Reactions of endocyclic linearly conjugated dienolates with Michael acceptors leading to bicyclo[2.2.2]octane derivatives. Application to the synthesis of C_{13} degradation products of carotenoids

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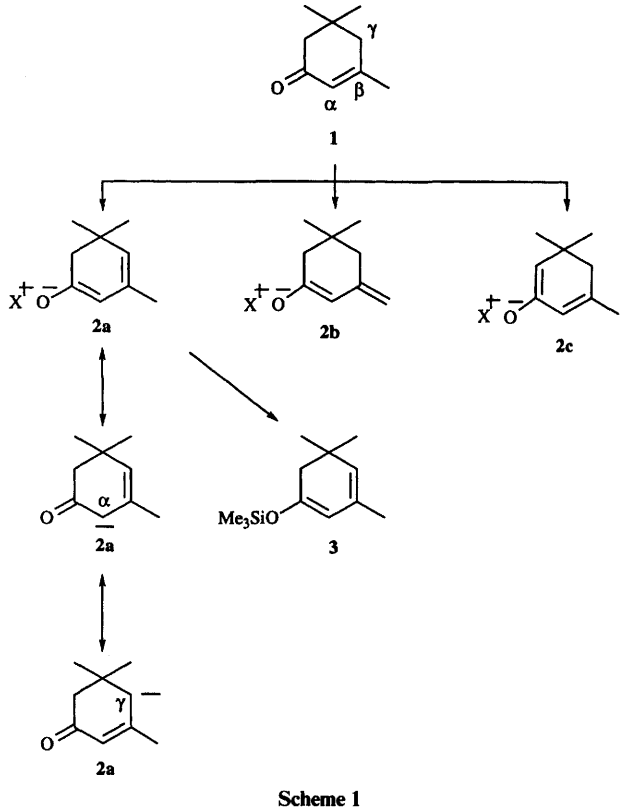
The endocyclic linearly conjugated dienolates from substituted cyclohex-2-enones react with but-3-en-2-one, substituted methyl propenoates, but-3-yn-2-one and methyl propiolate to afford bicyclo[2.2.2]-oct-2-en-1-ols 10a–c, 14a–c and bicyclo[2.2.2]octa-2,5-dien-1-ols 15a,b. The $AlCl_3$-catalysed reaction of 3,5,5-trimethyl-1-(trimethylsiloxy)cyclohexa-1,3-diene 3 with (*E*)-4-acetoxy- and (*E*)-4-methoxy-but-3-en-2-one provides *trans*-8-acetoxy-7-acetyl-3,5,5-trimethyl-1-(trimethylsiloxy)bicyclo[2.2.2]oct-2-enes 22, 23 and *trans*-7-acetyl-8-methoxy-3,5,5-trimethyl-1-(trimethylsiloxy)bicyclo[2.2.2]oct-2-enes 24, 25. Starting from these bicyclo[2.2.2]octenes, the C_{13} degradation products of carotenoids including 3-oxo-α-ionone 20, blumenol-C 27 and 1,3,7,7-tetramethyl-2-oxabicyclo[4.4.0]decan-9-one 29 have been synthesized.

Introduction

A large number of bicyclo[2.2.2]octane compounds, prepared by reactions of cross-conjugated dienolates derived from substituted cyclohex-2-enones with electron-deficient alkenes, have been utilized as convenient precursors for natural products syntheses,[1] and the mechanism related to the formation of bicycloadducts has often been discussed.[2,3] On the other hand, the reaction of linearly conjugated dienolates with electron-deficient alkenes and its application to natural product synthesis have been less extensively studied.[4] Regioselective formation of three conjugated dienolates **2a**,[5–7] **2b**[6,8] and **2c**[9] from isophorone **1** have been reported so far. We were interested in investigating the reactivity of the linearly conjugated dienolate **2a**, and expected that if the dienolate **2a** reacts at the γ-position to make a carbon–carbon bond, the carbon skeleton of C_{13} degradation products of carotenoids would be produced in a few steps. Many C_{13} degradation products of carotenoids have been isolated from various essential oils, black tea and tobaccos, and are considered to be formed by oxidative cleavage of conjugated double bonds of carotenoids,[10] such as lutein, which is well known as a colouring substance. Most C_{13} compounds possess an oxygen function at the C-3 position in the trimethylcyclohexene ring, as seen in 3-oxo-α-ionone **20**,[11] blumenol-C **27**[12] and 1,3,7,7-tetramethyl-2-oxabicyclo[4.4.0]decan-9-one **29**.[12b,13,14] A number of synthetic methods for these compounds have been reported because of their utility as flavour and fragrance constituents. We report here the reactions of two types of endocyclic linearly conjugated dienolates **2a**, **13a,b** and the corresponding trimethylsilyl enol ether **3**, derived from substituted cyclohex-2-enones with Michael acceptors, and synthesis of several C_{13} degradation products; 3-oxo-α-ionone **20**,[11] blumenol-C **27**[12] and 1,3,7,7-tetramethyl-2-oxabicyclo[4.4.0]decan-9-one **29**[12b,13,14] utilizing these reaction products.

Result and discussion

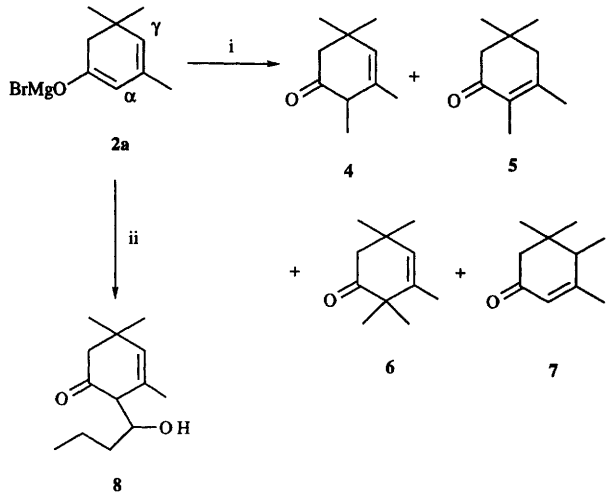
Electrophilic reaction of dienolate **2a** of isophorone **1** with electrophiles, including Michael acceptors, were investigated first. The magnesium dienolate **2a**,[5,6] generated by the reaction with methylmagnesium bromide in the presence of iron(III) chloride, can act as the tridentate anion through the three canonical forms and might react with electrophilic reagents at



Scheme 1

α- or γ-position as well as at the negatively charged oxygen atom (Scheme 1). In view of both theoretical predictions and experimental observations,[15] it was anticipated that the α-position of the linearly conjugated dienolate anion would participate preferentially. In fact, the reaction of the dienolate anion **2a** with methyl iodide gave exclusively α-alkylated and α,α-dialkylated products, **4–6**, and a trace amount of γ-alkylated product **7** was detected by means of gas chromatography. The reaction of butyraldehyde with the dienolate anion **2a** also afforded predominantly the aldol product **8** at the α-position in 44% yield (Scheme 2).

However, the reaction with but-3-en-2-one **9a** afforded



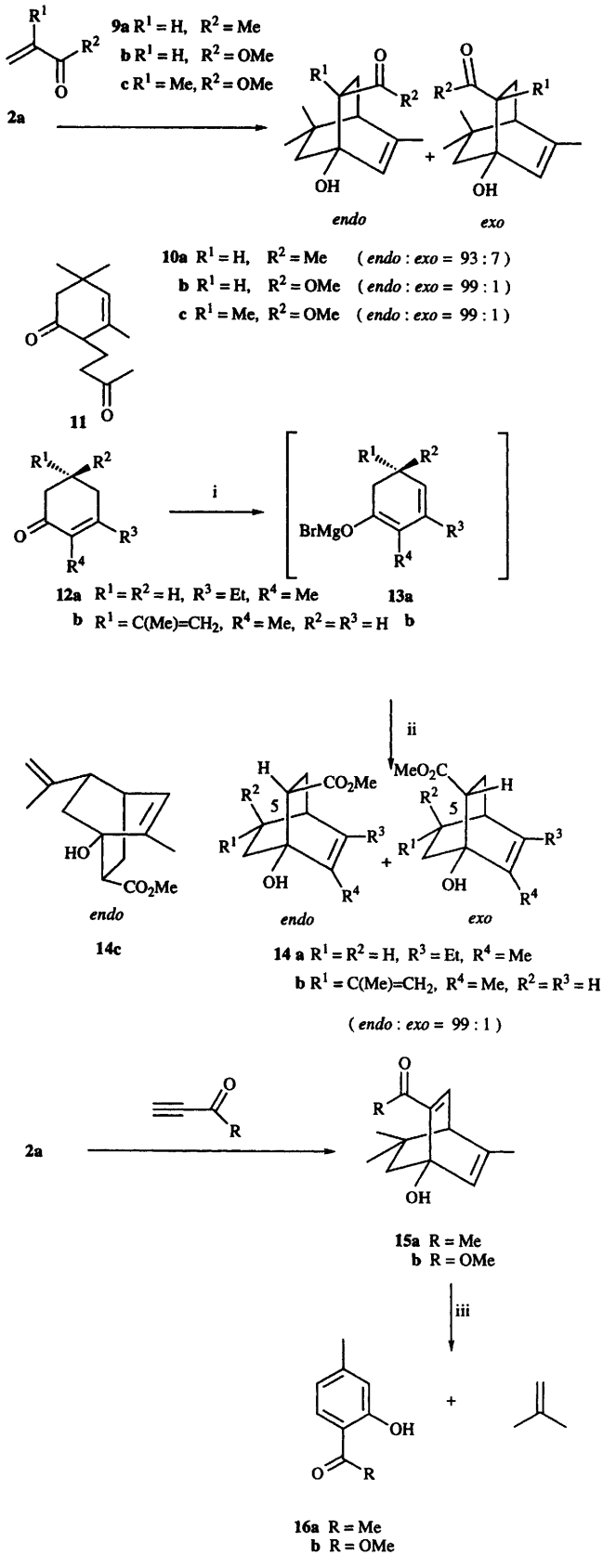
Scheme 2 *Reagents:* i, MeI, HMPA; ii, butyraldehyde

