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A Novel and Efficient Synthesis of Bicyclo[2.2.2]octenones and Sigmatropic Shifts in Ground and Excited States: Stereoselective Route to *cis*-Decalins and Diquinane Frameworks

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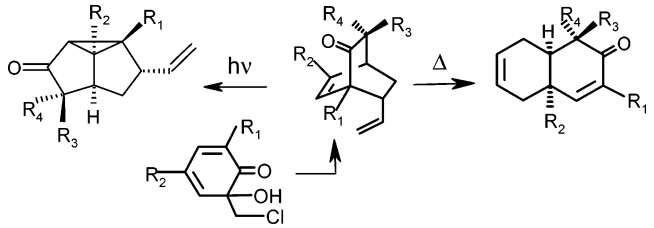

A new and efficient synthesis of a variety of highly embellished bicyclooctenones having an *endo*-vinyl moiety and their sigmatropic shifts in ground and excited states leading to a stereoselective route to substituted *cis*-decalins and diquinane frameworks have been described. Functionalized bicyclo[2.2.2]octenones having an *endo*-vinyl group and a β,γ-enone chromophore were prepared by in situ generation of 6-chloromethyl-6-hydroxycyclohexadienones and cycloaddition with butadiene (also generated in situ) followed by manipulation of the adducts. The presence of contiguous carbonyl, hydroxyl, and chloromethyl groups in adducts led to the introduction of various alkyl groups α to the ketone in a stereoselective fashion. The 3,3-sigmatropic shift in the bridged bicyclic compounds gave the corresponding *cis*-decalins, whereas the triplet sensitized irradiation led to the formation of diquinanes as a result of a 1,2-acyl shift.

Introduction

Recently, there has been an upsurge of interest in the synthesis of *cis*-decalins.[1,2] This is presumably due to the occurrence and isolation of a number of terpenoids such as agelasines[3] (**1**, **2**), kalihinene X[4a] (**3**) (Figure 1), and thelepoganes[4b,c] that contain a highly substituted *cis*-decalin core in their molecular architecture. Many of these natural products exhibit wide-ranging and interesting biological activities. For example, agelasine A (**1**) (Figure 1), a *cis*-clerodane diterpene, exhibits antimicrobial activity and strongly inhibits the activity of the enzyme NaK-ATPase.[3] The presence of a *cis*-decalin framework in their structure with varying degrees of substitution patterns and four or more contiguous stereocenters coupled with diverse biological activities has led

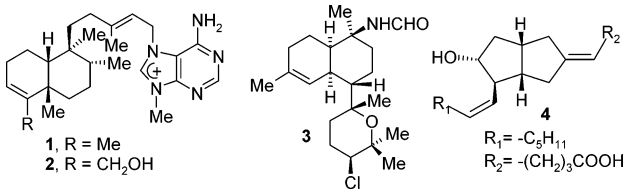

FIGURE 1. Agelasines, kalihinene terpenoids, and carbacyclin.

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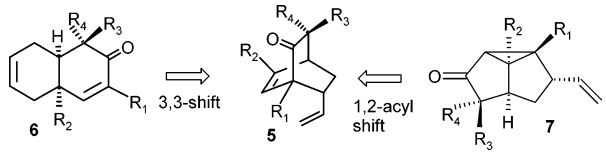
SCHEME 1



to significant interest in the development of new and efficient methods for the synthesis of functionalized *cis*-decalins.[1,2]

The diquinane or bicyclo[3.3.0]octane moiety is present in many natural products[5] and also constitutes an important building block for the synthesis of biologically active compounds such as carbacyclin **4** (Figure 1).[6] While there are a number of methods for the synthesis of diquinanes and polyquinanes,[7] the search for new and efficient methods is continuing.[8]

In view of the interest in the synthesis of *cis*-decalins and diquinanes and our interest in the chemistry of cyclohexadienones that have proved to be versatile reactive intermediates in synthesis,[9,10] we considered developing a general route to functionalized *cis*-decalins such as **6** and diquinane frameworks of the type **7** from a common precursor. It was contemplated that a 3,3-sigmatropic shift in the appropriately designed bicyclo-[2.2.2]octenones of type **5** would lead to the *cis*-decalins such as **6**, while a photochemical 1,2-acyl shift in **5** would give the diquinane framework of type **7** in a stereoselective fashion (Scheme 1).We report herein a new methodology for the synthesis of bridged bicyclic systems of type **5** and their sigmatropic shifts in ground and triplet excited states leading to a general, flexible, and stereoselective route to *cis*-decalins and diquinanes.[11]

