Studies on Cycloaddition of Cyclohexa-2,4-dienones and Transformation of Adducts: A General, Stereoselective Route to Multifunctional Bicyclo[2.2.2]octanes and Diquinanes

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Abstract: The cycloaddition of in situ generated cyclohexa-2,4-dienones with vinyl ethers, vinyl acetate, and phenyl vinyl sulfone leading to variously functionalized bicyclo[2.2.2]octanes has been examined. Functional group manipulation in the resulting adducts gave bicyclo[2.2.2]octanes endowed with a β,γ-enone chromophore. Triplet-sensitized irradiation of bicyclooctenones followed by reductive cleavage provided a stereoselective route to diquinane frameworks having diverse functionalities.

Key words: Diels–Alder reaction, photochemistry, pericyclic reaction, rearrangements

The π4s+π2s cycloaddition reaction is one of the most powerful synthetic methodologies by virtue of its diversity, versatility, and adaptability.[1] Recently, the cycloaddition of species derived from oxidative dearomatization of phenols such as *o*-benzoquinone masked ketals,[2,3] and spiroepoxycyclohexa-2,4-dienones[4,5] has stimulated intense interest since it provides molecular structures that are otherwise not readily accessible. 6-(Chloromethyl)-6-hydroxycyclohex-2,4-dienones of type **1** (Figure 1) constitute interesting 4π systems and generally undergo cycloaddition with electron rich dienophiles.[5] Recently, we have shown that these species, though electron deficient, undergo efficient cycloadditions even with electron-poor dienophiles such as acrylates.[5b,c]

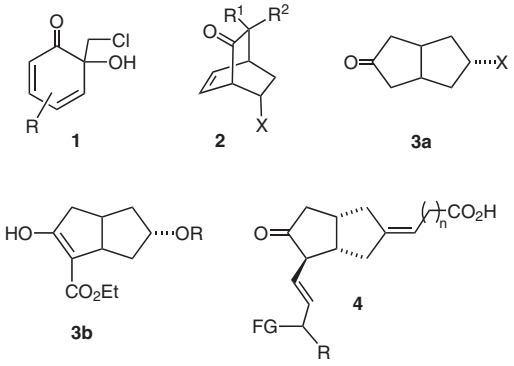

Figure 1

In continuation of our studies, we further considered examining the cycloadditions of 6-(chloromethyl)-6-hydroxycyclohexa-2,4-dienones with a range of dienophiles, such as vinyl ethers, vinyl acetates, and vinyl phenyl sulfone, so as to explore their reactivity and also develop a stereoselective route to novel bicyclo[2.2.2]octanes of type **2** since bicyclo[2.2.2]octanes are versatile synthetic precursors.[6] There are only a few routes to bicyclooctanes containing a β,γ-enone chromophore. It was also thought that the oxa-di-π-methane rearrangement of **2** would provide a stereoselective entry to diquinanes of type **3a**,**b** having distinguishable functional groups at central carbons of the five-membered rings, which are potential precursors to carbacyclins such as **4**.[7–9]

Moreover, diquinanes, in general, have elicited sustained interest[10] due their synthetic potential and the presence of this moiety in many natural products.[11] Though there are several methods for the synthesis of diquinane frameworks, there are only a few methods leading to diquinanes of type **3**.

We wish to report herein the stereoselective cycloaddition of cyclohexadienones of type **1** and manipulation of adducts to bicyclooctenones of type **2**. Photochemical reaction of the bicyclo[2.2.2]octenones and subsequent transformation to diquinanes of type **3a**,**b** is also reported.

Towards our objective, we thought to generate the cyclohexadienones of type **6** from dimers such as **5** by retro-Diels–Alder reaction and to examine its cycloaddition with ethyl vinyl ether. Thus, the dimer **5a**, readily prepared from salicyl alcohol[12] was heated in the presence of excess ethyl vinyl ether, which gave the *endo*-adduct **7a** in moderate yield, as a result of regio- and stereoselective cycloaddition (Scheme 1). Similarly, the dimers **5b** and **5c** were prepared from 2-(hydroxymethyl)-4,5-dimethylphenol and 2-(hydroxymethyl)-4,6-dimethylphenol, respectively, following an analogous procedure,[12] and heated with ethyl vinyl ether. Thus, while the dimer **5b** gave the *endo*-adduct **7b** exclusively, a mixture of *endo*- and *exo*-adducts **7c** (2:3) was obtained in the case of **5c**. Interestingly, the pyrolysis of **5a**,**b** in the presence of butyl vinyl ether also gave *endo*-adducts **8a**,**b** selectively, in better yields. Similarly, heating the dimer **5c** with butyl vinyl ether gave adducts **8c** as a mixture of *endo*- and *exo*-isomers, in good yields (Scheme 1). Though it is not clear at the moment, the formation of the *exo*-isomer in the case of

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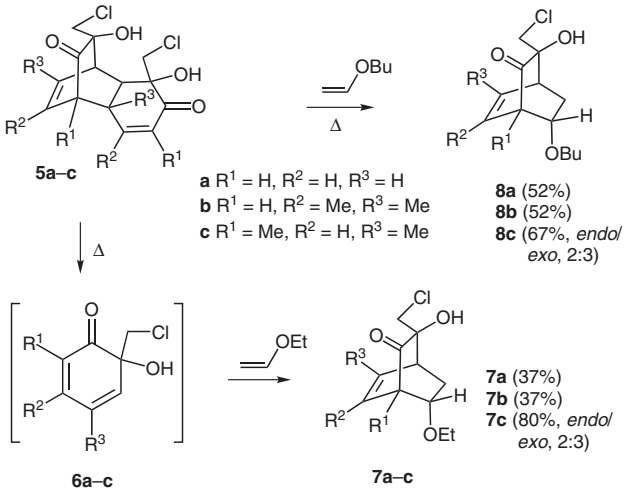
6c could be due to steric interactions between the methyl group and the ether moiety of the dienophile. The structures of all adducts were deduced from their spectral data and comparison with known data. The configuration of adduct **7b** was further confirmed by X-ray single crystal analysis (Figure 2).[13]



Scheme 1

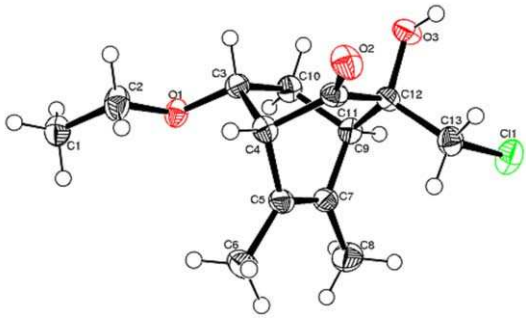
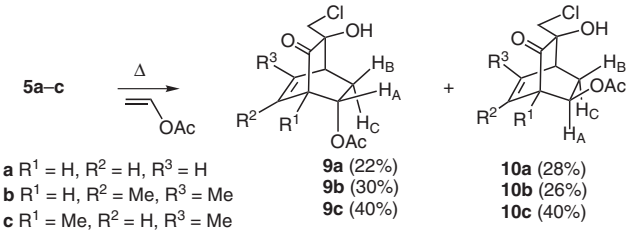


Figure 2 ORTEP diagram of compound **7b**

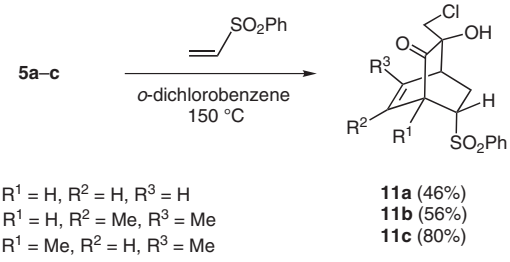
In order to extend the scope and generality, the above cycloaddition was also attempted with vinyl acetate, which is a poorly activated dienophile. Thus, when dimer **5a** was pyrolyzed in the presence of vinyl acetate in a sealed tube at 140 °C, it provided a mixture of adducts in good yield from which the *endo*- **9a** and *exo*-isomers **10a** (1.1:1) were isolated by chromatography. The *endo*- and *exo*-stereoisomers were distinguished by the chemical shift and coupling constants of H_A, H_B, and H_C. In general, the proton H_A in the *endo*-isomer appears downfield (compared to the *exo*-isomer). This is in agreement with an anisotropic shielding of the *endo* proton by the C5=C6 double bond.[4a] These trends were also observed for the other pairs of isomers.