bicyclic compounds **10a** and Michael adduct **11** at the α-position in 40% yield and a 3 : 1 ratio. Similarly, treatment with methyl acrylate **9b** and methyl α-methylacrylate **9c** afforded bicyclic compounds **10b** and **10c** in 81 and 41% yield, respectively. When the dienolate **13a**[6] from 2-methyl-3-ethylcyclohex-2-enone reacted with methyl acrylate **9b**, bicyclic compound **14a** was obtained in 66% yield. It is worthy of note that the reactions of these dienolates occurred with high stereoselectivity to give almost exclusively single diastereomers, *endo*-cycloadducts. In these reactions, the amount of *exo*-cycloadducts was too little for it to be isolated by column chromatography, and the ratio of cycloadducts was determined only by capillary gas chromatography. The authentic *exo*-adducts were obtained by thermal Diels–Alder cycloaddition[16] of dienoxysilanes derived from dienolates **2a** and **13a**. After desilylation of the cycloadducts (*endo*/*exo* = 1/1–4/1), the bicyclic compounds were chromatographed on silica gel to separate the *endo*- and *exo*-adduct, respectively; the *endo*/*exo* ratio of compound **10a** was determined after silylation using *N*-(trimethylsilyl)imidazole with a catalytic amount of tetrabutylammonium fluoride (TBAF),[17] because of thermal instability of the parent **10a** under gas chromatographic conditions. Reaction of the dienolate **13b** derived from (−)-carvone **12b** with methyl acrylate **9b** afforded also bicyclic compounds, **14b** and **14c**, in 37 and 8% yield, respectively. In this reaction, neither *exo* form of compound **14b** nor that of compound **14c** was detected even by capillary gas chromatography (Scheme 3).

Provided that conformer **17** of the dienolate **13b** is more stable than conformer **18** because of a disfavoured allylic interaction between an H-atom and the isopropenyl group as shown in Fig. 1, attack of methyl acrylate **9b** on the upper face of the conformer **17** is favoured, affording the stereoisomer **14b** preferentially.

The relative stereochemistry at C-5 and C-7 in bicyclic compounds **14b** and **14c** was established by difference nuclear Overhauser enhancement (NOE) measurements in the ^{1}H NMR spectra. Thus, the NOEs of compound **14b** were observed between H^a and H^d, H^a and H^c, and H^a and H^e, while that of compound **14c** was observed between H^c and OMe, H^c and H^a, and H^c and H^f as shown in Fig. 1. In addition, H^d in compound **14b** appeared upfield of H^d in compound **14c** due to the diamagnetic anisotropy of the carbon–carbon double bond, and, moreover, W-type long-range coupling was observed between H^b and H^d in compound **14c**. On the other hand, such long-range coupling was not observed with H^b of compound **14b**.

The reaction of dienolate **2a** with but-3-yn-2-one led to bicyclic octadiene compound **15a** in 50% yield. Methyl propiolate also afforded the corresponding bicyclic octadiene compound **15b** in 63% yield. These bicyclic compounds are



Scheme 3 *Reagents and conditions:* i, MeMgBr, $FeCl_3$; ii, methyl acrylate; iii, toluene, reflux

assumed to be unstable, and retro-Diels–Alder reactions are expected to proceed with elimination of alkene under thermal condition. In fact, refluxing toluene solution of the bicyclic compound **15a** and **15b** provided aromatic compounds **16a** and **16b** by elimination of isobutylene in 90 and 95% yield, respectively.

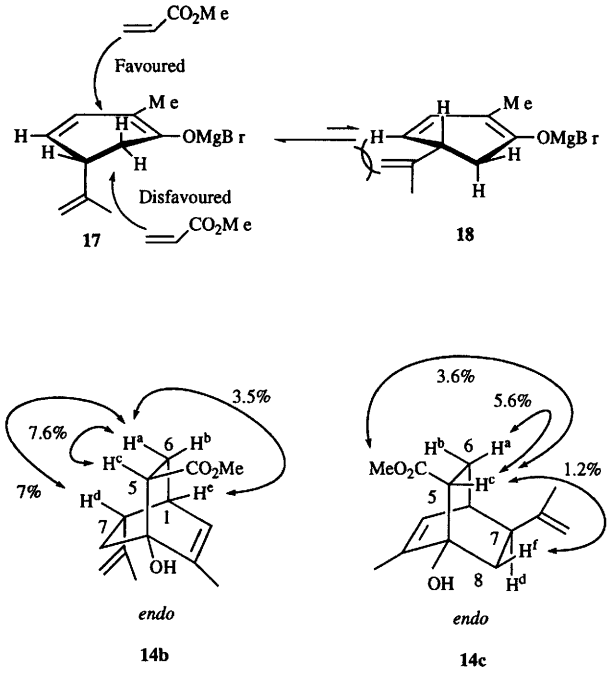
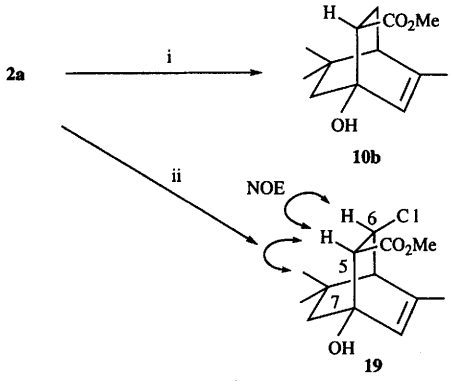


Fig. 1

Mechanistically, there are two possibilities, a Diels–Alder reaction or a sequential Michael and intramolecular aldol reaction, in the present formation of the bicyclic compounds. Several reactions of linearly conjugated dienolates with Michael acceptors have been reported,[4] but elucidation of their reaction mechanisms has still to be achieved. Much attention has been paid to the reactions of kinetically controlled cross-conjugated dienolate anions from substituted cyclohex-2-enones with methyl acrylate analogues.[1,2] White and Reusch have investigated whether this reaction proceeded by a Diels–Alder addition process or by a sequence of double Michael reactions.[3] When they carried out the reaction of cross-conjugated dienolate anion **2c** from isophorone **1** with methyl (*Z*)-β-chloroacrylate at −25 °C, the adduct having a bicyclic octane skeleton was not obtained but only an addition–elimination reaction product was afforded. This result supported a sequential Michael mechanism in their bicyclic octane formation. In our case, we treated the linear conjugate anion **2a** with the same ester to afford a single 5-*endo*-6-*endo* cycloadduct **19** in 68% yield retaining the *Z* stereochemistry of β-chloroacrylate (Scheme 4). This result indicates that formation of two



Scheme 4 *Reagents and conditions:* i, methyl acrylate, ether, −78 °C, 2 min; ii, methyl (*Z*)-β-chloroacrylate, ether, 0–25 °C, 2 h

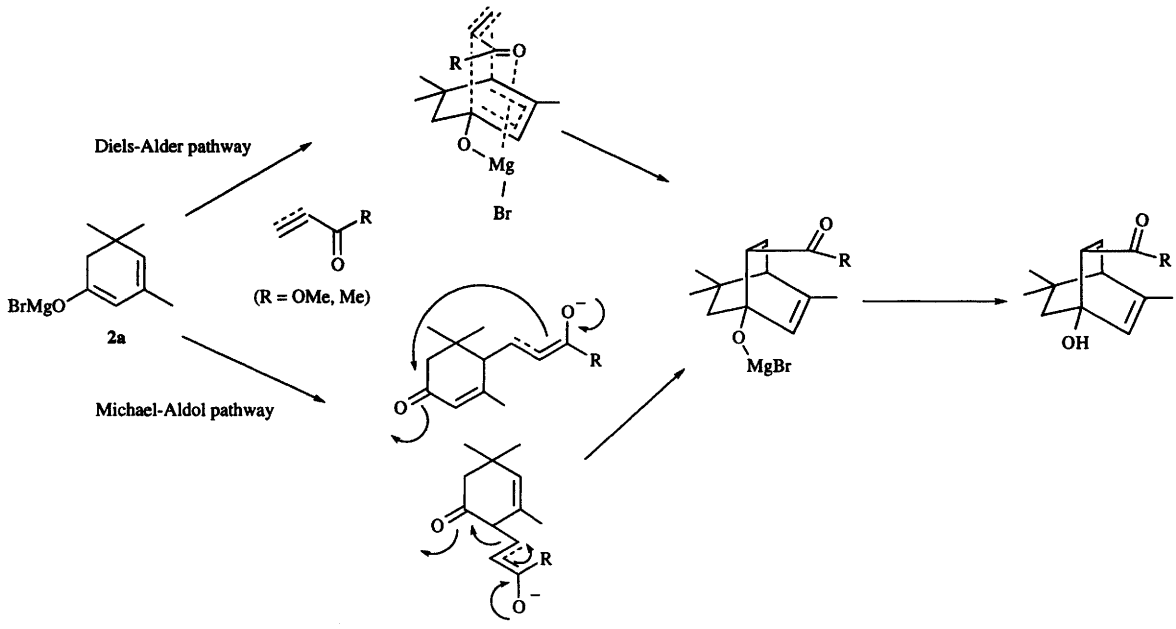
bonds is synchronous in the present reaction, eliminating a possible intervention of an intermediary ester enolate with longer lifetime.

