, 41.92 (each d, 3a- and 8a-C), 44.56 (d, 7a—C), 47.32, 47.79 (each t, 6-C), 124.88, 125.23, 126.75, 126.87, 127.11, 128.69 (each d), 140.08, 140.26, 142.72, 143.37 (each s), 174.78, 177.60, 177.78 (each s, 1- and 3-C), 202.02, and 202.43 (each s, 5-C).

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