Heating the dimers **5b** and **5c** in the presence of vinyl acetate also furnished the corresponding adducts **9b**,**c** and **10b**,**c** respectively (Scheme 2). Here again the cyclohexadienone **6c** having methyl groups at C2 and C4 of the dienone was found to be more reactive and furnished adducts **9c**, and **10c** in good yield. The loss of *endo* selectivity in the cycloaddition with vinyl acetate is presumably due to steric effects and lack of strong secondary orbital interactions. Such behavior of vinyl acetate during cycloadditions is known.[4a]



Scheme 2

We further explored the interception of 6-(chloromethyl)-6-hydroxycyclohexa-2,4-dienones **6a**–**c** with phenyl vinyl sulfone, a rarely used dienophile. Indeed, heating the dimer **5c** with phenyl vinyl sulfone ensued a smooth reaction and furnished a single *endo*-adduct **11c** in excellent yield (80%) as a result of regio- and stereoselective cycloaddition (Scheme 3). The structure of the adduct was deduced from ^{1}H and ^{13}C NMR spectra and the *endo* orientation of the sulfone group was revealed from the COSY spectrum and further confirmed by single crystal X-ray structure determination (Figure 3).[14] Cycloaddition of phenyl vinyl sulfone with cyclohexadienones generated from the other dimers **5a**,**b** also exclusively gave the corresponding *endo*-adducts in good yields (Scheme 3).



Scheme 3

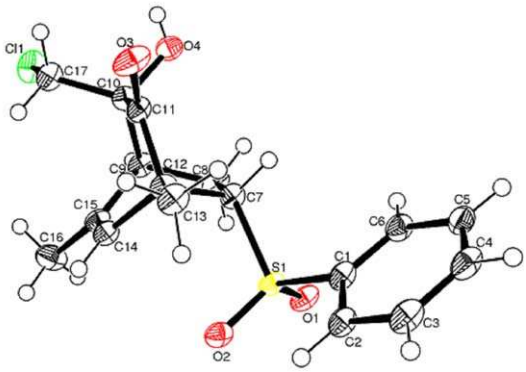
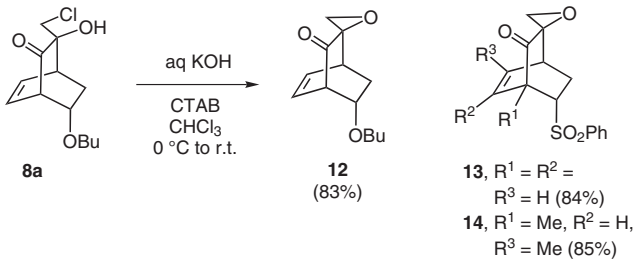


Figure 3 ORTEP diagram of compound **11c**

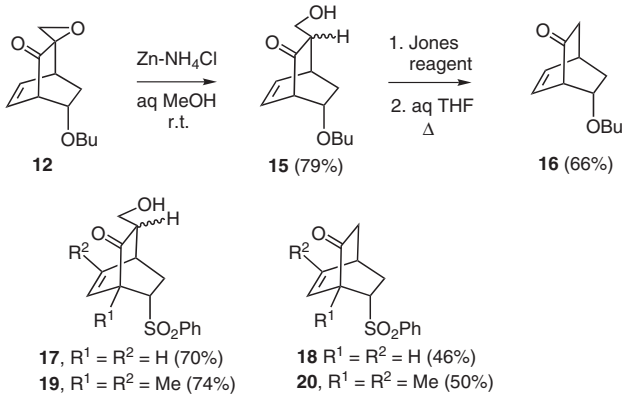
The presence of the chloromethyl and hydroxy groups in the above adducts provided further opportunities for manipulation. Thus, treatment of adduct **8a** with aqueous potassium hydroxide in the presence of cetyltrimethylammonium bromide (CTAB) as a phase-transfer catalyst gave the keto epoxide **12** in very good yield (Scheme 4).



Scheme 4

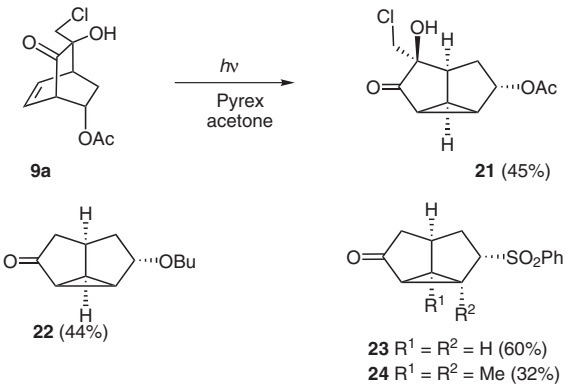
Similarly, other chloromethyl-hydroxy adducts **11a** and **11c** were also converted into the keto epoxides **13** and **14**, respectively (Scheme 4).

Further, reduction of **12** with zinc/ammonium chloride in aqueous methanol at ambient temperature selectively furnished the β-keto alcohol **15** (79%, as a mixture of *syn*/*anti*-isomers, ^{1}H NMR) as the major product. Oxidation of the β-keto alcohol **15** with Jones reagent followed by decarboxylation gave ketone **16** (Scheme 5). Similarly, the keto epoxides **13** and **14** were also transformed into the keto sulfones **18** and **20**, respectively, via the corresponding β-keto alcohols **17** and **19**.



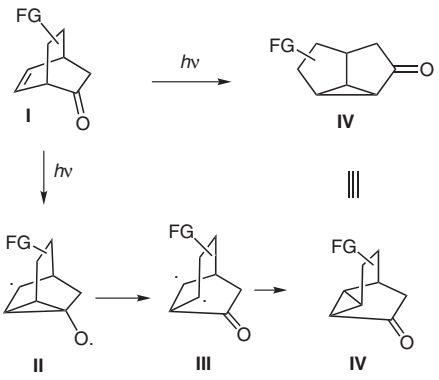
Scheme 5

Photoreactions of β,γ-enones have generated significant interest recently due to their synthetic applications.[15–17] In general, the sensitized irradiation of rigid β,γ-enones causes a 1,2-acyl shift or oxa-di-π-methane rearrangement and direct irradiation leads to a 1,3-acyl shift. During their seminal studies on the photoreactions of β,γ-enones, Demuth and co-workers examined 1,2-acyl shifts in some bicyclo[2.2.2]octanes and demonstrated their synthetic potential.[15a,b] However, the photoreactions of compounds of type **9**, **18**, and **20** have not been previously explored. We first examined the photoreaction of **9a** upon sensitized irradiation. Thus, a solution of ketone **9a** in degassed acetone (both solvent and sensitizer) was irradiated under nitrogen with a mercury vapor lamp (125 W, APP) during which a clean reaction occurred. Removal of the solvent followed by chromatography furnished the photoproduct **21**, whose structure was deduced from its spectral features and comparison with its precursor. Similar irradiation of other chromophoric systems **16**, **18**, and **20** also gave the corresponding oxa-di-π-methane products **22**–**24** respectively, in reasonably good yields (Scheme 6).



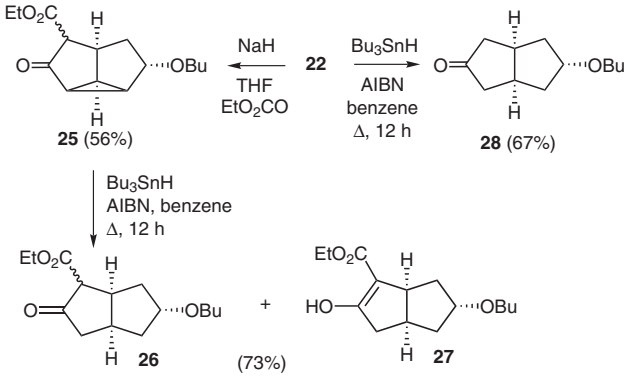
Scheme 6

A simplified mechanism for the oxa-di-π-methane reaction is presented in Scheme 7. The triplet sensitized irradiation of a β,γ-enone such as **I** proceeds through initial formation of the species **II**, which rearranges to the diradical **III** that upon ring closure gives the photoproduct **IV** (Scheme 7).