The stereochemistry of the stereocentres at the C-5 and C-6 in cycloadduct **19** was assigned by NOE measurements in the ^{1}H NMR spectrum. The NOEs were observed between 5-H and 6-H, as well as between 5-H and 7-*exo*-Me. The ^{1}H NMR signals at δ 4.78 (dd, *J* 9.2 and 3.4 Hz) and 3.10 (d, *J* 9.2 Hz) were assigned to 5-H and 6-H, respectively. The coupling pattern of these protons indicated that the adduct **19** has a 5-*endo*-6-*endo* configuration. When the reaction mixture of the dienolate **2a** with methyl acrylate **9b** at −78 °C was worked up within 2 *min*, cycloadduct **10b** was obtained in 35% yield without Michael adducts at the α- or γ-position. Failure to trap an intermediary Michael adduct as well as the clear formation of compound **19** indicate that the present reaction would proceed *via* an oxyanion-accelerated Diels–Alder reaction (Scheme 5).

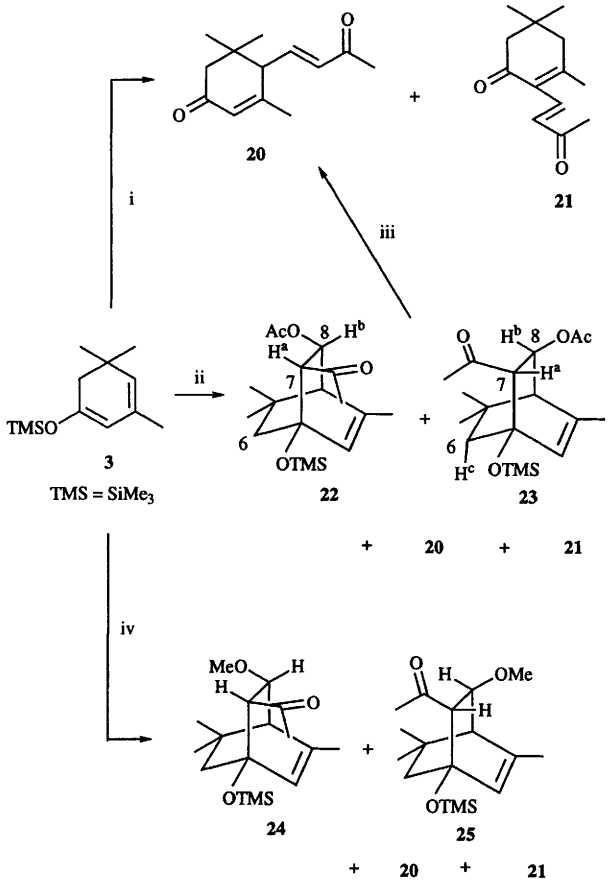
Next, the reaction of dienoxysilane **3** with Michael acceptors possessing a leaving group at the β-position was investigated. As previously described, it was reported that dienoxysilane **3** from dienolate **2a** reacted with several dienophiles, for example, but-3-en-2-one, to give the corresponding Diels–Alder adducts at 200 °C.[16] When we carried out the reactions of dienoxysilane **3** with (*E*)-4-acetoxy- and (*E*)-4-methoxy-but-3-en-2-one, Diels–Alder adducts were not obtained under the same thermal reaction conditions. However, treatment with (*E*)-4-acetoxybut-3-en-2-one in the presence of an equivalent amount of $AlCl_3$ in CH_2Cl_2 for 2 h gave 3-oxo-α-ionone **20**, *via* an addition–elimination at the γ-position, was isolated in 60% yield along with another addition–elimination product, **21**, at the α-position in 10% yield. Compound **20** is a degradation product of carotenoids,[11] key intermediates for producing C_{13} carotenoid degradation products,[18] and cyclic carotenoids.[19] In order to confirm the mechanism of formation of the 3-oxo-α-ionone **20**, the same reaction was quenched in 15 min. In this case, not only were addition–elimination products **20** and **21** but also cyclic adducts **22** and **23** were obtained in 13 and 15% yield, respectively. The stereochemistry of adducts **22** and **23** were assigned on the basis of the coupling constants of the bridgehead hydrogen in the ^{1}H NMR spectra. Since the coupling was observed between H^a and H^c in adduct **23**, the relative stereochemistry at C-7 of compound **23** was determined to be *exo* to the olefinic linkage. H^a in adducts **22** and **23** has coupling constants of 6.0 (doublet) and 6.0 and 2.0 Hz, (dd), respectively. Thus, orientations of acetyl and acetoxy groups on compounds **22** and **23** were established to be *anti* in each other. Moreover, H^a in adduct **22** appeared upfield ($\Delta\delta$ 0.17 ppm) to that of adduct **23**, and H^b in adduct **22** appeared downfield ($\Delta\delta$ 0.5 ppm) to that of adduct **23** due to the diamagnetic anisotropy of double bond. These coupling patterns as well as the difference of chemical shift values indicated that adducts **22** and **23** have 7-*endo*-8-*exo* and 7-*exo*-8-*endo* configuration, respectively, as indicated. Lack of 7-*endo* selectivity was presumably due to the steric hindrance between the *gem*-dimethyl group of the dienoxysilane **3** and the acetoxy group of the (*E*)-4-acetoxybut-3-en-2-one. When the reaction of a mixture of cyclic adducts **22** and **23** with $AlCl_3$ at 0 °C in CH_2Cl_2 for 1 h, the 3-oxo-α-ionone **20** was isolated as a single product in 92% yield. When the reaction of compound **3** with (*E*)-4-methoxybut-3-en-2-one was performed, a similar reaction took place to afford the diones **20** and **21** in 54 and 6% yield, respectively. Moreover, when the reaction was quenched in 5 min, corresponding cyclic adducts **24** and **25** were obtained in 13 and 8% yield, respectively (Scheme 6).

These results indicated that 3-oxo-α-ionone **20** was not produced *via* the Michael addition followed by elimination at the γ-position of the dienoxysilane but *via* the Diels–Alder reaction followed by retro-aldol and a β-elimination reaction (Scheme 7).

Transformation of the bicyclic compounds **10a** and **10b** into the γ-substituted isophorones **26** and **28** was accomplished by using a retro-aldol reaction in hydrochloric acid. Dione **26** is a key intermediate for syntheses of C_{13} carotenoid degradation products[16] and had been reduced with an equivalent amount



Scheme 5



Scheme 6 *Reagents and conditions:* i, (*E*)-4-acetoxybut-3-en-2-one or (*E*)-4-methoxybut-3-en-2-one, $AlCl_3$, CH_2Cl_2, 0 °C, 2 h; ii, (*E*)-4-acetoxybut-3-en-2-one, $AlCl_3$, CH_2Cl_2, 0 °C, 15 min; iii, $AlCl_3$, CH_2Cl_2, 0 °C, 1 h; iv, (*E*)-4-methoxybut-3-en-2-one, $AlCl_3$, CH_2Cl_2, 0 °C, 5 min

of $NaBH_4$ in methanol to give blumenol-C **27**.[12,14] This compound was treated with NaH in benzene to give the oxabicyclo[4.4.0]decanone **29**[12b,13,14] as a mixture of two diastereomers in 55% yield, whose ratio was determined to be 97:3 by capillary gas chromatography. Although Roberts and his co-workers[14] alternatively synthesized compound **29** from blumenol-C **27** with toluene-*p*-sulfonic acid in benzene, the stereochemistry of bicycle **29** has not been reported. The configuration of major diastereomer **29** was assigned by NOE measurements in the ^1H NMR spectrum as indicated by arrows in the formulae (Scheme 8).

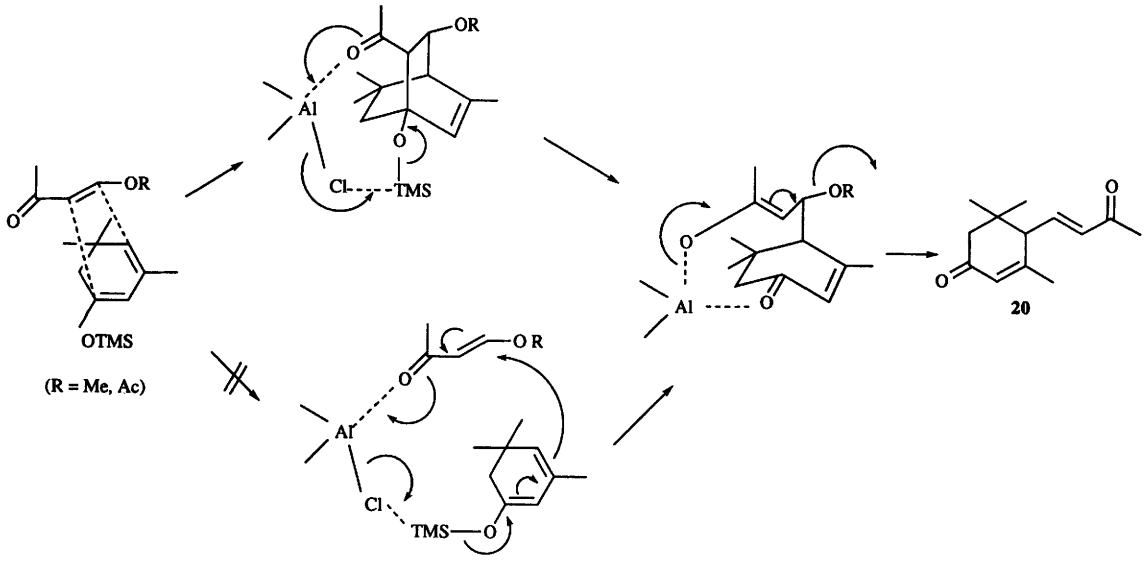
In summary, we have shown that endocyclic linearly conjugated dienolates and enol ethers reacted with Michael acceptors to give bicyclo[2.2.2]octane compounds which led to several C_{13} degradation products of carotenoids.