Results and Discussion

Synthesis of Bicyclo[2.2.2]octenones Having an *endo*-Vinyl Moiety. To develop a route to the *cis*-decalins of type **6** and the diquinanes **7**, it was necessary to devise an efficient method for the synthesis of bicyclo-[2.2.2]octenones of type **5**. While such types of bicyclic systems are not known in the literature, simpler vinyl-substituted bicyclo[2.2.2]octanes are prepared by addition of a vinyl group to bicyclo[2.2.2]octenones that gives a mixture of stereoisomers.[12] Recently, some other methods involving double Michael addition,[13] Michael addition followed by reductive amination,[14] homoallyl−homoallyl radical rearrangement,[15] and cycloaddition of *o*-quinone ketals and related species have been developed for the synthesis of bicyclo[2.2.2]octenones.[16] However, most of these methods have several limitations with regard to introduction of functional groups and substituents on the bicyclo[2.2.2]octane framework and often give a mixture of regioisomers.

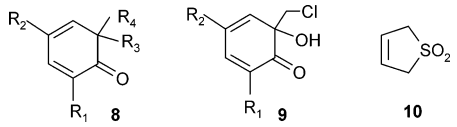


FIGURE 2. Potential intermediates for cycloaddition.

Conceptually, the desired bicyclooctenones of type **5** should be available via inverse electron demand cycloaddition of cyclohexa-2,4-dienones of type **8** with acyclic 1,3-dienes (Figure 2). Although there are some methods for preparation of 6,6-disubstituted cyclohexadienones viz., the alkylation of ortho-substituted phenols and rearrangement of epoxyfulvene,[17] these methods are not easily adaptable for our purpose. Therefore, we developed an indirect route to bicyclooctenones of type **5** by in situ generation and cycloaddition of 6-chloromethyl-6-hydroxycyclohexadienones of type **9** with the butadiene equivalent sulfolene **10** followed by manipulation of the adducts as presented below.

Thus, sulfolene **10** was slowly added to a preheated solution of the readily available dimer **11a**[18] in *o*-dichlorobenzene at 140 °C. Chromatography of the reaction mixture gave the adduct **12a** as the major product along with a minor amount of the enone **13a** (Scheme 2), whose structures were deduced from their spectral data and chemical transformation. The *endo* stereochemistry of the vinyl group was proved through Cope rearrangement (vide infra), and the orientation of chloromethyl and hydroxyl groups was suggested on the basis of general tendency of cyclohexadienones during cycloaddition.[19,20]

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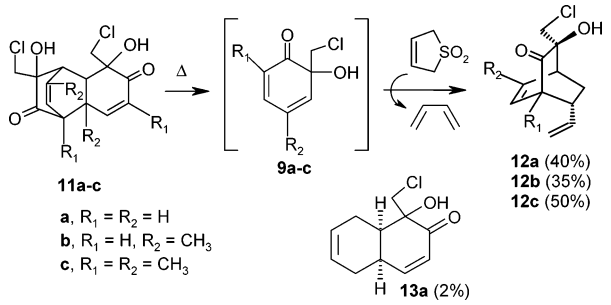
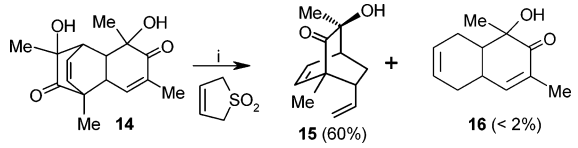
SCHEME 2

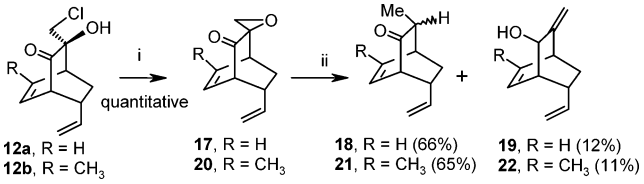


SCHEME 3[a]



[a] Reagents/conditions: i, *o*-dichlorobenzene, 115 °C.