Scheme 7

The photoproduct **22** was further manipulated to give the functionalized diquinanes **25**–**28**. Ketone **22** was alkylated with diethyl carbonate to give compound **25** as a mixture of stereoisomers containing the isomer having a β-ethoxycarbonyl group as the major product. Subsequent treatment of **25** with tributyltin hydride/2,2′-azobis(isobutyronitrile)[18] furnished the keto ester **26**, as a mixture with its enol tautomer **27** (^{1}H NMR, ^{13}C NMR). Ketone **22** was also treated with tributyltin hydride/2,2′-azobis(isobutyronitrile) to give the diquinane **28** (Scheme 8). The



Scheme 8

diquinanes **26**–**28** are potential precursors for the synthesis of a variety of compounds including carbacyclins.[9a,19]

In summary, we have demonstrated that cyclohexa-2,4-dienones **6a**–**c** are versatile 4π-partners and undergo Diels–Alder reactions with a variety of dienophiles leading to multifunctional bicyclo[2.2.2]octenones **7a**–**c** to **11a**–**c**. This method is flexible, readily adaptable and permits the introduction of various substituents on the bicyclo[2.2.2]octane framework. Manipulation of the adducts provided other functionalized bicyclo[2.2.2]octenones **12**–**20**, which are otherwise not easily available. Triplet-sensitized photochemical reaction of bicyclooctenones **9a**, **16**, **18**, and **20** provided functionalized diquinane frameworks **21**, **22**, **23**, and **24** respectively, in stereoselective fashion. Alkylation and radical-induced cleavage of the peripheral cyclopropane bond furnished diquinanes **26**–**28**, which are versatile synthetic intermediates.

IR spectra were recorded on a Nicolet Impact 400 FT-IR. ^{1}H NMR (300 MHz) and ^{13}C (75 MHz) were recorded on a Varian VXR 300. ^{1}H NMR (400 MHz) and ^{13}C (100 MHz) were recorded on a Mercury Varian 400 MHz. The samples were dissolved in $CDCl_3$ with TMS as internal standard. HRMS were recorded on a Q-Tof micro (YA-105). Melting points were determined on a Veego apparatus of Buchi type and are uncorrected. All organic extracts were dried over anhyd Na_2SO_4. Reactions were monitored with TLC and spots were visualized with I_2 vapor. Column chromatography was performed using SRL/Thomas Baker silica gel (60–120 and 100–200 mesh) with elution using PE [petroleum ether (bp 60–80 °C)] and EtOAc mixtures.

3-(Chloromethyl)-7-*endo*-ethoxy-3-hydroxybicyclo[2.2.2]oct-5-en-2-one (7a); Typical Procedure

Chlorohydroxy dimer **5a** (1.0 g, 3.14 mmol) was taken up in a round-bottomed flask fitted with a reflux condenser through which cold H_2O was circulated and *o*-dichlorobenzene (8 mL) was added. An inert atmosphere was created by displacement of air by N_2 and freshly distilled ethyl vinyl ether (10 mL, excess) was added to the mixture. The mixture was heated at 125 °C for 14 h with stirring during time which more ethyl vinyl ether was added at regular intervals. The mixture was brought to r.t. and charged as such on to a column (silica gel, 60–120 mesh). Elution with PE gave *o*-dichlorobenzene. Continued elution with PE–EtOAc (9:1) gave **7a** (0.540 g, 37%) as a solid; mp 102–103 °C.

IR (KBr): 3442, 1726 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.61 (superimposed dd, J = 8.5 Hz, 1 H), 6.14 (superimposed dd, J = 6.1 Hz, 1 H), 4.08–3.98 (m, 1 H), 3.72–3.38 (set of complex multiplets, 5 H), 3.24–3.16 (m, 1 H), 2.78 (br s, 1 H), 2.64 (ddd, J_1 = 10.9 Hz, J_2 = 8.5 Hz, J_3 = 2.4 Hz, 1 H), 1.37–1.34 (dt, J_1 = 6.1 Hz, J_2 = 3.6 Hz, 1 H), 1.17 (t, J = 7.3 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.5, 135.4, 126.0, 75.6, 73.2, 64.4, 53.5, 50.8, 39.2, 29.1, 15.4.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{11}H_{15}ClNaO_3$: 253.0607; found: 253.0598.

3-(Chloromethyl)-7-*endo*-ethoxy-3-hydroxy-5,6-dimethylbicyclo[2.2.2]oct-5-en-2-one (7b)

Following the typical procedure for **7a** using **5b** (0.5 g, 1.34 mmol), ethyl vinyl ether (5 mL), and *o*-dichlorobenzene (5 mL) and heating at 130 °C for 20 h. Chromatography of the mixture (PE–EtOAc, 92:8) gave **7b** (0.256 g, 37%) as a solid; mp 97–99 °C.

IR (KBr): 3452, 1707 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.98 (dt, J_1 = 6.1 Hz, J_2 = 3.0 Hz, 1 H), 3.63 (part of an AB pattern, J_{AB} = 11.8 Hz, 1 H), 3.6–3.36 (cluster of multiplet, 4 H), 2.88 (superimposed dd, J = 2.6 Hz, 1 H), 2.55 (ddd, J_1 = 10.9 Hz, J_2 = 8.3 Hz, J_3 = 2.6 Hz, 1 H), 2.4 (br s, 1 H), 1.9 (d, J = 1.3 Hz, 3 H), 1.78 (d, J = 1.3 Hz, 3 H), 1.3 (dt, J_1 = 13.6 Hz, J_2 = 3.0 Hz, 1 H), 1.17 (t, J = 7.0 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 208.1, 134.9, 125.3, 75.9, 73.3, 64.3, 58.7, 50.1, 44.4, 29.0, 17.7, 17.1, 15.4.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{19}ClNaO_3$: 281.0920; found: 281.0930.

3-(Chloromethyl)-7-*endo*-ethoxy-3-hydroxy-1,5-dimethylbicyclo[2.2.2]oct-5-en-2-one (7c)

Following the typical procedure for **7a** using **5c** (0.5 g, 1.34 mmol), ethyl vinyl ether (5 mL), and *o*-dichlorobenzene (5 mL) and heating at 125 °C for 12 h. Chromatography of the mixture (PE–EtOAc, 94:6) gave **7c** (0.558 g, 80%) as an oily liquid as a inseparable mixture of *endo*- and *exo*-adducts (2:3).

IR (neat): 3491, 1705 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) (signals for the major isomer): δ = 5.47–5.39 (m, 1 H), 3.72–3.34 (cluster of multiplet, 5 H), 2.98–2.94 (m, 1 H), 2.63 (ddd, J_1 = 11 Hz, J_2 = 8.0 Hz, J_3 = 2.9 Hz, 1 H), 2.47 (br s, 1 H), 1.95 (d, J = 1.8 Hz, 3 H), 1.44 (dt, J_1 = 6.5 Hz, J_2 = 3.2 Hz, 1 H), 1.29 (s, 3 H), 1.15 (t, J = 6.9 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.6, 144.4, 123.7, 79.2, 73.2, 65.5, 58.0, 50.3, 43.0, 38.2, 21.0, 18.1, 15.4.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{19}ClNaO_3$: 281.0920; found: 281.0925.

7-*endo*-Butoxy-3-(chloromethyl)-3-hydroxybicyclo[2.2.2]oct-5-en-2-one (8a)

Following the typical procedure for **7a** using **5a** (0.5 g, 1.57 mmol), *o*-dichlorobenzene (5 mL), and butyl vinyl ether (4 mL, excess) and heating at 140 °C for 20 h under N_2. Chromatography (PE–EtOAc, 96:4) gave **8a** (0.418 g, 52%) as a thick liquid.

IR (neat): 3455, 1734 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.60 (superimposed dd, J = 7.3 Hz, 1 H), 6.12 (superimposed dd, J = 7.3 Hz, 1 H), 4.02–3.98 (m, 1 H), 3.66–3.65 (m, 1 H), 3.63–3.52 (m, 2 H), 3.54–3.33 (m, 2 H), 3.22–3.16 (m, 1 H), 3.0–2.9 (br s, 1 H), 2.63 (ddd, J_1 = 10.9 Hz, J_2 = 8.5 Hz, J_3 = 2.4 Hz, 1 H), 1.54–1.47 (m, 2 H), 1.39–1.30 (m, 3 H), 0.90 (t, J = 7.3 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 208.6, 135.3, 125.8, 75.6, 73.1, 68.7, 53.3, 50.5, 39.0, 31.7, 28.9, 19.2, 13.8.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{19}ClNaO_3$: 281.0920; found: 281.0914.