Experimental

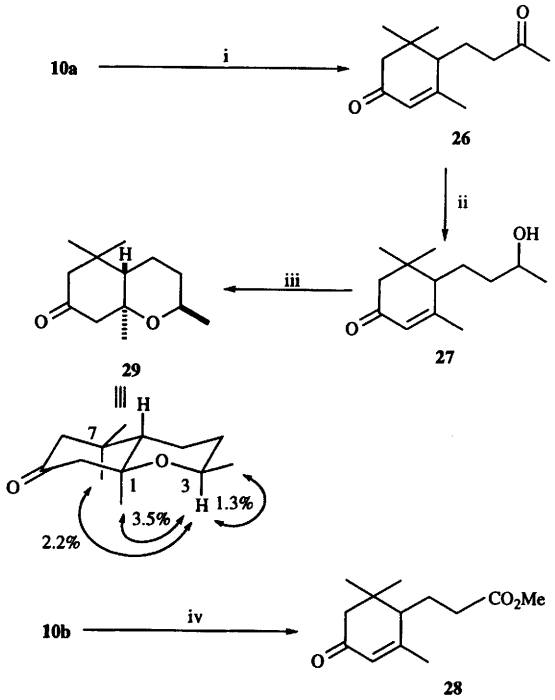
All mps were determined with a Mettler FP62 hot-stage apparatus and were uncorrected. IR spectra were recorded on a JASCO FT/IR-7000 spectrophotometer. NMR spectra were obtained for solutions in deuteriochloroform with JEOL LA-600 (600 MHz), GX-400 (400 MHz) and LA-400 (400 MHz) and Hitachi R-24B (60 MHz) instruments for ^1H with tetramethylsilane as an internal standard and JEOL LA-600 (150 MHz) and LA-400 (100 MHz) instruments for ^{13}C. *J* Values are given in Hz. Mass spectra were run on Hewlett Packard 5992B and Hitachi M-80B spectrometers with a Hitachi MO101 data system. Capillary gas chromatographic analyses were carried out on Shimadzu GC-7A and Hewlett Packard 5890 series II. Specific rotations, $[\alpha]_D$, were run on a JASCO DIP-370 polarimeter for solutions in chloroform; $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. Microanalysis was carried out in the microanalytical laboratory of the Institute for Chemical Reaction Science, Tohoku University. Ether and DME refer to diethyl ether and 1,2-dimethoxyethane, respectively. Ether, CH_2Cl_2, benzene and DME were used after being dried with 4 Å molecular sieves, 80–100 mesh.

General procedure for the reaction of the linearly conjugated dienolate anions 2a or 13b from substituted cyclohex-2-enones 1 or 12b with electrophiles

Method I. To a solution of methylmagnesium bromide (3.69 cm^3, 10.9 mmol, 2.94 mol dm^{-3} solution in ether) in anhydrous ether (15 cm^3) was added anhydrous iron(III) chloride (22 mg, 0.14 mmol) under nitrogen at 0 °C. After the reaction mixture had been stirred for 15 min, a solution of a substituted cyclohex-2-enone (9.1 mmol) **1** or **12b** in ether (2 cm^3) was added dropwise to the mixture for a period of 15 min and the resulting solution was stirred for an additional 30 min at that temperature. A solution of an electrophile (10.9 mmol) in ether (2 cm^3) was added over a period of 5 min and the mixture was



Scheme 7



Scheme 8 *Reagents and conditions:* i, aq. HCl, THF, 25 °C; ii, $NaBH_4$ (0.65 mol equiv.), MeOH; iii, NaH (3 mol equiv.), benzene; iv, aq. HCl, MeOH, 85 °C

stirred for 1 h at 0 °C and for 1 h at room temperature. The reaction was quenched by addition of aq. ammonium chloride and the product was extracted with ethyl acetate. The extract was washed with brine, dried over anhydrous magnesium sulfate and evaporated. The crude product was chromatographed on silica gel with ethyl acetate–hexane as eluent.

Preparation of authentic *exo*- and *endo*-cycloadducts 10b,c and 14a

Method II. A mixture of dienoxysilane **3**[6,16] or 3-ethyl-2-methyl-1-(trimethylsiloxy)cyclohexa-1,3-diene[6] (0.5 mmol) and Michael acceptors (0.6 mmol) was heated at 200 °C for 7 h in a steel autoclave. To the reaction mixture were added tetrahydrofuran (THF) (2.0 cm^3) and HCl (1 mol dcm^{-3} solution; 0.5 cm^3, 0.5 mmol) and the solution was stirred for 1 h at room temperature. The product was extracted with ethyl acetate. The extract was washed successively with aq. sodium hydrogen carbonate and brine, dried over anhydrous magnesium sulfate and evaporated. The crude product was chromatographed on silica gel with ethyl acetate–hexane as eluent.

Reaction of the dienolate anions 2a with methyl iodide

According to Method I of the general procedure, the dienolate anions **2a** was treated with methyl iodide (1.67 g, 11.8 mmol) in the presence of hexamethylphosphoric triamide (HMPA) (14 cm^3). The reaction was quenched by addition of aq. ammonium chloride. Extraction with hexane, followed by chromatography on silica gel, afforded an oil (1.06 g, 74%), which was analysed by capillary GC (FFAP; 50 m; 70–200 °C; 4 °C min^{-1}) to be a mixture of compounds **4**, **5**, **6** and **7** in proportions 45:15:39:1. Analytically pure samples of the four compounds were isolated by repeated silica gel chromatography.

2,3,5,5-Tetramethylcyclohex-3-enone 4. ν_{max}(KBr)/cm^{-1} 2952 (C–H), 1712 (C=O), 1440 and 1282; δ_H(60 MHz) 1.05 (6 H, s, 2 × Me), 1.21 (3 H, d, *J* 7, 2-Me), 2.21 (3 H, d, *J* 1, 3-Me), 2.35 (2 H, br s, 6-H_2), 2.63 (1 H, q, *J* 7, 2-H) and 5.49 (1 H, br s, 4-H); *m/z* 152 (M^+, 35%), 137 (15), 100 (94), 109 (44), 95 (100), 81 (16), 67 (29) and 41 (35) (Found: M^+, 152.1172. $C_{10}H_{16}O$ requires *M*, 152.1200).

2,3,5,5-Tetramethylcyclohex-2-enone 5. ν_{max}(KBr)/cm^{-1} 2950 (C–H), 1682 (C=O), 1642 (C=C), 1370 and 1282; δ_H(60 MHz) 1.00 (6 H, s, 2 × Me), 1.73 (3 H, s, C=CMe), 1.90 (3 H, s, C=CMe) and 2.15–2.35 (4 H, m); *m/z* 152 (M^+, 27%), 96 (100), 68 (20), 67 (19) and 41 (13) (Found: M^+, 152.1181).

2,3,3,5,5-Pentamethylcyclohex-3-enone 6. ν_{max}(KBr)/cm^{-1} 2965 (C–H), 1718 (C=O) and 1442; δ_H(60 MHz) 1.00 (6 H, s, 2 × Me), 1.17 (6 H, s, 2 × Me), 1.69 (3 H, d, *J* 4, 3-Me), 2.88 (2 H, s, 6-H_2) and 5.45 (1 H, br s, 4-H); *m/z* 166 (M^+, 47%), 151 (38), 124 (79), 123 (62), 110 (70), 109 (100), 95 (25), 81 (43), 67 (29) and 41 (57) (Found: M^+, 166.1380. $C_{11}H_{18}O$ requires *M*, 166.1357).

3,4,5,5-Tetramethylcyclohex-2-enone 7. ν_{max}(KBr)/cm^{-1} 2960 (C–H) and 1665 (C=O); δ_H(60 MHz) 0.98 (3 H, s, 5-Me), 1.00 (3 H, s, 5-Me), 1.08 (3 H, d, *J* 8, 4-Me), 1.85 (3 H, d, *J* 2, 3-Me), 2.01–2.71 (3 H, m) and 5.80 (1 H, br s, 2-H); *m/z* 152 (M^+, 17%), 96 (100), 81 (16), 67 (14) and 41 (14) (Found: M^+, 152.1201. $C_{10}H_{16}O$ requires *M*, 152.1200).

2-(1-Hydroxybutyl)-3,5,5-trimethylcyclohex-3-enone 8. According to Method I of the general procedure, the reaction of dienolate anions **2a** with butyraldehyde afforded a *threo*/*erythro* mixture of aldol **8** (841 mg, 44%), ν_{max}(KBr)/cm^{-1} 3435 (OH), 2930 (C–H) and 1695 (C=O); δ_H(60 MHz) 0.93 (3 H, t, *J* 7,

CH_3CH_2), 1.02 (3 H, s, 5-Me), 1.07 (3 H, s, 5-Me), 1.1–1.7 (4 H, m), 1.71 (3 H, d, *J* 1, 3-Me), 2.29–2.38 (2 H, m, 6-H_2), 3.07 (1 H, m, 2-H), 3.49 (0.3 H, s, OH), 3.67 (0.7 H, s, OH), 3.89 (1 H, m, C*H*OH) and 5.54 (1 H, m, 4-H); *m/z* 192 ($M^+ - H_2O$, 51%), 177 (81), 167 (100), 179 (32), 149 (32), 135 (52), 121 (50), 91 (34), 71 (43), 55 (65) and 41 (37) (Found: $M - H_2O^+$, 192.1505. $C_{13}H_{20}O$ requires $M - H_2O$, 192.1512).