SCHEME 4[a]

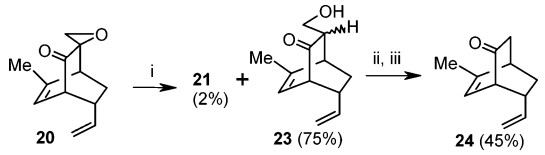


[a] Reagents/conditions: i, KOH, $H_2O-CHCl_3$, CTAB, rt; ii, Zn, NH_4Cl, dioxane, Δ.

Further, the dimers **11b** and **11c** were also prepared[21] and subjected to pyrolysis in the presence of sulfolene, which furnished the corresponding adducts **12b** and **12c**, respectively (Scheme 2). Similarly, pyrolysis of the dimer **14**[18b] and sulfolene gave the adduct **15** in good yield along with a very minor amount of the enone **16** (Scheme 3). Although the yields in the aforementioned cycloadditions are moderate, the generation of molecular complexity is noteworthy.[22]

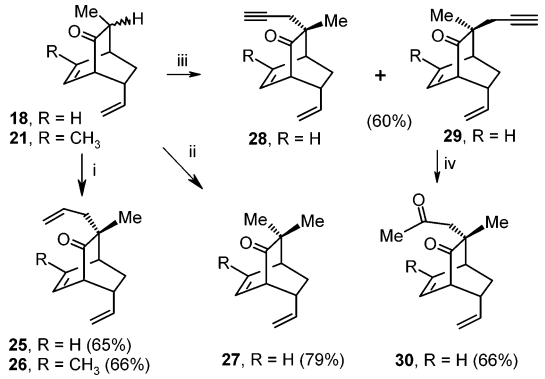
Manipulation of Chloromethyl and Hydroxyl Groups in 12a and 12b into Alkyl Groups: Synthesis of Bicyclo[2.2.2]octenones of Type 5. The presence of contiguous functional groups in adducts **12a**−**c** provided a unique opportunity for further manipulation. Thus, the adduct **12a** was readily converted into epoxy ketone **17** in a quantitative fashion on treatment with aqueous KOH in chloroform containing cetyltrimethylammonium bromide (CTAB) as a phase-transfer catalyst (Scheme 4). The reduction of the epoxy-ketone **17** with activated zinc in refluxing dry dioxane containing ammonium chloride, following a methodology developed in our group, furnished the ketone **18** [as a syn/anti mixture (1:2), ^{1}H NMR (300 MHz) spectrum] as a major product along with the alcohol **19** as a minor product. Similarly, the adduct **12b** was also transformed into the ketone **21**

SCHEME 5[a]



[a] Reagents/conditions: i, Zn, NH_4Cl, $MeOH-H_2O$ (6:1), 33 °C; ii, Jones oxidation; iii, aq ThF, Δ.

SCHEME 6[a]



[a] Reagents/conditions: i, NaH, THF, allyl bromide, Δ; ii, NaH, methyl iodide, THF, Δ; iii, NaH, propargyl bromide, THF, Δ; iv, HgO, 4% H_2SO_4, MeOH, 60 °C.

via the ketoepoxide **20** (Scheme 4). Alternatively, the epoxide **20** was manipulated to bicyclooctenone **24** as shown in Scheme 5. The reduction of ketoepoxide **20** with zinc-NH_4Cl in an aqueous protic solvent ($MeOH-H_2O$) at ambient temperature selectively gave the β-keto alcohol **23** as the major product [syn/anti mixture (1:3), ^{1}H NMR spectrum] that upon oxidation and decarboxylation furnished **24** (Scheme 5).

Further, the treatment of ketone **18** with allyl bromide in the presence of NaH−THF yielded a mixture of syn/anti (85:15) isomers (^{1}H NMR) from which the major syn isomer **25** was isolated by column chromatography on $AgNO_3$-impregnated silica gel in good yield (Scheme 6). The syn stereochemistry of the allyl chain was indicated from the chemical shift of the methyl group at C-3 that appeared downfield (δ 1.09) compared to the anti isomer (δ 1.06) in accordance with earlier observation in related systems. Such types of stereoselective alkylations have also been observed by us as well as others.[23] Similarly, the ketone **21** was also alkylated with allyl bromide to give the syn isomer **26** as a major product. The ketone **18** was also alkylated with methyl iodide to furnish the compound **27** in good yield.