7-*endo*-Butoxy-3-(chloromethyl)-3-hydroxy-5,6-dimethylbicyclo[2.2.2]oct-5-en-2-one (8b)

Following the typical procedure for **7a** using **5b** (0.1 g, 0.268 mmol), butyl vinyl ether (2 mL, excess), and *o*-dichlorobenzene (3 mL) and heated at 130 °C for 10 h. Chromatography of the mixture (PE–EtOAc, 95:5) gave **8b** (0.08 g, 52%) as a thick liquid.

IR (neat): 3431, 1719 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.93 (dt, J_1 = 5.8 Hz, J_2 = 2.9 Hz, 1 H), 3.66–3.58 (m, 1 H), 3.48–3.28 (cluster of m, 4 H), 3.0 (s, 1 H), 2.86 (superimposed dd, J = 2.9 Hz, 1 H), 2.52 (ddd, J_1 = 10.9 Hz, J_2 = 8.4 Hz, J_3 = 2.5 Hz, 1 H), 1.87 (s, 3 H), 1.86 (s, 3 H), 1.54–1.42 (m, 2 H), 1.40–1.22 (m, 3 H), 0.87 (t, J = 7.3 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 208.5, 135.0, 125.2, 76.0, 73.3, 68.7, 58.7, 49.9, 44.3, 31.8, 28.8, 19.2, 17.6, 17.0, 13.8.

HRMS (ESI): *m*/*z* [M + K]$^+$ calcd for $C_{15}H_{23}ClKO_3$: 325.0973; found: 325.0965.

7-*endo*-Butoxy-3-(chloromethyl)-3-hydroxy-1,5-dimethylbicyclo[2.2.2]oct-5-en-2-one (8c)

Following the typical procedure for **7a** using **5c** (0.5 g, 1.34 mmol), butyl vinyl ether (4 mL, excess), and *o*-dichlorobenzene (4 mL) and heating at 120 °C for 6 h under N_2. Chromatography of the mixture (PE–EtOAc, 97:3) gave **8c** (0.510 g, 67%) as a thick liquid as an inseparable mixture of *endo*- and *exo*-adducts.

IR (neat): 3435, 1726 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) (signals due to major isomer): δ = 5.45–5.41 (m, 1 H), 3.87 (dt, J_1 = 5.8 Hz, J_2 = 2.7 Hz, 1 H), 3.72–3.68 (m, 1 H), 3.6 (part of an AB system, J_{AB} = 12.0 Hz, 1 H), 3.5 (part of an AB system, J_{AB} = 11.7 Hz, 1 H), 3.55–3.45 (m, 1 H), 3.38–3.27 (m, 1 H), 2.96 (s, 1 H), 2.6 (ddd, J_1 = 10.9 Hz, J_2 = 8.1 Hz, J_3 = 2.7 Hz, 1 H), 1.94 (d, J = 1.5 Hz, 3 H), 1.56–1.48 (m, 2 H), 1.38–1.32 (m, 3 H), 1.29 (s, 3 H), 0.90 (t, J = 6.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.7, 131.8, 123.8, 79.4, 74.0, 69.9, 58.1, 50.3, 43.1, 38.3, 32.0, 30.0, 21.1, 19.4, 14.1.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{23}ClNaO_3$: 309.1233; found: 309.1241.

7-*endo*-Acetoxy-3-(chloromethyl)-3-hydroxybicyclo[2.2.2]oct-5-en-2-one (9a) and 7-*exo*-Acetoxy-3-(chloromethyl)-3-hydroxybicyclo[2.2.2]oct-5-en-2-one (10a); Typical Procedure

A mixture of **5a** (0.5 g, 1.57 mmol), and vinyl acetate (3 mL) in *o*-dichlorobenzene (2 mL) was heated in a sealed tube at 140 °C for 20 h. The mixture was filtered through a small pad of silica gel and eluted with PE to remove the solvent and excess dienophile. Elution with PE–EtOAc (75:25) gave the mixture of adducts (TLC). The mixture of adducts thus obtained was rechromatographed (silica gel 100–200 mesh). Elution with PE–EtOAc (91:9) first gave the *endo*-adduct **9a** (0.166 g, 22%) as a colorless solid. Further elution with PE–EtOAc (9:1) gave the *exo*-adduct **10a** (0.211 g, 28%) as a colorless solid.

***endo*-Adduct 9a**

Mp 130–131 °C.

IR (KBr): 3471, 1739, 1713 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.63 (superimposed dd, J = 7.0 Hz, 1 H), 6.15 (superimposed dd, J = 7.0 Hz, 1 H), 5.36–5.27 (m, 1 H), 3.65 (part of an AB pattern, J_{AB} = 12 Hz, 1 H), 3.61–3.56 (m, 1 H), 3.5 (part of an AB system J_{AB} = 12 Hz, 1 H), 3.26–3.18 (m, 1 H), 2.79 (ddd, J_1 = 10.9 Hz, J_2 = 8.5 Hz, J_3 = 2.3 Hz, 1 H), 2.7 (br s, 1 H), 2.01 (s, 3 H), 1.36 (dt, J_1 = 6.6 Hz, J_2 = 3.5 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 206.0, 170.3, 136.2, 125.8, 72.6, 69.6, 53.0, 50.5, 38.8, 28.7, 21.1.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{11}H_{13}ClNaO_4$: 267.0190; found: 267.0200.

***exo*-Adduct 10a**

Mp 80–82 °C.

IR (KBr): 3501, 1739 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.60 (superimposed dd, J = 7.3 Hz, 1 H), 6.18 (superimposed dd, J = 7.3 Hz, 1 H), 5.16–4.96 (m, 1 H), 3.67 (part of an AB pattern, J_{AB} = 12 Hz, 1 H), 3.55 (part of an AB system J_{AB} = 12 Hz, 1 H), 3.54–3.40 (m, 1 H), 3.27 (s, 1 H), 2.8 (br s, 1 H), 2.25–1.90 (m, 2 H), 2.05 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 206.8, 170.6, 137.8, 126.2, 73.9, 71.9, 52.2, 50.7, 39.3, 26.5, 21.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{14}ClO_4$: 245.0581; found: 245.0574.

7-*endo*-Acetoxy-3-(chloromethyl)-3-hydroxy-5,6-dimethylbicyclo[2.2.2]oct-5-en-2-one (9b) and 7-*exo*-Acetoxy-3-(chloromethyl)-3-hydroxy-5,6-dimethylbicyclo[2.2.2]oct-5-en-2-one (10b)

Following the typical procedure for **10a** using **5b** (0.5 g, 1.34 mmol), vinyl acetate (3 mL), and *o*-dichlorobenzene (2 mL) and heating at 150 °C for 17 h. The mixture was charged on a small pad of silica gel and washed with PE to remove the solvent and excess dienophile. Elution with PE–EtOAc (75:25) gave the mixture of adducts (TLC) which was further chromatographed on silica gel (100–200 mesh). Elution with PE–EtOAc (93:7) first gave the *endo*-adduct **9b** (0.219 g, 30%). Further elution with PE–EtOAc (9:1) gave the *exo*-adduct **10b** (0.184 g, 26%) as a colorless solid.

***endo*-Adduct 9b**

Mp 92–94 °C.

IR (KBr): 3447, 1732, 1713 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.26 (dt, J_1 = 6.2 Hz, J_2 = 2.9 Hz, 1 H), 3.7 (part of an AB pattern, J_{AB} = 12 Hz, 1 H), 3.46 (part of an AB pattern J_{AB} = 12 Hz, 1 H), 3.30 (d, J = 3.6 Hz, 1 H), 2.96 (superimposed dd, J = 2.9 Hz, 1 H), 2.70 (ddd, J_1 = 10.9 Hz, J_2 = 8.4 Hz, J_3 = 2.5 Hz, 1 H), 2.63 (br s, 1 H), 2.03 (s, 3 H), 1.92 (d, J = 1.0 Hz, 3 H), 1.76 (d, J = 1.0 Hz, 3 H), 1.35 (dt, J_1 = 6.2 Hz, J_2 = 2.9 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.6, 170.3, 135.9, 125.4, 72.9, 70.4, 58.6, 50.0, 44.2, 28.5, 21.1, 17.7, 17.2.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{17}ClNaO_4$: 295.0713; found: 295.0709.

***exo*-Adduct 10b**

Mp 110–111 °C.