7-*endo*-Acetyl-3,5,5-trimethylbicyclo[2.2.2]oct-2-en-1-ol 10a and 4-(2,4,4-trimethyl-6-oxocyclohex-2-enyl)butan-2-one 11

In the same manner, the reaction of dienolate anions **2a** with but-3-en-2-one **9a** afforded *endo*-adduct **10a** (568 mg, 30%) and the Michael adduct **11** (189 mg, 10%). To a solution of 100 mg of crude **10a** in dimethylformamide (1 cm^3) under nitrogen was added *N*-(trimethylsilyl)imidazole (144 mg, 1.03 mmol), followed by a solution of TBAF (1 mol dm^{-3} solution in THF; 0.01 cm^3, 0.01 mmol) and the mixture was stirred for 2 h at room temperature. The reaction was quenched with 10% aq. sodium hydrogen carbonate, extracted with hexane and the organic layer was washed with brine. The extract was analysed by GLC (FFAP; 2 m; 70–200 °C; 5 °C min^{-1}) and shown to be a mixture of *endo*-*O*-silyl derivative[16] of **10a** and *exo*-*O*-silyl compound[16] of **10a** in the ratio 93:7. The *endo*-adduct **10a** had ν_{max}(KBr)/cm^{-1} 3401 (OH), 2925 (C–H), 1695 (C=O), 1440 and 1080; δ_H(60 MHz) 0.85 (3 H, s, 5-Me), 1.08 (3 H, s, 5-Me), 1.29 (2 H, s), 1.05–1.81 (2 H, m), 1.76 (3 H, d, *J* 2, 3-Me), 2.05 (3 H, s, COMe), 1.96–2.85 (2 H, m), 4.61 (1 H, s, OH) and 5.70 (1 H, br s, 2-H); *m/z* 208 (M^+, 7%), 151 (7), 138 (42), 123 (100), 109 (43), 91 (11), 77 (10), 55 (9) and 41 (44). The Michael adduct **11** had ν_{max}(KBr)/cm^{-1} 2950 (C–H) and 1705 (C=O); δ_H(60 MHz) 1.01 (3 H, s, 4-Me), 1.06 (3 H, s, 4-Me), 1.74 (3 H, d, *J* 2, 2-Me), 1.5–2.7 (7 H, m), 2.12 (3 H, s, COMe) and 5.44 (1 H, br s, 3-H); *m/z* 208 (M^+, 6%), 193 (6), 135 (100), 123 (8), 107 (7), 93 (8), 79 (6) and 43 (41) (Found: M^+, 208.1464. $C_{13}H_{20}O_2$ requires *M*, 208.1462).

Methyl 5-*endo*-4-hydroxy-2,7,7-trimethylbicyclo[2.2.2]oct-2-ene-5-carboxylate 10b and methyl 5-*exo*-4-hydroxy-2,7,7-trimethylbicyclo[2.2.2]oct-2-ene-5-carboxylate 10b

According to Method I of the general procedure, the reaction of dienolate anions **2a** with methyl acrylate **9b** afforded a crude product which was shown by capillary GC (FFAP; 50 m; 70–200 °C; 4 °C min^{-1}) to be a mixture of *endo*-adduct **10b** and *exo*-adduct **10b** in the ratio 99:1. Chromatography of the crude product provided *endo*-adduct **10b** (1.65 g, 81%); ν_{max}-(KBr)/cm^{-1} 3450 (OH), 2945 (C–H), 1710 (C=O), 1435 and 1160 (OMe); δ_H(60 MHz) 0.83 (3 H, s, 7-Me), 1.04 (3 H, s, 7-Me), 1.30 (2 H, s), 1.21–1.65 (2 H, m), 1.86 (3 H, d, *J* 2, 2-Me), 1.96–2.79 (2 H, m), 3.62 (3 H, s, OMe), 3.85 (1 H, s, OH) and 5.58 (1 H, br s, 3-H); *m/z* 224 (M^+, 1%), 168 (2), 138 (45), 123 (100), 109 (21), 80 (13), 55 (14) and 41 (10).

According to Method II, the reaction of dienoxysilane **3** and methyl acrylate **9b** afforded *exo*-adduct (17 mg, 15%) **10b** and *endo*-adduct **10b** (63 mg, 56%). *exo*-Adduct **10b** had ν_{max}(KBr)/cm^{-1} 3445 (OH), 2948 (C–H), 1720 (C=O), 1439 and 1160 (OMe); δ_H(60 MHz) 0.83 (3 H, s, 7-Me), 1.05 (3 H, s, 7-Me), 0.9–1.49 (2 H, m), 1.68 (3 H, d, *J* 2, 2-Me), 1.49–2.63 (4 H, m), 3.20 (1 H, s, OH), 3.23 (3 H, s, OMe) and 5.72 (1 H, br s, 3-H); *m/z* 224 (M^+, 3%), 168 (15), 138 (56), 123 (100), 109 (32), 80 (16), 55 (15) and 41 (10).

Methyl 5-*endo*-4-hydroxy-2,5,7,7-tetramethylbicyclo[2.2.2]oct-2-ene-5-carboxylate 10c and methyl 5-*exo*-4-hydroxy-2,5,7,7-tetramethylbicyclo[2.2.2]oct-2-ene-5-carboxylate 10c

According to Method I of the general procedure, the reaction of dienolate anions **2a** with methyl α-methylacrylate **9c** afforded a crude product, which was shown by capillary GC (FFAP; 50 m; 70–210 °C, 4 °C min^{-1}) to be a mixture of *endo*-adduct **10c** and *exo*-adduct **10c** in the ratio 99:1. Chromatography of the crude product provided *endo*-adduct **10c** (888 mg, 41%); ν_{max}-(KBr)/cm^{-1} 3499 (OH), 2950 (C–H), 1707 (C=O), 1439, 1295, 1260 and 1160; δ_H(400 MHz) 0.87 (3 H, s, 7-Me), 1.09 (3 H, s, 7-Me), 1.13 (1 H, d, *J* 13.1, 8-H), 1.34 (3 H, s, 5-Me), 1.65 (1 H, d, *J* 13.1, 8-H), 1.66–1.76 (2 H, m, 6-H_2), 1.74 (3 H, d, *J* 1.4, 2-Me), 2.14 (1 H, dd, *J* 13.9 and 3.8, 1-H), 3.67 (3 H, s, OMe), 4.36 (1 H, s, OH) and 5.70 (1 H, br s, 3-H); *m/z* 238 (M^+, 0.1%), 138 (44), 123 (100), 108 (2), 69 (2) and 41 (4) [Found: $M^+ - (Me)_2C{=}CH_2$, 182.0962. $C_{10}H_{14}O_3$ requires $M - C_4H_8$, 182.0942].

According to Method II, the reaction of dienoxysilane **3** and methyl α-methylacrylate **9c** afforded *exo*-adduct (18 mg, 15%) **10c** and *endo*-adduct **10c** (15 mg, 13%). exo-*Adduct* **10c** had ν_{max}(KBr)/cm^{-1} 3500 (OH), 2925 (C–H), 1700 (C=O), 1439, 1288, 1220 and 1100; δ_H(60 MHz) 0.86 (3 H, s, 7-Me), 0.97 (3 H, s, 7-Me), 1.17 (3 H, s, 5-Me), 1.25–1.41 (2 H, m), 1.57–2.10 (2 H, m), 1.79 (3 H, d, *J* 2, 2-Me), 2.76 (1 H, dd, *J* 14 and 3.2, 1-H), 3.73 (3 H, s, OMe), 3.85 (1 H, s, OH) and 5.60 (1 H, br s, 3-H); *m/z* 238 (M^+, 0.2%), 138 (48), 123 (100), 108 (5), 69 (2) and 41 (5) (Found: M^+, 238.1600. $C_{14}H_{22}O_3$ requires *M*, 238.1568).

Methyl 5-*endo*-2-ethyl-4-hydroxy-3-methylbicyclo[2.2.2]oct-2-ene-5-carboxylate 14a and methyl 5-*exo*-2-ethyl-4-hydroxy-3-methylbicyclo[2.2.2]oct-2-ene-5-carboxylate 14a

To a solution of methylmagnesium bromide (3.07 cm^3, 9.1 mmol; 2.94 mol dm^{-3} in ether) was added DME (12 cm^3) under nitrogen at 0 °C. Anhydrous iron(III) chloride (489 mg, 3 mmol) was added and the solution was stirred for 1 h at room temperature, then at 0 °C. A solution of 3-ethyl-2-methylcyclohex-2-enone **12a** (174 mg, 1.26 mmol) in DME (2 cm^3) was added to the mixture over a period of 15 min and the resulting solution was stirred for an additional 35 min at that temperature. A second solution of methylmagnesium bromide (1.25 cm^3, 3.77 mmol; 2.94 mol dm^{-3} in ether) was added over a period of 10 min and the mixture was stirred for 35 min. A solution of methyl acrylate **9b** (433 mg, 5 mmol) in DME (2 cm^3) was added over a period of 5 min and the resulting solution was stirred for 1 h at 0 °C and then for 1 h at room temperature. The reaction mixture was quenched by addition of aq. ammonium chloride and the product was extracted with ethyl acetate. The extract was washed with brine, dried over anhydrous magnesium sulfate, and evaporated. The crude product was shown by capillary GC (DB-1; 60 m; 70–20 °C; 4 °C min^{-1}) to be a mixture of *endo*-adduct **14a** and *exo*-adduct **14a** in the ratio 99:1. Chromatography of the crude product on silica gel provided endo-*adduct* **14a** (186 mg, 66%); ν_{max}(KBr)/cm^{-1} 3500 (OH), 2947 (C–H), 1725, 1711, 1430 and 1199; δ_H(600 MHz) 0.96 (3 H, t, *J* 7.7, CH_2CH_3), 1.34 (1 H, m), 1.42 (1 H, m), 1.57–1.67 (3 H, m), 1.74 (3 H, s, 3-Me), 1.94 (1 H, ddd, *J* 13.0, 10.6 and 2.5, 6-H), 2.09 (2 H, q, *J* 7.3, CH_2CH_3), 2.38 (1 H, m, 1-H), 2.70 (1 H, dd, *J* 10.6 and 5.1, 5-H), 3.66 (3 H, s, OMe) and 4.00 (1 H, s, OH); δ_C(150 MHz) 10.85 (CH_2CH_3), 12.93 (3-CH_3), 24.27 (CH_2CH_3), 25.98 (CH_2), 31.11 (CH_2), 32.65 (CH_2), 33.50 (CH-1), 49.09 (CH-5), 51.71 (OCH_3), 74.57 (C-4), 132.13 (C=C), 138.45 (C=C) and 175.99 (CO); *m/z* 224 (M^+, 14%), 193 (4), 163 (7), 138 (100), 123 (28), 109 (32), 91 (9), 55 (13) and 41 (5) (Found: M^+, 224.1459. $C_{13}H_{20}O_3$ requires *M*, 224.1411).