In addition, alkylation of **18** with propargyl bromide gave the propargyl analogue as a mixture of syn/anti isomers **28** and **29** in a selective fashion, from which some of the syn isomer **28** was separated after repeated chromatography on silica gel (Scheme 6). Further, hydration of the syn/anti mixture of **28** and **29** with HgO in aqueous H_2SO_4 gave a mixture of diones from which the dione **30** was isolated as the major product (66%) by chromatography on $AgNO_3$-impregnated silica gel (Scheme

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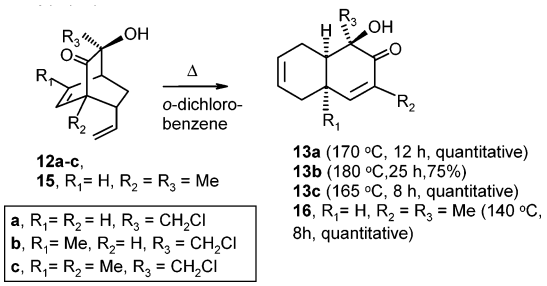
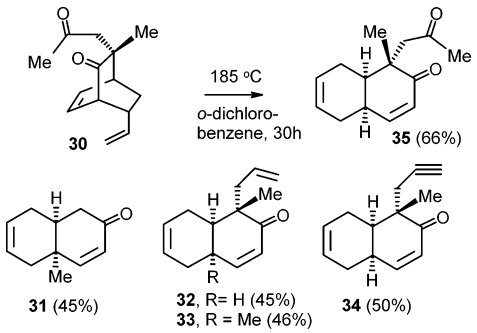
SCHEME 7



SCHEME 8



6). However, the minor isomer could not be separated. The structure and stereochemistry of the compound **30** was deduced from its spectral data and further confirmed through its chemical transformation to **35** (vide infra).

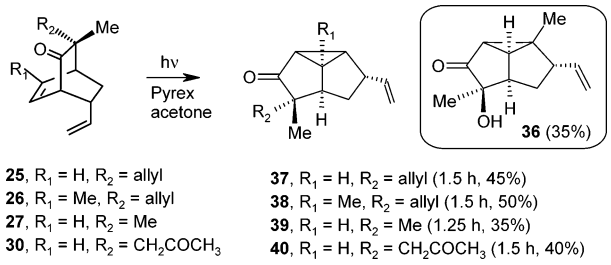
[3,3]-Sigmatropic Shift of Substituted Bicyclo-[2.2.2]octenones: A Novel, General, and Stereoselective Route to Functionalized *cis*-Decalins. Cope rearrangement or 3,3-sigmatropic shift is a general process.[24] While the oxy Cope and the oxy-anion Cope have been widely used in synthesis,[24b–d] the Cope rearrangement is not often used due to its reversibility and harsh reaction conditions. Toward the synthesis of *cis*-decalins, 3,3-sigmatropic shift in bicyclooctenones **12a–c**, **15**, **24–26**, **28**, and **30** was explored.

Thus, heating a solution of **12a** in *o*-dichlorobenzene at ~170 °C led to a clean 3,3-sigmatropic shift and furnished the *cis*-decalin **13a** in quantitative yield (Scheme 7). Similarly, heating the bicyclic compounds **12b**, **12c**, and **15** furnished the corresponding *cis*-decalins **13b**, **13c**, and **16** in good yields (Scheme 7).

The bicyclooctenones **25**, **26**, **28**, and **30** (Scheme 6) required a little higher temperature for 3,3-shift and gave the corresponding *cis*-decalins **32–35** respectively (Scheme 8). The structure of **35** was confirmed by its single X-ray structure determination. Thus, the structures and stereochemistry of the preceding intermediates leading to **35** were also established. The 3,3-sigmatropic shift in compound **24** gave the enone **31**, the *cis*-diastereoisomer of the Woodward's precursor for steroids[25] (Scheme 8).