IR (KBr): 3490, 1744, 1723 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.08–5.0 (m, 1 H), 3.7 (part of an AB system, J_{AB} = 12 Hz, 1 H), 3.46 (part of an AB system, J_{AB} = 12 Hz, 1 H), 3.18 (d, J = 3.6 Hz, 1 H), 2.96 (superimposed dd, J = 2.9 Hz, 1 H), 2.5 (br s, 1 H), 2.06–2.03 (m, merged with singlet, 2 H), 2.03 (s, 3 H), 1.87 (d, J = 1.0 Hz, 3 H), 1.76 (d, J = 1.0 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 206.9, 170.6, 138.2, 125.4, 74.2, 72.1, 58.0, 50.2, 45.0, 27.0, 21.2, 17.2, 16.5.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{17}ClNaO_4$: 295.0503; found: 295.0671.

7-*endo*-Acetoxy-3-(chloromethyl)-3-hydroxy-1,5-dimethylbicyclo[2.2.2]oct-5-en-2-one (9c) and 7-*exo*-Acetoxy-3-(chloromethyl)-3-hydroxy-1,5-dimethylbicyclo[2.2.2]oct-5-en-2-one (10c)

Following the typical procedure for **10a** using **5c** (0.5 g, 1.34 mmol), vinyl acetate (3 mL, excess), and *o*-dichlorobenzene (2 mL) and heating at 140 °C for 12 h. Chromatography with elution with PE–EtOAc (94:6) first gave the adduct **9c** (0.290 g, 40%) as a colorless solid. Further elution with PE–EtOAc (9:1) gave the *exo*-adduct **10c** (0.293 g, 40%) as a colorless solid.

***endo*-Adduct 9c**

Mp 92–93 °C.

IR (KBr): 3442, 1729, 1265 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 5.47–5.42 (m, 1 H), 4.98 (ddd, J_1 = 4.3 Hz, J_2 = 3.2 Hz, J_3 = 1 Hz, 1 H), 3.68 (part of an AB system, J_{AB} = 12 Hz, 1 H), 3.46 (part of an AB system, J_{AB} = 12 Hz, 1 H), 3.01–2.96 (m, 1 H), 2.84 (ddd, J_1 = 10.9 Hz, J_2 = 8.4 Hz, J_3 = 2.5 Hz, 1 H), 2.45 (br s, 1 H), 2.04 (s, 3 H), 1.98 (d, J = 1.8 Hz, 3 H), 1.33 (dt, J_1 = 6.5, J_2 = 3.2 Hz, 1 H), 1.21 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.6, 170.3, 145.2, 123.3, 73.5, 72.8, 53.6, 50.0, 43.0, 30.4, 20.9, 20.8, 13.8.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{17}ClNaO_4$: 295.0713; found: 295.0706.

***exo*-Adduct 10c**

Mp 96–98 °C.

IR (KBr): 3451, 1735, 1265 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 5.42–5.39 (m, 1 H), 4.83 (dd, J_1 = 9.3 Hz, J_2 = 3.1 Hz, 1 H), 3.71 (part of an AB pattern, J_{AB} = 12 Hz, 1 H), 3.5 (part of an AB pattern, J_{AB} = 12 Hz, 1 H), 3.02–2.99 (m, 1 H), 2.51 (br s, 1 H), 2.21–2.12 (m, 1 H), 2.06–1.97 (m, 4 H), 1.94 (d, J = 1.5 Hz, 3 H), 1.19 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.0, 170.6, 147.7, 123.5, 76.4, 73.6, 52.5, 50.0, 43.9, 28.4, 20.8, 20.6, 14.2.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{17}ClNaO_4$: 295.0713; found: 295.0709.

3-(Chloromethyl)-3-hydroxy-7-*endo*-(phenylsulfonyl)bicyclo[2.2.2]oct-5-en-2-one (11a)

Following the typical procedure for **10a** using **5a** (1.0 g, 3.15 mmol), phenyl vinyl sulfone (0.8 g, 4.73 mmol), and *o*-dichlorobenzene (5 mL) and heating at 150 °C for 22 h. Chromatography (silica gel, 60–120 mesh) with continued elution with PE–EtOAc (80:20) gave some unreacted dimer (0.200 g, 20%). Further elution with PE–EtOAc (78:22) gave **11a** (0.935 g, 46%) as a colorless solid; mp 130–132 °C.

IR (KBr): 3452, 1733 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.92–7.85 (m, 2 H), 7.74–7.67 (m, 1 H), 7.64–7.57 (m, 2 H), 6.56 (superimposed dd, J = 8.1 Hz, 1 H), 6.29–6.21 (m, 1 H), 3.73–3.65 (m, 3 H), 3.45 (d, J = 12 Hz, 1 H), 3.38–3.33 (m, 1 H), 2.65 (s, 1 H), 2.47 (ddd, J_1 = 12.8 Hz, J_2 = 9.7 Hz, J_3 = 3.1 Hz, 1 H), 1.95 (ddd, J_1 = 9.3 Hz, J_2 = 6.6 Hz, J_3 = 2.7 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 203.2, 138.0, 135.8, 134.3, 129.6 (2 C), 128.6 (2 C), 125.7, 72.9, 59.3, 50.3, 47.2, 39.3, 22.8.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{15}ClNaO_4S$: 349.0277; found: 349.0287.

3-(Chloromethyl)-3-hydroxy-5,6-dimethyl-7-*endo*-(phenylsulfonyl)bicyclo[2.2.2]oct-5-en-2-one (11b)

Following the typical procedure for **10a** using **5b** (0.230 g, 0.616 mmol), phenyl vinyl sulfone (0.142 g, 0.845 mmol), and *o*-dichlorobenzene (3 mL) and heating at 140 °C for 20 h. Chromatography (PE–EtOAc, 78:22) gave **11b** (0.240 g, 56%) as a colorless solid; mp 158–159 °C.

IR (KBr): 3356, 1725 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.83–7.77 (m, 2 H), 7.63–7.55 (m, 1 H), 7.54–7.45 (m, 2 H), 3.62 (d, J = 11.9 Hz, 1 H), 3.57–3.50 (m, 1 H), 3.32–3.27 (m, 2 H), 3.0–2.95 (m, 1 H), 2.50 (s, 1 H), 2.25 (ddd, J_1 = 13.1 Hz, J_2 = 9.7 Hz, J_3 = 3.0 Hz, 1 H), 1.83–1.74 (cluster of m, 7 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.4, 138.2, 136.8, 134.1, 129.5, 128.5, 125.4, 73.1, 59.3, 52.5, 49.7, 44.7, 22.4, 17.25, 17.20.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{19}ClNaO_4S$: 377.0590; found: 377.0591.

3-(Chloromethyl)-3-hydroxy-1,5-dimethyl-7-*endo*-(phenylsulfonyl)bicyclo[2.2.2]oct-5-en-2-one (11c)

Following the typical procedure for **10a** using **5c** (0.1 g, 0.268 mmol), phenyl vinyl sulfone (0.068 g, 0.402 mmol), and *o*-dichlorobenzene (1.0 mL) and heating at 125 °C for 6 h. Chromatography (PE–EtOAc, 80:20)] gave **11c** (0.152 g, 80%) as a colorless solid; mp 178–180 °C.

IR (KBr): 3453, 1729 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.88–7.83 (m, 2 H), 7.69–7.62 (m, 1 H), 7.60–7.54 (m, 2 H), 5.50 (s, 1 H), 3.69 (part of AB system, J = 12.0 Hz, 1 H), 3.51 (dd, J_1 = 9.75, J_2 = 7.0 Hz, 1 H), 3.40 (part of AB system, J = 12.0 Hz, 1 H), 3.01–2.98 (m, 1 H), 2.56 (s, 1 H), 2.26 (ddd, J_1 = 13.6 Hz, J_2 = 9.7 Hz, J_3 = 2.7 Hz, 1 H), 1.90 (d, J = 1.5 Hz, 3 H), 1.79 (ddd, J_1 = 9.7 Hz, J_2 = 7.0 Hz, J_3 = 2.73 Hz, 1 H), 1.54 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.4, 144.5, 139.7, 133.83, 129.3, 128.5, 123.9, 72.8, 63.2, 50.6, 49.7, 43.1, 25.9, 20.7, 16.2.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{19}ClNaO_4S$: 377.0590; found: 377.0605.