According to Method II, the reaction of 3-ethyl-2-methyl-1-(trimethylsiloxy)cyclohexa-1,3-diene with methyl acrylate **9b** afforded *exo*-adduct (4 mg, 4%) **14a** and *endo*-adduct **14a** (24 mg, 21%). exo-*Adduct* **14a** had ν_{max}(KBr)/cm^{-1} 3447 (OH), 2950 (C–H), 1725, 1710, 1435 and 1175; δ_H(600 MHz) 0.98 (3 H, t, *J* 7.7, CH_2CH_3), 1.29 (1 H, m), 1.35 (1 H, m), 1.57 (1 H, s), 1.65 (1 H, m), 1.74 (3 H, s, 3-Me), 1.87–1.94 (2 H, m), 2.11 (2 H, q, *J* 7.7, CH_2CH_3), 2.37 (1 H, m, 1-H), 2.45 (1 H, ddd, *J* 12.1, 5.8 and 3.3, 5-H), 3.13 (1 H, s, OH) and 3.74 (3 H, s, OMe); δ_C(150 MHz) 9.51 (CH_2CH_3), 12.83 (3-CH_3), 24.06 (CH_2CH_3), 25.98 (CH_2), 29.78 (CH_2), 30.63 (CH_2), 33.36 (CH-1), 47.58 (CH-5), 51.83 (OCH_3), 74.66 (C-4), 133.92

(C=C) and 175.68 (CO); *m/z* 224 (M^+, 13%), 193 (5), 163 (6), 138 (100), 123 (32), 109 (35), 91 (8), 55 (18) and 41 (7) (Found: M^+, 224.1462).

Methyl (1*R*,4*R*,5*R*,7*S*)-4-hydroxy-7-isopropenyl-3-methylbicyclo[2.2.2]oct-2-ene-5-carboxylate 14c and methyl (1*S*,4*S*,5*S*,7*S*)-4-hydroxy-7-isopropenyl-3-methylbicyclo[2.2.2]oct-2-ene-5-carboxylate 14b

According to Method I of the general procedure, the reaction of dienolate anions **13b** from (−)-carvone **12b** with methyl acrylate **9b** afforded 5-*endo*-7-*exo* adduct **14c** (172 mg, 8%) and 5-*endo*-7-*endo* adduct **14b** (795 mg, 37%). Compound **14c** had $[\alpha]_D$ −37.3 (*c* 0.354); ν_{max}(KBr)/cm^{-1} 3450 (OH), 2945 (C–H), 1710 (C=O), 1639 (C=C), 1432, 1201 (OMe), 1011 and 883; δ_H(400 MHz) 1.52 (1 H, dddd, *J* 13.0, 5.1, 3.5 and 1.8, 6-H), 1.59–1.66 (2 H, m, 8-H_2), 1.76 (3 H, s, CH_2=C*Me*), 1.84 (3 H, d, *J* 1.6, 3-Me), 2.10 (1 H, ddd, *J* 13.1, 10.8 and 2.1, 6-H), 2.15 (1 H, m, 7-H), 2.47 (1 H, m, 1-H), 2.65 (1 H, dd, *J* 10.6 and 4.8, 5-H), 3.67 (3 H, s, OMe), 4.08 (1 H, s, OH), 4.88 (1 H, s, C=CH), 4.94 (1 H, dd, *J* 2.8 and 1.3, C=CH) and 5.97 (1 H, dd, *J* 6.8 and 1.6, 2-H); δ_C(100 MHz) 16.41 (CH_3), 23.24 (CH_3), 25.61 (CH_2-6), 32.39 (CH-7), 35.68 (CH_2-8), 44.08 (CH-1), 48.81 (CH-5), 51.83 (OCH_3), 74.94 (C-4), 109.83 (C=*C*H_2), 127.16 (CH-2), 142.93 (C), 146.10 (C) and 175.85 (CO); *m/z* 236 (M^+, 10%), 168 (100), 150 (25), 136 (39), 109 (57), 108 (88), 91 (16), 80 (16), 79 (14), 77 (13), 55 (28) and 41 (13) (Found: M^+, 236.1420. $C_{14}H_{20}O_3$ requires *M*, 236.1411). Compound **14b** had $[\alpha]_D$ +25.5 (*c* 0.932); ν_{max}(KBr)/cm^{-1} 3449 (OH), 2940 (C–H), 1711 (C=O), 1640 (C=C), 1430, 1205 (OMe) and 881; δ_H(600 MHz) 1.35 (1 H, dd, *J* 12.3 and 6.4, 8-H), 1.65 (1 H, m, 6-H), 1.65 (3 H, s, CH_2=C*Me*), 1.57 (1 H, s), 1.84 (3 H, d, *J* 1.7, 3-Me), 1.85 (1 H, dd, *J* 12.4 and 9.8, 8-H), 2.03 (1 H, ddd, *J* 12.9, 10.4 and 2.5, 6-H), 2.41 (1 H, dd, *J* 9.9 and 6.4, 7-H), 2.52 (1 H, m, 1-H), 2.73 (1 H, dd, *J* 10.6 and 5.7, 5-H), 3.68 (3 H, s, OMe), 3.91 (1 H, s, OH), 4.58 (1 H, s, C=CH), 4.66 (1 H, s, C=CH) and 5.78 (1 H, dd, *J* 6.3, 1.1, 2-H); δ_C(100 MHz) 16.12 (CH_3), 21.84 (CH_3), 32.89 (CH_2-6), 34.00 (CH-7), 38.92 (CH_2-8), 44.91 (CH-1), 47.46 (CH-5), 51.81 (OCH_3), 74.79 (C-4), 109.35 (C=*C*H_2), 124.29 (CH-2), 142.09 (C), 148.51 (C) and 176.05 (CO); *m/z* 236 (M^+, 7%), 168 (93), 150 (34), 136 (48), 109 (88), 108 (100), 91 (17), 80 (24), 55 (26) and 41 (13) (Found: M^+, 236.1407).

6-Acetyl-3,8,8-trimethylbicyclo[2.2.2]octa-2,5-dien-1-ol 15a

According to Method I of the general procedure, the reaction of dienolate anions **2a** with but-3-yn-2-one afforded bicyclic octadiene **15a** (937 mg, 50%); ν_{max}(KBr)/cm^{-1} 3410 (OH), 3075 (C–H), 2952 (C–H), 1645 (C=O) and 1601 (C=C); δ_H(60 MHz) 0.92 (3 H, s, 8-Me), 1.01 (3 H, s, 8-Me), 1.32 [1 H, d (of AB q), *J* 12, 7-H], 1.53 [1 H, d (of AB q), *J* 12, 7-H], 1.84 (3 H, d, *J* 2, 3-Me), 2.29 (3 H, s, COMe), 2.91 (1 H, dd, *J* 6 and 2, 4-H), 5.91 (1 H, m, 2-H), 6.55 (1 H, s, OH) and 7.32 (1 H, d, *J* 6, 5-H); *m/z* 150 [M^+ − C=C(Me)$_2$, 43%], 135 (100), 107 (10), 77 (20) and 43 (14) (Found: M^+ − CHCOMe, 138.1068. $C_9H_{14}O$ requires *M* − C_3H_4O, 138.1044).

Methyl 1-hydroxy-5,8,8-trimethylbicyclo[2.2.2]octa-2,5-diene-2-carboxylate 15b

According to Method I of the general procedure, the reaction of dienolate anions **2a** with methyl propiolate afforded bicyclic octadiene **15b** (1.27 g, 63%); ν_{max}(KBr)/cm^{-1} 3452 (OH), 2948 (C–H), 1648 (C=O) and 1603 (C=C); δ_H(60 MHz) 0.90 (3 H, s, 7-Me), 0.97 (3 H, s, 7-Me), 1.27 [1 H, d (of AB q), *J* 11, 8-H], 1.47 [1 H, d (of AB q), *J* 11, 8-H], 1.79 (3 H, d, *J* 2, 2-Me), 2.86 (1 H, dd, *J* 6 and 2, 1-H), 3.72 (3 H, s, OMe), 5.78 (1 H, s, OH), 5.89 (1 H, m, 3-H) and 7.27 (1 H, d, *J* 6, 6-H); *m/z* (CI) 223 (MH^+, 82%), 207 (5), 191 (6), 167 (100), 166 (34), 134 (19) and 106 (5) [Found: M^+ − C=C(Me)$_2$, 166.0644. $C_9H_{10}O_3$ requires *M* − C_4H_6, 166.0629].