Photochemical 1,2-Acyl Shift in Bicyclo[2.2.2]-octenones and Synthesis of Diquinane Frame-works. The photochemical reactions of β,γ-enones have evoked a great deal of interest in the past,[26,27] which has been further enhanced recently[28] because of their synthetic potential and versatility. In general, the direct irradiation of constrained β,γ- enones causes a 1,3-shift of the acyl group, and sensitized irradiation results in a 1,2-acyl shift or oxa-di-π-methane rearrangement. Oxa-di-π-methane reaction of bicyclo[2.2.2]octenones is well documented.[26c,27a,28] Although the range of the oxa-di-π-methane rearrangement appears to be wide, it is quite sensitive to the nature of both functional groups and substituents.[28b,c] The triplet-sensitized photoreaction of **15**, **25–27**, and **30** was examined.

SCHEME 9



Thus, a solution of **27** in acetone (both solvent and sensitizer) was irradiated in a Pyrex immersion well for 1.25 h. Removal of solvent followed by chromatography of the photolysate gave the tricyclic ketone **39** in moderate yield (35%) in addition to the recovered starting material (15%) (Scheme 9).

Similarly, irradiation of the bicyclo[2.2.2]octenones **25** and **26** having an allyl group in addition to the *endo*-vinyl moiety and β,γ-enone group furnished the oxa-di-π-methane products **37** and **38**, respectively (Scheme 9). Irradiation of the compound **30**, having another photochemically reactive carbonyl group in addition to the β,γ-enone moiety, also underwent oxa-di-π-methane rearrangement to give the diquinane framework **40** (Scheme 9). Similar irradiation of the compound **15**, having a hydroxyl group at the α position to the carbonyl group, also gave the tricyclic ketone **36** in moderate yield as a result of the oxa-di-π-methane rearrangement (Scheme 9).

Conclusion

In summary, we have described a new and efficient synthesis of a variety of functionalized bicyclooctenones of type **12a–c**, **15**, **17–28**, **30** having an *endo*-vinyl moiety and their sigmatropic shifts in ground and excited states. A new method for the synthesis of bicyclo[2.2.2]-octenones was developed via in situ generation of 6-chlo-

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romethyl-6-hydroxycyclohexadienones and cycloaddition with butadiene (also generated in situ) followed by stereoselective manipulation of the adducts. While Cope rearrangement provided a highly efficient and stereoselective route to highly functionalized *cis*-decalins, the photochemical 1,2-acyl shift led to synthesis of a bicyclo-[3.3.0]octane framework. The present work also demonstrates the creation of structural diversity from a common precursor via modulation of chemical reactivity. Application of this methodology toward synthesis of agelasines and other biologically active compounds is underway.

Experimental Section

3-Chloromethyl-3-hydroxy-7-*endo*-vinyl-bicyclo[2.2.2]-oct-5-en-2-one (12a). To a solution of dimer **11a** (3 g, 9.46 mmol) in *o*-dichlorobenzene (12 mL) at 140 °C was added the sulfolene **10** (12 g, excess) at regular intervals using a solid-addition funnel over a period of 7 h. Reaction mixture was brought to room temperature and chromatographed on silica gel. Elution with petroleum ether first gave *o*-dichlorobenzene. Continued elution with petroleum ether/ethyl acetate (98:2) gave the adduct **12a** (1.60 g, 40%) as a solid, which was recrystallized from petroleum ether/ethyl acetate (96:4). Further elution with petroleum ether/ethyl acetate (97:3) gave the enone **13a** (0.065 g, ∼2%) as a liquid.

Data for **12a**: mp 83−84 °C; IR (film) ν_{max} 1726 cm^{-1}; ^{1}H NMR (300 MHz, CCl_4 + $CDCl_3$) δ 6.54 (superimposed dd, $J_1 = J_2 = 7$ Hz, 1H), 6.16 (superimposed dd, $J_1 = J_2 = 7$ Hz, 1H), 5.61−5.50 (m, 1H), 5.01 (d, $J = 16.8$ Hz, 1H), 4.97 (d, $J = 10.2$ Hz, 1H), 3.60 (part of an AB system, $J_{AB} = 11.7$ Hz, 1H), 3.48 (part of an AB system, $J_{AB} = 11.7$ Hz, 1H), 3.19 (br m, 2H), 2.85−2.77 (m overlapped with s, 2H), 2.45 (superimposed dd, $J_1 = J_2 = 11.2$ Hz, 1H), 1.20 (d, $J = 13.2$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$ + CCl_4) δ 208.4, 140.1, 136.0, 126.9, 114.9, 73.33, 53.3, 50.55, 40.21, 40.00, 26.20. Analysis found: C, 61.72; H, 5.93%. Calcd for $C_{11}H_{13}O_2Cl$: C, 62.10; H, 6.11%. Mass (*m/z*) 212 (M^+).