8-*endo*-Butoxyspiro[bicyclo[2.2.2]oct-5-ene-2,2′-oxiran]-3-one (12); Typical Procedure

To a soln of **8a** (2.40 g, 9.28 mmol) in $CHCl_3$ (200 mL) containing CTAB (0.3 g) was added a soln of KOH (0.6 g, 10.7 mmol) in H_2O (25 mL). The mixture was stirred at r.t. (~30 °C) for 7 h, after which the organic phase was separated and the aqueous layer extracted with $CHCl_3$ (3 × 25 mL). The combined organic extracts were washed with brine and dried (anhyd Na_2SO_4). Removal of solvent followed by column chromatography (silica gel, PE–EtOAc, 95:5) gave **12** (1.7 g, 83%) as a colorless thick liquid.

IR (neat): 1736 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 6.68–6.61 (m, 1 H), 6.20–6.12 (m, 1 H), 4.10–4.02 (m, 1 H), 3.78–3.72 (m, 1 H), 3.52–3.34 (m, 2 H), 3.13 (d, J = 6.2 Hz, 1 H), 2.84 (d, J = 6.2 Hz, 1 H), 2.60–2.52 (m, 1 H), 2.52–2.44 (m, 1 H), 1.64–1.48 (m, 3 H), 1.42–1.28 (m, 2 H), 0.90 (t, J = 7.3 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.8, 134.6, 126.3, 75.2, 68.8, 57.7, 53.7, 53.5, 37.6, 31.8, 31.6, 19.3, 13.9.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{18}NaO_3$: 245.1154; found: 245.1152.

8-*endo*-(Phenylsulfonyl)spiro[bicyclo[2.2.2]oct-5-ene-2,2′-oxiran]-3-one (13)

Following the typical procedure for **12** using **11a** (1.27 g, 3.89 mmol), $CHCl_3$ (120 mL), CTAB (0.125 g), and a soln of KOH (0.350 g, 6.23 mmol) in H_2O (25 mL) and stirring at r.t. (~30 °C) for 8 h. Column chromatography (silica gel, PE–EtOAc, 4:1) gave **13** (0.941 g, 84%) as a colorless solid; mp 168–170 °C.

IR (KBr): 1736 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92–7.86 (m, 2 H), 7.74–7.67 (m, 1 H), 7.64–7.54 (m, 2 H), 6.67–6.6 (m, 1 H), 6.33–6.25 (m, 1 H), 3.78–3.74 (m, 1 H), 3.72–3.62 (m, 1 H), 3.17 (d, J = 5.8 Hz, 1 H), 2.88 (d, J = 6.2 Hz, 1 H), 2.56–2.5 (m, 1 H), 2.38 (ddd, J_1 = 13.5 Hz, J_2 = 9.8 Hz, J_3 = 2.9 Hz, 1 H), 2.22–2.14 (ddd, J_1 = 10.9 Hz, J_2 = 6.2 Hz, J_3 = 3.6 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.6, 137.9, 134.9, 134.2, 129.5, 128.4, 125.9, 59.3, 56.9, 52.9, 47.6, 37.7, 24.6.

HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{15}H_{14}NaO_4S$: 313.0511; found: 313.0519.

4,6-Dimethyl-8-*endo*-(phenylsulfonyl)spiro[bicyclo[2.2.2]oct-5-ene-2,2′-oxiran]-3-one (14)

Following the typical procedure for **12** using **11c** (3.8 g, 10.71 mmol), $CHCl_3$ (200 mL), CTAB (0.2 g), and a soln of KOH (0.78 g, 13.92 mmol) in H_2O (25 mL) and stirring for 8 h. Chromatography (PE–EtOAc, 4:1) gave **14** (2.9 g, 85%) as a colorless solid; mp 186 °C.

IR (KBr): 1737 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89–7.83 (m, 2 H), 7.69–7.63 (m, 1 H), 7.61–7.53 (m, 2 H), 5.52 (s, 1 H), 3.53 (dd, J_1 = 10.2, J_2 = 6.5 Hz, 1 H), 3.16 (part of AB pattern, J_{AB} = 6.2 Hz, 1 H), 2.90 (part of AB pattern, J_{AB} = 6.2 Hz, 1 H), 2.32 (dd, J_1 = 4.7 Hz, J_2 = 2.5 Hz, 1 H), 2.20 (ddd, J_1 = 13.8 Hz, J_2 = 10.2 Hz, J_3 = 2.9 Hz, 1 H), 2.02 (ddd, J_1 = 9.1 Hz, J_2 = 6.5 Hz, J_3 = 2.5 Hz, 1 H), 1.87 (d, J = 1.4 Hz, 3 H), 1.56 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 202.6, 143.6, 139.9, 133.8, 129.3, 128.4, 124.4, 63.3, 56.8, 52.5, 51.4, 42.1, 27.8, 20.4, 16.3.

HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{17}H_{18}NaO_4S$: 341.0824; found: 341.0833.

7-*endo*-Butoxy-3-(hydroxymethyl)bicyclo[2.2.2]oct-5-en-2-one (15); Typical Procedure

To a suspension of activated Zn (13 g, excess) in MeOH–H_2O (5:1, 90 mL) was added a soln of **12** (2.4 g, 10.8 mmol) in MeOH (10 mL) followed by NH_4Cl (2.6 g, excess) and the mixture was stirred at r.t. (~30 °C) for 12 h. It was filtered through a Celite pad and the filtrate was concentrated in vacuo and the residue was diluted with H_2O and extracted with EtOAc (3 × 50 mL). The combined extracts were washed with brine and dried (Na_2SO_4). The solvent was removed under reduced pressure and the product was purified by column chromatography (PE–EtOAc, 80:20) to give **15** (1.9 g, 79%, mixture of *syn*/*anti*-isomers) as a colorless liquid.

IR (KBr): 1740 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.74–6.50 (m, 2 H), 6.12–6.00 (m, 2 H), 4.0–3.80 (m, 2 H), 3.74–3.68 (m, 2 H), 3.64–3.50 (m, 6 H), 3.48–3.42 (m, 4 H), 3.38–3.30 (m, 4 H), 2.99–2.90 (m, 2 H), 2.60–2.50 (br s, 1 H), 2.30–2.12 (m, 3 H), 1.60–1.42 (m, 3 H), 1.40–1.26 (m, 3 H), 0.98–0.94 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.9, 137.9, 125.0, 75.3, 68.6, 61.6, 54.4, 48.8, 34.9, 31.7, 29.9, 19.2, 13.8 (signals due to major isomer).

HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{13}H_{21}O_3$: 225.1491; found: 225.1492.

7-*endo*-Butoxybicyclo[2.2.2]oct-5-en-2-one (16); Typical Procedure

To a soln of **15** (3.0 g, 13.3 mmol) in acetone (60 mL) was added dropwise freshly prepared Jones reagent with stirring at 0 °C. When the reaction was complete (TLC, ~30 min), the solvent was removed under vacuum and the residue was diluted with H_2O and extracted with EtOAc (4 × 50 mL). The combined extracts were washed with H_2O and brine and dried (anhyd Na_2SO_4). Removal of solvent gave a β-keto acid that was directly subjected to decarboxylation as described below. The β-keto acid thus obtained was taken in THF–H_2O (1:1, 120 mL) and the mixture was refluxed for 8 h. THF was removed under vacuum and the aqueous medium was further diluted with H_2O and extracted with EtOAc (3 × 50 mL). The combined extracts were washed with $NaHCO_3$ soln, H_2O, and brine and dried (anhyd Na_2SO_4). Removal of solvent followed by chromatography (PE–EtOAc, 95:5) of the residue gave **16** (1.68 g, 66%) as a colorless liquid.

IR (KBr): 1732 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.61 (superimposed dd, J = 7.6 Hz, 1 H), 6.07 (superimposed dd, J = 6.9 Hz, 1 H), 3.98–3.88 (m, 1 H), 3.62–3.58 (m, 1 H), 3.48–3.40 (m, 1 H), 3.38–3.30 (m, 1 H), 3.04–2.96 (m, 1 H), 2.13 (ddd, J_1 = 10.9 Hz, J_2 = 8.4 Hz, J_3 = 2.5 Hz, 1 H), 2.05–1.98 (m, 1 H), 1.91–1.86 (m, 1 H), 1.54–1.44 (m, 3 H), 1.38–1.28 (m, 2 H), 0.89 (t, J = 7.3 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 211.8, 137.0, 125.1, 74.8, 68.7, 54.5, 39.7, 34.9, 31.9, 31.6, 19.4, 13.9.

HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{12}H_{18}NaO_2$: 217.1204; found: 217.1199.