6-Acetyl-5-methylphenol 16a

A solution of bicyclic octadiene **15a** (129 mg, 0.63 mmol) in toluene (2 cm^3) was refluxed for 1 h. After evaporation off of toluene, the residue was chromatographed on silica gel to afford the phenol **16a** (85 mg, 90%); ν_{max}(KBr)/cm^{-1} 3420, 1620 (C=O), 1241, 1220 and 792; δ_H(60 MHz) 2.32 (3 H, s, Me), 2.57 (3 H, s, COMe), 6.58–6.78 (2 H, m, ArH), 7.62 (1 H, d, *J* 8, ArH) and 14.28 (1 H, s, OH); *m/z* 150 (M^+, 43%), 135 (100), 107 (10), 77 (20) and 43 (14).

Methyl 2-hydroxy-4-methylbenzoate 16b

A solution of bicyclic octadiene **15b** (96 mg, 0.43 mmol) in toluene (2 cm^3) was refluxed for 1 h. After evaporation off of toluene, the residue was chromatographed on silica gel to afford the phenol **16b** (68 mg, 95%); ν_{max}(KBr)/cm^{-1} 3150, 2952 (C–H), 1680 (C=O) and 770; δ_H(60 MHz) 2.30 (3 H, s, Me), 3.89 (3 H, s, OMe), 6.55–6.85 (2 H, m, ArH), 7.68 (1 H, d, *J* 8, ArH) and 10.69 (1 H, s, OH); *m/z* 166 (M^+, 10%), 134 (33), 106 (8), 78 (7), 56 (53) and 41 (100).

Methyl 5-*endo*-6-*endo*-6-chloro-4-hydroxy-2,7,7-trimethylbicyclo[2.2.2]oct-2-ene-5-carboxylate 19

According to Method I of the general procedure, the reaction of dienolate anions **2a** with methyl (*Z*)-β-chloroacrylate [20] afforded *cycloadduct* **19** (1.60 g, 68%), mp 80–81 °C (Found: C, 60.4; H, 7.4; Cl, 13.7. $C_{13}H_{19}ClO_3$ requires C, 60.35; H, 7.4; Cl, 13.7%); ν_{max}[KBr(pellet)]/cm^{-1} 3550 (OH), 3532 (OH), 2951 (C–H), 1720 (C=O), 1365 and 1200; δ_H(400 MHz) 0.93 (3 H, s, 7-Me), 1.11 (3 H, s, 7-Me), 1.32 (2 H, s, 8-H_2), 1.90 (3 H, d, *J* 1.5, 2-Me), 2.28 (1 H, s, 1-H), 3.10 (1 H, d, *J* 9.2, 5-H), 3.29 (1 H, s, *J* 13.1, OH), 3.71 (3 H, s, OMe), 4.78 (1 H, dd, *J* 9.2 and 3.4, 6-H) and 5.90 (1 H, s, 3-H); *m/z* 258 (M^+, 3%), 223 (33), 207 (16), 167 (43), 138 (57), 123 (100), 107 (23), 91 (11), 77 (18) and 59 (13).

(*E*)-4-(2,4,4-Trimethyl-6-oxo-cyclohex-1-enyl)but-3-en-2-one 21 and 3-oxo-α-ionone, (*E*)-4-(2,6,6-trimethyl-4-oxocyclohex-2-enyl)but-3-en-2-one 20

To a solution of dienoxysilane **3** (525 mg, 2.5 mmol) and (*E*)-4-acetoxybut-3-en-2-one [21] (320 mg, 2.5 mmol) in CH_2Cl_2 (5 cm^3) was added $AlCl_3$ (333 mg, 2.5 mmol) and the mixture was stirred at 0 °C for 2 h under nitrogen. The reaction mixture was poured into cold aq. sodium hydrogen carbonate and extracted with ethyl acetate. The extract was washed with brine, dried over anhydrous magnesium sulfate and evaporated. The residue was chromatographed on silica gel to afford adduct **21** (52 mg, 10%) and 3-oxo-α-ionone **20** (309 mg, 60%). *Compound* **21** had ν_{max}(KBr)/cm^{-1} 2965 (C–H), 1670 (C=O), 1600 (C=C), 1368, 1254 and 980; δ_H(60 MHz) 1.03 (6 H, s, 2 × 4-Me), 2.10 (3 H, s, COMe), 2.28–2.50 (7 H, m), 6.80 (1 H, d, *J* 16, C=CH) and 7.35 (1 H, d, *J* 16, C=CH); *m/z* 206 (M^+, 1%), 163 (100), 122 (17), 107 (10), 79 (16) and 43 (38) (Found: M^+, 206.1352. $C_{13}H_{18}O_2$ requires *M*, 206.1306).

3-Oxo-α-ionone **20** had ν_{max}(KBr)/cm^{-1} 2960 (C–H), 1670 (C=O), 1379, 1265 and 995; δ_H(60 MHz) 1.02 (3 H, s, 6-Me), 1.08 (3 H, s, 6-Me), 1.90 (3 H, d, *J* 1, 2-Me), 2.05–2.25 (2 H, s, 5-H_2), 2.27 (3 H, s, COMe), 2.75 (1 H, d, *J* 9, 1-H), 5.93 (1 H, br s, 3-H), 6.13 (1 H, d, *J* 16, C=CHCO) and 6.72 (1 H, dd, *J* 16 and 9, C–C*H*=CH); *m/z* 206 (M^+, 1%), 150 (17), 108 (100), 91 (12), 77 (18), 55 (8) and 43 (97).

To a solution of dienoxysilane **3** (483 mg, 2.3 mmol) and (*E*)-4-methoxybut-3-en-2-one (230 mg, 2.3 mmol) in CH_2Cl_2 (5 cm^3) was added $AlCl_3$ (306 mg, 2.3 mmol) and the mixture was stirred at 0 °C for 2 h under nitrogen. The reaction mixture was worked up in a similar manner as above to afford adduct **21** (28 mg, 6%) and 3-oxo-α-ionone **20** (256 mg, 54%).

8-*endo*-Acetoxy-7-*exo*-acetyl-3,5,5-trimethyl-1-(trimethylsiloxy)bicyclo[2.2.2]oct-2-ene 23 and 8-*exo*-acetoxy-7-*endo*-acetyl-3,5,5-trimethyl-1-(trimethylsiloxy)bicyclo[2.2.2]oct-2-ene 22

To a solution of dienoxysilane **3** (504 mg, 2.4 mmol) and (*E*)-4-acetoxybut-3-en-2-one [21] (307 mg, 2.4 mmol) in CH_2Cl_2 (5 cm^3)

was added $AlCl_3$ (319 mg, 2.4 mmol) and the mixture was stirred at 0 °C for 15 min under nitrogen. The reaction mixture was worked up in a similar manner as above to afford 7-*exo*-8-*endo* adduct **23** (122 mg, 15%), 7-*endo*-8-*exo* adduct **22** (105 mg, 13%), adduct **21** (49 mg, 10%) and 3-oxo-α-ionone **20** (148 mg, 30%). 7-exo-8-endo *Adduct* **23** had ν_{max}(KBr)/cm^{-1} 3051, 2975 (C–H), 1740 (C=O), 1720 (C=O), 1661 (C=C), 1259, 882 and 845; δ_H(60 MHz) 0.12 (9 H, s, $SiMe_3$), 0.86 (3 H, s, 5-Me), 1.23 (3 H, s, 5-Me), 0.99–1.23 (2 H, m, 6-H_2), 1.80 (3 H, d, *J* 2, 3-Me), 1.92 (3 H, s, COMe), 1.99 (1 H, m, 4-H), 2.20 (3 H, s, OCOMe), 2.59 (1 H, dd, *J* 6 and 2, 7-H), 5.07 (1 H, dd, *J* 3 and 3, 8-H) and 5.82 (1 H, br s, 2-H); *m*/*z* 338 (M^+, 0.8%), 263 (8), 210 (63), 207 (40), 196 (18), 195 (100), 143 (8), 73 (43) and 43 (57) (Found: M^+, 338.1881. $C_{18}H_{30}O_4Si$ requires *M*, 338.1911).

7-endo-8-exo *Adduct* **22** had ν_{max}(KBr)/cm^{-1} 3053, 2975 (C–H), 1738 (C=O), 1720 (C=O), 1660 (C=C), 880 and 840; δ_H(60 MHz) 0.12 (9 H, s, $SiMe_3$), 0.87 (3 H, s, 5-Me), 1.22 (3 H, s, 5-Me), 1.41 [1 H, d (of AB q), *J* 12, 6-H], 1.64 [1 H, d (of AB q), *J* 12, 6-H], 1.83 (3 H, d, *J* 2, 3-Me), 1.89 (1 H, m, 4-H), 1.97 (3 H, s, COMe), 2.15 (3 H, s, OCOMe), 2.76 (1 H, d, *J* 6, 7-H), 4.57 (1 H, dd, *J* 6 and 3, 8-H) and 5.60 (1 H, br s, 2-H); *m*/*z* 338 (M^+, 1%), 263 (10), 210 (55), 207 (43), 196 (17), 195 (100), 143 (14), 73 (42) and 43 (61) (Found: M^+, 338.1907).

Transformation of a mixture of cycloadducts 23 and 22 into 3-oxo-α-ionone 20

To a solution of 7-*exo*-8-*endo* adduct **23** (53 mg, 0.16 mmol) and 7-*endo*-8-*exo* adduct **22** (47 mg, 0.14 mmol) in CH_2Cl_2 (1 cm^3) was added $AlCl_3$ (40 mg, 0.3 mmol) and the mixture was stirred at 0 °C for 1 h under nitrogen. The reaction mixture was worked up in a similar manner as above to afford 3-oxo-α-ionone **20** (56 mg, 92%).