3-Chloromethyl-3-hydroxy-5-methyl-7-*endo*-vinyl-bicyclo[2.2.2]oct-5-en-2-one (12b). Pyrolysis of dimer **11b** (3 g, 8.69 mmol) and sulfolene (12 g, excess) in *o*-dichlorobenzene (12 mL) at 140 °C for 7 h as described above followed by chromatography [petroleum ether/ethyl acetate (98:2)] gave the adduct **12b** (1.37 g, 35%) as a solid, which was recrystallized from petroleum ether/ethyl acetate (96:4): mp 91−92 °C; IR (film) ν_{max} 1727 cm^{-1}; ^{1}H NMR (300 MHz, CCl_4 + $CDCl_3$) δ 5.74 (s, 1H), 5.62−5.50 (m, 1H), 5.0 (d, $J = 17.4$ Hz, 1H), 4.93 (d, $J = 9.9$ Hz, 1H), 3.61 (part of an AB system, $J_{AB} = 12$ Hz, 1H), 3.44 (d of a part of an AB system, $J_1 = 12$ Hz, $J_2 = 3.4$ Hz, 1H), 3.03 (m, 2H), 2.81−2.66 (m, 2H), 2.44 (m, 1H), 1.96 (s, 3H), 1.16 (superimposed dd of a d, $J_1 = 13$ Hz, $J_2 = J_3 = 2.7$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$ + CCl_4) δ 208.68, 145.84, 140.37, 118.80, 114.67, 73.31, 52.98, 49.83, 44.94, 40.63, 26.05, 20.93. Analysis found: C, 63.38; H, 6.66%. Calcd for $C_{12}H_{15}O_2Cl$: C, 63.57; H, 6.62%. Mass (*m/z*) 226 (M^+).

3-Chloromethyl-3-hydroxy-1,5-dimethyl-7-*endo*-vinyl-bicyclo[2.2.2]oct-5-en-2-one (12c). Pyrolysis of dimer **11c** (3 g, 8.04 mmol) and sulfolene (12 g, excess) in *o*-dichlorobenzene (12 mL) at 115 °C for 5 h as described above followed by chromatography [petroleum ether/ethyl acetate (98:2)] gave the adduct **12c** as a colorless liquid (1.93 g, 50%): IR (neat) ν_{max} 3475, 1717 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.48−5.36 (s merged with m, 2H), 4.96 (m, 2H), 3.55 (part of an AB system, $J_{AB} = 11.8$ Hz, 1H), 3.45 (part of an AB system, $J_{AB} = 11.8$ Hz, 1H), 2.98 (m, 1H), 2.56 (s, 1H), 2.51 (m, 1H), 2.40 (m, 1H), 1.95 (s, 3H), 1.22 (dd of a d, $J_1 = 13$ Hz, $J_2 = 4.9$ Hz, $J_3 = 2.8$ Hz, 1H), 1.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.04, 145.07, 139.10, 124.35, 116.02, 73.96, 51.39, 50.26, 46.94, 44.37, 28.06, 20.90, 15.78. HRMS (EI): found 240.0920 (M^+); calcd for $C_{13}H_{17}O_2Cl$ 240.0917 (M^+).

3-Hydroxy-1,3-dimethyl-7-*endo*-vinyl-bicyclo[2.2.2]oct-5-en-2-one (15). The dimer **14** (3 g, 10.86 mmol) and sulfolene (12 g, excess) were heated in *o*-dichlorobenzene (12 mL) at 115 °C for 5 h as described above, and the reaction mixture was chromatographed on silica gel. Elution with petroleum ether first gave *o*-dichlorobenzene. Continued elution with petroleum ether/ethyl acetate (98:2) gave the adduct **15** (2.50 g, 60%) as a solid, which was recrystallized from petroleum ether. Further elution with petroleum ether/ethyl acetate (97:3) then gave the enone **16** (0.075 g, ∼2%) as a colorless liquid.