7-*endo*-(Phenylsulfonyl)bicyclo[2.2.2]oct-5-en-2-one (18)

Following the typical procedure for **15**, using a suspension of activated zinc (18 g, excess) in MeOH–H_2O (7:1, 80 mL), a soln of **13** (1.4 g, 4.82 mmol) in MeOH (20 mL), NH_4Cl (2 g, excess) and stirring at r.t. (~30 °C) for 10 h. Column chromatography (PE–EtOAc, 60: 40) gave **17** (0.980 g, 70%, mixture of *syn*/*anti*-isomers) as a colorless liquid that was subjected to oxidation and decarboxylation.

To a soln of keto alcohol **17** (0.970 g, 3.32 mmol) in acetone (40 mL) was added dropwise freshly prepared Jones reagent with stirring at 0 °C. After the reaction was complete (TLC, ~1 h) the solvent was removed under vacuum and the residue was diluted with H_2O and extracted with EtOAc (4 × 50 mL). The combined extracts were washed with H_2O and brine and dried (anhyd Na_2SO_4). Removal of solvent gave a β-keto acid, which was directly subjected to decarboxylation. The β-keto acid thus obtained was taken in THF–H_2O (1:1, 44 mL) and the mixture was refluxed for 16 h. The THF was removed under vacuum and the aqueous medium was further diluted with H_2O and extracted with EtOAc (3 × 50 mL). The combined extracts were washed with $NaHCO_3$ soln, H_2O, and brine and dried (anhyd Na_2SO_4). Removal of solvent followed by chromatography (PE–EtOAc, 90:10) gave **18** (0.400 g, 46%) as a colorless solid; mp 120–121 °C.

IR (KBr): 1732 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90–7.85 (m, 2 H), 7.76–7.65 (m, 1 H), 7.66–7.55 (m, 2 H), 6.62–6.54 (m, 1 H), 6.19–6.10 (m, 1 H), 3.60–3.48 (m, 2 H), 3.20–3.12 (m, 1 H), 2.18–1.98 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.8, 138.3, 137.4, 134.2, 129.6, 128.8, 124.7, 59.2, 48.6, 38.6, 31.9, 27.8.

HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{14}H_{15}O_3S$: 263.0742; found: 263.0739.

3-(Hydroxymethyl)-1,5-dimethyl-7-*endo*-(phenylsulfonyl)bicyclo[2.2.2]oct-5-en-2-one (19)

Following the typical procedure for **15** using activated Zn (21 g, excess), MeOH–H_2O (5:1, 120 mL,) a soln of **14** (3.0 g, 9.4 mmol) in MeOH (20 mL), and NH_4Cl (3.5 g, excess) and stirring at r.t. (~30 °C) for 14 h. Chromatography (PE–EtOAc, 70:30) gave **19** (2.2 g, 74%, mixture of *syn*/*anti*-isomers) as a colorless solid; mp 176–177 °C.

IR (KBr): 3432, 1721 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) (major isomer): δ = 7.87–7.80 (m, 2 H), 7.69–7.60 (m, 1 H), 7.60–7.52 (m, 2 H), 5.40 (s, 1 H), 3.75–3.25 (set of m, 3 H), 2.70–2.68 (m, 1 H), 2.28–2.24 (m, 1 H), 2.20–1.90 (set of m, 2 H), 1.86–1.74 (set of m, 4 H), 1.5 (s, 3 H).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{21}O_4S$: 321.1161; found: 321.1154.

1,5-Dimethyl-7-*endo*-(phenylsulfonyl)bicyclo[2.2.2]oct-5-en-2-one (20)

Following the typical procedure for **16** using **19** (0.5 g, 1.56 mmol) in acetone (15 mL) was added dropwise a freshly prepared Jones reagent with stirring at 0 °C and the mixture was stirred for 1 h to give a β-keto acid that was directly subjected to decarboxylation. The β-keto acid thus obtained was taken up in THF–H_2O (1:1, 22 mL) and the mixture was refluxed for 16 h. THF was removed under vacuum and the aqueous medium was further diluted with H_2O and extracted with EtOAc (3 × 25 mL). The combined extracts were washed with $NaHCO_3$ soln, H_2O, and brine and dried (anhyd Na_2SO_4). Removal of solvent followed by chromatography (PE–EtOAc, 88:12) gave **20** (0.225 g, 50%); mp 162–64 °C.

IR (KBr): 1725 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87–7.83 (m, 2 H), 7.68–7.62 (m, 1 H), 7.60–7.53 (m, 2 H), 5.35 (s, 1 H), 3.41 (dd, J_1 = 9.7 Hz, J_2 = 7.4 Hz, 1 H), 2.71 (dd, J_1 = 5.4 Hz, J_2 = 2.3 Hz, 1 H), 2.19–2.01 (m, 2 H), 1.97–1.87 (m, 2 H), 1.80 (d, J = 1.5 Hz, 3 H), 1.50 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.0, 145.8, 140.0, 133.6, 129.1, 128.5, 123.0, 63.4, 51.0, 38.1, 36.0, 31.1, 19.8, 16.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{19}O_3S$: 291.1055; found: 291.1053.

7-*exo*-Acetoxy-4-(chloromethyl)-4-hydroxytricyclo[3.3.0.0^{2,8}]octan-3-one (21); Typical Procedure

A soln of **9a** (0.110 g, 0.45 mmol) in degassed acetone (110 mL, solvent as well as sensitizer) was irradiated with a Hg vapor lamp (125 W, Applied Photophysics) in a Pyrex immersion well for 4 h, under N_2. Acetone was removed under vacuum and the residue was chromatographed (silica gel, PE–EtOAc, 85:15) to afford **21** (0.050 g, 45%) as a colorless liquid.

IR (neat): 3524, 1736 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.84 (t, J = 6.9 Hz, 1 H), 3.64 (part of AB pattern, J = 11.3 Hz, 1 H), 3.57 (part of AB pattern, J = 11.3 Hz, 1 H), 3.06 (br s, 1 H), 2.99 (dd, J_1 = 8.0, J_2 = 5.1 Hz, 1 H), 2.76 (dd, J_1 = 10.2, J_2 = 5.1 Hz, 1 H), 2.62 (dd, J_1 = 13.1 Hz, J_2 = 6.2 Hz, 1 H), 2.21 (ddd, J_1 = 16.1 Hz, J_2 = 10.6 Hz, J_3 = 5.8 Hz, 2 H), 2.06 (s, 3 H), 2.02–1.90 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 209.5, 170.2, 83.0, 74.2, 49.7, 43.9, 39.1, 36.9, 30.9, 30.7, 21.0.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{11}H_{13}ClNaO_4$: 267.0400; found: 267.0410.

7-*exo*-Butoxytricyclo[3.3.0.0^{2,8}]octan-3-one (22)

Following the typical procedure for **21**, irradiation of a soln of **16** (0.105 g, 1.54 mmol) in acetone (110 mL) for 2 h followed by removal of the solvent and chromatography (PE–EtOAc, 93:7) gave **22** (0.048 g, 44%) as a colorless liquid.

IR (neat): 1742 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.85 (superimposed dd, J = 7.69 Hz, 1 H), 3.54–3.38 (m, 2 H), 2.96–2.88 (m, 1 H), 2.82 (dd, J_1 = 10.9 Hz, J_2 = 5.4 Hz, 1 H), 2.49 (dd, J_1 = 17.9 Hz, J_2 = 9.5 Hz, 1 H), 2.12–1.98 (m, 3 H), 1.75 (d, J = 17.9 Hz, 1 H), 1.58–1.52 (m, 3 H), 1.42–1.32 (m, 2 H), 0.92 (t, J = 7.3 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 214.7, 79.4, 70.2, 47.8, 47.8, 36.8, 35.6, 35.4, 32.0, 19.4, 14.0.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{19}O_2$: 195.1385; found: 195.1389.

7-*exo*-(Phenylsulfonyl)tricyclo[3.3.0.0^{2,8}]octan-3-one (23)

Following the typical procedure for **21**, irradiation of a soln of **18** (0.100 g, 0.33 mmol) in acetone (110 mL) for 1.5 h followed by removal of the solvent and chromatography (PE–EtOAc, 75:25) gave **23** (0.060 g, 60%) as a thick colorless liquid.