7-*exo*-Acetyl-8-*endo*-methoxy-3,5,5-trimethyl-1-(trimethylsiloxy)bicyclo[2.2.2]oct-2-ene 25 and 7-*endo*-acetyl-8-*exo*-acetoxy-3,5,5-trimethyl-1-(trimethylsiloxy)bicyclo[2.2.2]oct-2-ene 24

To a solution of dienoxysilane **3** (525 mg, 2.5 mmol) and (*E*)-4-methoxybut-3-en-2-one (250 mg, 2.5 mmol) in CH_2Cl_2 (5 cm^3) was added $AlCl_3$ (333 mg, 2.5 mmol) and the mixture was stirred at 0 °C for 5 min under nitrogen. The reaction mixture was worked up in a similar manner as above to afford 7-*exo*-8-*endo* adduct **25** (62 mg, 8%), 7-*endo*-8-*exo* adduct **24** (101 mg, 13%), adduct **21** (31 mg, 6%) and 3-oxo-α-ionone **20** (175 mg, 34%).

7-exo-8-endo *Adduct* **25** had ν_{max}(KBr)/cm^{-1} 3071, 2965 (C–H), 1715 (C=O), 1663 (C=C), 1100, 890 and 840; δ_H(400 MHz) 0.14 (9 H, s, $SiMe_3$), 0.88 (3 H, s, 5-Me), 1.02 (1 H, dd, *J* 12.2 and 2, 6-H), 1.22 (3 H, s, 5-Me), 1.50 (1 H, d, *J* 12.2, 6-H), 1.83 (3 H, d, *J* 2, 3-Me), 2.08 (1 H, m, 4-H), 2.30 (3 H, s, COMe), 2.63 (1 H, dd, *J* 6 and 2, 7-H), 3.18 (3 H, s, OMe), 4.04 (1 H, dd, *J* 2.9 and 2.9, 8-H) and 5.84 (1 H, s, 2-H); *m*/*z* 310 (M^+, 0.2%), 295 (1), 263 (1), 211 (19), 210 (57), 196 (18), 195 (100), 179 (8), 73 (36) and 43 (23) (Found: M^+, 310.1967. $C_{17}H_{30}O_3Si$ requires *M*, 310.1962).

7-endo-8-exo *Adduct* **24** had ν_{max}(KBr)/cm^{-1} 3051, 2935 (C–H), 1770 (C=O), 1661 (C=C), 1100 and 840; δ_H(60 MHz) 0.12 (9 H, s, $SiMe_3$), 0.85 (3 H, s, 5-Me), 1.25 (3 H, s, 5-Me), 1.52 (2 H, m, 6-H_2), 1.82 (3 H, d, *J* 2, 3-Me), 2.13 (1 H, m, 4-H), 2.22 (3 H, s, COMe), 2.80 (1 H, d, *J* 6, 7-H), 3.20 (3 H, s, OMe), 3.49 (1 H, dd, *J* 6 and 3, 8-H) and 5.60 (1 H, br s, 2-H); *m*/*z* 310 (M^+, 0.3%), 295 (1), 267 (1), 211 (35), 210 (56), 196 (18), 195 (100), 179 (9), 73 (38) and 43 (26) (Found: M^+, 310.1999).

4-(2,6,6-Trimethyl-4-oxocyclohex-2-enyl)butan-2-one 26

To a solution of *endo*-adduct **10a** (102 mg, 0.5 mmol) in THF (2 cm^3) was added HCl (1 mol dm^{-3} solution; 0.5 cm^3, 0.5 mmol) and the mixture was stirred for 1 h at room temperature. The solution was extracted with ethyl acetate. The extract was washed successively with aq. sodium hydrogen carbonate and brine, dried over anhydrous magnesium sulfate and evaporated. The crude product was chromatographed on silica gel with ethyl acetate–hexane (1:2) to afford dione **26** (86 mg, 84%); ν_{max}(KBr)/cm^{-1} 2947 (C–H), 1710 (C=O), 1660 (C=O) and 1250; δ_H(60 MHz) 1.03 (3 H, s, 6-Me), 1.08 (3 H, s, 6-Me), 1.75–2.80 (7 H, m), 2.01 (3 H, d, *J* 2, 2-Me), 2.15 (3 H, s, COMe) and 5.84 (1 H, s, 3-H); *m*/*z* 208 (M^+, 21%), 151 (72), 138 (14), 135 (64), 123 (29), 109 (70), 95 (42) and 43 (100).

Blumenol-C [4-(2,6,6-trimethyl 4-oxocyclohex-2-enyl)butan-2-ol] 27

To a solution of dione **26** (415 mg, 2 mmol) in methanol (5 cm^3) and water (5 cm^3) was added $NaBH_4$ (50 mg, 1.3 mmol) and the mixture was stirred for 3 h at room temperature. The reaction mixture was poured into water and extracted with ethyl acetate. The extract was washed with brine, dried over anhydrous magnesium sulfate and evaporated. The crude product was chromatographed on silica gel with ethyl acetate–hexane (1:1) to afford Blumenol-C **27** (316 mg, 75%); ν_{max}(KBr)/cm^{-1} 3430 (OH), 2950 (C–H), 1655 (C=O), 1378 and 1255; δ_H(60 MHz) 1.02 (3 H, s, 6-Me), 1.07 (3 H, s, 6-Me), 1.22 (3 H, d, *J* 6, *Me*COH), 1.3–2.1 (6 H, m), 2.00 (3 H, d, *J* 1, 2-Me), 2.03 (1 H, d, *J* 17, 2-H), 2.39 (1 H, d, *J* 17, 2-H), 3.77 (1 H, m, *CH*OH) and 5.84 (1 H, s, 3-H).

Methyl 3-(2,6,6-trimethyl 4-oxocyclohex-2-enyl)propionate 28

To a solution of *endo*-adduct **10b** (752 mg, 3.4 mmol) in methanol (8.0 cm^3) was added HCl (12 mol dm^{-3} solution; 8 cm^3, 96 mmol) and the mixture was stirred for 0.5 h at 85 °C. The solution was evaporated at 40 °C under reduced pressure to remove methanol and the residue was extracted with ethyl acetate. The extract was washed successively with aq. sodium carbonate and brine, dried over anhydrous magnesium sulfate, and evaporated. The crude product was chromatographed on silica gel with ethyl acetate–hexane (1:2) to give keto ester **28** (587 mg, 78%); ν_{max}(KBr)/cm^{-1} 2985 (C–H), 1745 (C=O), 1674 (C=O), 1445 and 1260; δ_H(60 MHz) 1.02 (3 H, s, 6-Me), 1.65–2.55 (7 H, m), 1.95 (3 H, d, *J* 1, 2-Me), 3.61 (3 H, s, OMe) and 5.69 (1 H, s, br s); *m*/*z* 224 (M^+, 30%), 193 (12), 151 (55), 135 (100), 123 (26), 109 (59), 95 (33), 79 (33), 67 (56), 55 (34) and 41 (65).

(1*RS*,3*SR*,6*RS*)-1,3,7,7-Tetramethyl-2-oxabicyclo[4.4.0]decan-9-one 29

To sodium hydride (60%; 288 mg, 7.2 mmol) washed three times with benzene at room temperature was added a solution of Blumenol-C **27** (505 mg, 2.4 mmol) in benzene (3.0 cm^3) and the resulting slurry was stirred for 70 h at room temperature under nitrogen. The reaction mixture was poured into ice–water and extracted with ethyl acetate. The extract was washed with brine, dried over anhydrous magnesium sulfate and evaporated. The crude product was chromatographed on silica gel with ethyl acetate–hexane (1:3) to afford bicyclic compound **29** (278 mg, 55%), which was shown by capillary GC (DB-WAX; 60 m; 80–200 °C; 4 °C min^{-1}) to be a mixture of two diastereomers in the ratio 97:3, mp 58–59 °C (lit.,[14] 40–41 °C). Major isomer **29** had ν_{max}(KBr)/cm^{-1} 2949 (C–H), 1712 (C=O), 1285, 1261 and 1095; δ_H(400 MHz) 0.78 (3 H, s, 7-Me), 1.06 (3 H, s, 7-Me), 1.13 (3 H, d, *J* 6, 3-Me), 1.22 (3 H, s, 1-Me), 1.34 (1 H, m), 1.52 (1 H, m), 1.73–1.84 (3 H, m), 2.18 (1 H, dd, *J* 13.5 and 2.2, COCH), 2.24 (1 H, d, *J* 13.5, COCH) 2.47 (1 H, dd, *J* 12.4 and 2.2, COCH), 2.55 (1 H, d, *J* 12.4, COCH) and 3.76 (1 H, ddq, *J* 11.6, 6 and 2.2, 3-H); δ_C(100 MHz) 19.84 (CH_2), 20.57 (CH_3), 22.09 (CH_3), 22.28 (CH_3), 31.92 (CH_3), 34.86 (CH_2), 35.64 (C-7), 52.69 (CH-6), 56.69 (CH_2), 56.74 (CH_2), 66.17 (CH-3), 76.26 (CH-1) and 208.93 (CO); *m*/*z* 210 (M^+, 7%), 196 (15), 195 (93), 153 (100), 111 (51), 95 (35), 68 (56), 55 (35) and 43 (68). Minor isomer **29** had *m*/*z* 210 (M^+, 5%), 195 (12), 153 (100), 111 (23), 95 (20) and 43 (19).

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