Data for **15**: mp 52−54 °C; IR (film) ν_{max} 3466, 1724 cm^{-1}; UV (MeOH) λ_{max} 305.6 (w), 216.6 (s) nm; ^{1}H NMR (300 MHz, CCl_4 + $CDCl_3$) δ 6.46 (superimposed dd, $J_1 = J_2 = 7.4$ Hz, 1H), 5.87 (d, $J = 8.4$ Hz, 1H), 5.44−5.32 (m, 1H), 4.95 (m, 2H), 2.80 (s merged with m, 2H), 2.58 (m, 1H), 2.35 (m, 1H), 1.24 (s, 3H), 1.20−1.08 (s merged with m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$ + CCl_4) δ 213.92, 139.46, 136.17, 131.57, 115.78, 72.17, 51.31, 46.21, 43.31, 28.82, 26.08, 15.84. HRMS (EI): found 192.1140 (M^+); calcd for $C_{12}H_{16}O_2$ 192.1150 (M^+).

3-Spiroepoxy-7-*endo*-vinyl-bicyclo[2.2.2]oct-5-en-2-one (17). To a solution of the adduct **12a** (0.5 g, 2.35 mmol) in chloroform (50 mL) containing cetyltrimethylammonium bromide (CTAB) (0.035 g) as a phase-transfer catalyst was added an aqueous solution of potassium hydroxide (0.145 g, 2.58 mmol in H_2O, 10 mL). The reaction mixture was stirred at room temperature (∼30 °C) for 5 h, after which the organic phase was separated and the aqueous layer extracted with chloroform (2 × 15 mL). The combined organic extract was washed with brine (20 mL) and dried over anhydrous sodium sulfate. Removal of solvent followed by column chromatography [petroleum ether/ethyl acetate, (98:2)] of the residue on silica gel gave the epoxy ketone **17** as a colorless liquid: IR (neat) ν_{max} 1740 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$ + CCl_4) δ 6.57 (superimposed dd, $J_1 = J_2 = 7.2$ Hz, 1H), 6.20 (superimposed dd, $J_1 = J_2 = 7.2$ Hz, 1H), 5.68−5.56 (m, 1H), 5.06 (d, $J = 18$ Hz, 1H), 4.98 (d, $J = 10.2$ Hz, 1H), 3.27 (d, $J = 6.3$ Hz, 1H), 3.11 (part of an AB system, $J_{AB} = 6.3$ Hz, 1H), 2.89 (m, 1H), 2.80 (part of an AB system, $J_{AB} = 6.3$ Hz, 1H), 2.54 (m, 1H), 2.42−2.33 (m, 1H), 1.42 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$ + CCl_4) δ 204.10, 139.91, 135.06, 127.40, 114.95, 57.20, 53.72, 52.88, 39.45, 38.64, 28.49. HRMS (EI): found 176.0828 (M^+); calcd for $C_{11}H_{12}O_2$ 176.0832 (M^+).

3-Methyl-7-*endo*-vinyl-bicyclo[2.2.2]oct-5-en-2-one (18). To a suspension of activated zinc (7 g, excess) and ammonium chloride (1 g, excess) in dry dioxane (20 mL) was added a solution of the compound **17** (1.5 g, 8.52 mmol) in dry dioxane (15 mL) and refluxed for 12 h. The reaction mixture was filtered on a Celite pad to remove zinc and washed with ethyl acetate. The filtrate was concentrated in vacuo and diluted with water (15 mL) and extracted with ethyl acetate (3 × 25 mL). The combined organic layer was washed with brine (25 mL) and dried over anhydrous sodium sulfate. The solvent was removed under vacuum, and the residue was chromatographed on silica gel. Elution with petroleum ether/ethyl acetate (99:1) first gave the compound **18** (0.91 g, 66%) as a syn/anti mixture. Further elution with petroleum ether/ethyl acetate (94:6) furnished the alcohol **19** in minor amounts (0.16 g, 12%) as a colorless liquid.