IR (neat): 1725 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95–7.88 (m, 2 H), 7.73–7.65 (m, 1 H), 7.63–7.55 (m, 2 H), 3.56–3.0 (m, 1 H), 3.12–3.04 (m, 1 H), 2.93 (dd, J_1 = 10.9 Hz, J_2 = 5.4 Hz, 1 H), 2.74–2.66 (m, 1 H), 2.56 (dd, J_1 = 17.9 Hz, J_2 = 9.5 Hz, 1 H), 2.42–2.34 (m, 1 H), 2.06–2.0 (m, 1 H), 1.82–1.74 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.8, 138.5, 134.1, 129.6, 128.6, 63.8, 47.2, 42.2, 37.4, 37.1, 35.6, 30.8.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{15}O_3S$: 263.0742; found: 263.0742.

1,8-Dimethyl-7-*exo*-(phenylsulfonyl)tricyclo[3.3.0.0^{2,8}]octan-3-one (24)

Following the typical procedure for **21**, irradiation of a soln of **20** (0.098 g, 0.337 mmol) in degassed acetone (110 mL) for 1.5 h followed by removal of the solvent and chromatography (PE–EtOAc, 88:12) first gave the starting material (0.007 g, 7%). Further elution (PE–EtOAc, 85:15) afforded **24** (0.03 g, 32%) as a colorless solid; mp 128–129 °C.

IR (neat): 1716 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89–7.82 (m, 2 H), 7.69–7.62 (m, 1 H), 7.60–7.52 (m, 2 H), 3.56 (dd, J_1 = 11.3 Hz, J_2 = 5.8 Hz, 1 H), 2.74–2.52 (m, 3 H), 1.62 (s, 1 H), 1.55 (s, 3 H), 1.47 (s, 3 H), 1.27 (dd, J_1 = 17.2 Hz, J_2 = 5.8 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 212.8, 139.7, 133.8 (2 C), 129.3 (2 C), 128.3, 67.2, 51.0, 50.2, 47.0, 42.9, 41.9, 41.3, 16.2, 13.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{19}O_3S$: 291.1055; found: 291.1055.

Ethyl 7-*exo*-Butoxy-3-oxotricyclo[3.3.0.0^{2,8}]octane-4-carboxylate (25)

NaH (0.450 g of 60% w/w suspension in oil, excess) was placed in a dry two-necked flask and mineral oil was washed with anhyd PE. Anhyd THF (20 mL) and ethyl carbonate (1.0 mL, 8.26 mmol) were added. The mixture was heated to reflux and a soln of **22** (0.200 g, 1.03 mmol) in anhyd THF (10 mL) was added dropwise over a period of 30 min at r.t. After the addition was complete, the mixture was allowed to reflux for 2 h. The mixture was then cooled and quenched by careful addition of H_2O. The mixture was diluted with H_2O and extracted with EtOAc (3 × 50 mL). The combined extracts were washed with H_2O and brine and dried (anhyd Na_2SO_4). The solvent was removed under reduced pressure and residue was purified by column chromatography (PE–EtOAc, 9:1) to give **25** (0.150 g, 56%) as a colorless liquid.

IR (neat): 1726 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.24–4.12 (m, 2 H), 3.83 (superimposed dd, J = 6.5 Hz, 1 H), 3.54–3.36 (m, 2 H), 3.20–3.14 (m, 1 H), 3.03 (dd, J_1 = 10.6, J_2 = 5.1 Hz, 1 H), 2.79 (s, 1 H), 2.18–2.15 (m, 2 H), 2.06–2.0 (m, 2 H), 1.60–1.54 (m, 2 H), 1.42–1.33 (m, 2 H), 1.30–1.24 (m, 3 H), 0.96–0.88 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.4, 168.5, 79.5, 70.3, 64.5, 61.8, 46.4, 43.5, 40.6, 37.4, 36.1, 34.5, 32.0, 19.4, 14.2 (signals due to major isomer).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{23}O_4$: 267.1596; found: 267.1601.

Ethyl 7-*exo*-Butoxy-3-oxobicyclo[3.3.0]octane-2-carboxylate (26) and Its Enol Tautomer 27

To a stirred soln of **25** (0.550 g, 2.075 mmol) in anhyd benzene (15 mL), AIBN 0.100 g, 0.609 mmol) and Bu_3SnH (2.0 mL, 7.42 mmol) were added and the mixture was refluxed for 12 h (TLC) under N_2. Benzene was removed and the residue was column chromatographed (silica gel). First PE eluted the tin impurity, then PE–EtOAc (92:8) eluted **26** and **27** (0.40 g, 73%) as a colorless liquid.

IR (neat): 1751, 1723, 1658 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) (keto–enol mixture): δ = 10.44 (br s, 1 H), 4.30–4.10 (m, 4 H), 4.04–3.94 (m, 1 H), 3.90–3.80 (m, 1 H), 3.44–3.30 (m, 5 H), 3.22–3.10 (m, 1 H), 3.02–2.92 (m, 1 H), 2.84–2.60 (m, 3 H), 2.28–2.06 (m, 4 H), 2.02–1.90 (m, 2 H), 1.76–1.64 (m, 2 H), 1.54–1.42 (m, 5 H), 1.40–1.20 (m, 12 H), 0.95–0.88 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.6, 174.5, 170.1, 169.4, 104.4, 80.9, 80.6, 68.7, 68.6, 61.5, 61.4, 59.8, 57.8, 44.3, 43.2, 42.9, 42.7, 39.9, 39.5, 39.3, 39.0, 38.4, 36.2, 34.4, 32.2, 32.1,19.5, 14.4, 14.2, 13.9.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{15}H_{25}O_4$: 269.1753; found: 269.1740.

7-*exo*-Butoxybicyclo[3.3.0]octan-3-one (28)

To a stirred soln of **22** (0.490 g, 2.52 mmol) in anhyd benzene (20 mL), AIBN (0.100 g, 0.609 mmol) and Bu_3SnH (1.0 mL, 3.71 mmol) were added and the mixture was refluxed for 12 h (TLC) under N_2. Benzene was removed and the residue was column chromatographed (silica gel). First PE eluted the tin impurity then (PE–EtOAc, 96:4) eluted **28** (0.330 g, 67%) as a colorless liquid.

IR (neat): 1741 cm^{-1}.

1H NMR (400 MHz, $CDCl_3$): δ = 4.03–3.96 (m, 1 H), 3.36 (superimposed dd, *J* = 6.5 Hz, 2 H), 2.94–2.82 (m, 2 H), 2.58–2.46 (m, 2 H), 2.22–1.96 (m, 4 H), 1.64–1.48 (m, 4 H), 1.42–1.30 (m, 2 H), 0.91 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 220.7, 81.3, 68.6, 44.7, 39.7, 37.7, 32.2, 19.5, 14.0.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{12}H_{21}O_2$: 197.1542; found: 197.1543.

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(13) *Crystal data* **7b**: $C_{13}H_{19}O_3Cl$, MW 258.09, space group, monoclinic, $P2_1/c$, a = 10.256(2), b = 7.6274(12), c = 15.360(7) Å, α = 90.0, β = 107.44(3), γ = 90.0°, U = 1146.3(6) A^3, Z = 4, D_c = 1.218 g/m^3, T = 293(2) K, $F(000)$ = 456, size = 0.26 × 0.16 × 0.12 mm. Reflections/collected/unique 10532/2012 [R(int) = 0.0258], final R indices [$I > 2\sigma(I)$] = $R1$ = 0.0369, w$R2$ = 0.105c, R indices

(all data) $R1 = 0.0554$, w$R2 = 0.1107$. The complete crystal data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif quoting the CCDC number 674959.

(14) *Crystal data* **11c**: $C_{17}H_{19}ClO_4S$, MW 354.83, space group, monoclinic, $P2_1/c$, $a = 8.3197(6)$, $b = 23.0608(19)$, $c = 15.360(7)$ Å, $\alpha = 90.0$, $\beta = 96.045(6)$, $\gamma = 90.0°$, $U = 1600.8(2)$ A^3, $Z = 4$, $D_c = 1.472$ mg/m^3, $T = 120(2)$ K, $F(000) = 744$, size = $0.33 \times 0.27 \times 0.21$ mm. Reflections/collected/unique 8932 / 2801 [R(int) = 0.0732], final R indices [$I > 2\sigma(I)$] = $R1 = 0.0826$, w$R2 = 0.2139$, R indices (all data) $R1 = 0.0965$, w$R2 = 0.2226$. The complete crystal data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif quoting the CCDC number 674960.

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