Data for **18**: IR (neat) ν_{max} 1724 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.6 (superimposed dd, $J_1 = J_2 = 7.3$ Hz, 1H), 6.08 (superimposed dd, $J_1 = J_2 = 7.3$ Hz, 1H), 5.64−5.52 (m, 1H), 4.99 (d, $J = 17$ Hz, 1H), 4.92 (d, $J = 9.7$ Hz, 1H), 3.1 (m, 1H), 2.66 (m, 1H), 2.60 (m, 1H), 2.18 (m, 1H), 2.04 (m, 1H), 1.20 (d with structure, $J = 12$ Hz, 1H), 1.12 (d, $J = 7.3$ Hz, 3H) (data for major isomer). HRMS (EI): found 162.1032 (M^+); calcd for $C_{11}H_{14}O$ 162.1039 (M^+).

Data for **19**: IR (neat) ν_{max} 3456 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$ + CCl_4) δ 6.28 (superimposed dd, $J_1 = J_2 = 7$ Hz, 1H), 6.09 (superimposed dd, $J_1 = J_2 = 7$ Hz, 1H), 5.62−5.51 (m, 1H), 4.97−4.91 (m, 3H), 4.84 (d, $J = 10.2$ Hz, 1H), 3.99 (s, 1H), 3.04 (m, 1H), 2.85 (dd, $J_1 = 15.7$ Hz, $J_2 = 7.6$ Hz, 1H), 2.66 (m, 1H), 1.96−1.88 (m, 1H), 1.76 (br s with structure, 1H),

1.24 (dd of a d, J_1 = 12.3 Hz, J_2 = 5.8 Hz, J_3 = 2.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$ + CCl_4) δ 152.29, 143.51, 134.22, 130.35, 113.23, 107.65, 71.45, 45.69, 40.96, 35.25, 33.58; mass (*m/z*) 162 (M^+). HRMS (ESI): found 163.1130 [M^+ + H];. calcd for $C_{11}H_{15}O$ 163.1123 [M^+ + H].

3-Spiroepoxy-5-methyl-7-*endo*-vinyl-bicyclo[2.2.2]oct-5-en-2-one (20). To a solution of the adduct **12b** (0.53 g, 2.35 mmol) in chloroform (50 mL) containing cetyltrimethylammonium bromide (CTAB) (0.035 g) was added an aqueous solution of KOH (0.145 g, 2.58 mmol in 10 mL H_2O). The reaction mixture was stirred at room temperature (~30 °C) for 5 h, after which the organic phase was separated and the aqueous layer extracted with chloroform (2 × 15 mL). The combined organic extract was washed with brine (20 mL) and dried over anhydrous sodium sulfate. Removal of solvent followed by column chromatography [petroleum ether/ethyl acetate, (98:2)] of the residue on silica gel gave the epoxy ketone **20** (0.440 g, ~100%) as a colorless liquid: IR (neat) ν_{max} 1738 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.78 (d with structure, J = 6.2 Hz, 1H), 5.71−5.59 (m, 1H), 5.05 (d with structure, J = 17 Hz, 1H), and 4.98 (d with structure, J = 10.6 Hz, 1H), 3.2 (dd, J_1 = 6.2 Hz, J_2 = 2.1 Hz, 1H), 3.13 (part of an AB system, J_{AB} = 6.2 Hz, 1H), 2.88 (part of an AB system merged with a multiplet, J_{AB} = 6.2 Hz, 2H), 2.39−2.29 (m, 2H), 1.94 (d, J = 1.8 Hz, 3H), 1.4 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.42, 145.05, 140.23, 119.23, 114.77, 57.43, 53.66, 52.33, 44.03, 40.21, 28.23, 20.64. HRMS (EI): found 190.0979 (M^+); calcd for $C_{12}H_{14}O_2$ 190.0988 (M^+).

3,5-Dimethyl-7-*endo*-vinyl-bicyclo[2.2.2]oct-5-en-2-one (21). A solution of the compound **20** (1.5 g, 7.89 mmol) in dry dioxane (15 mL) was added to a suspension of activated zinc (7 g, excess) and NH_4Cl (1 g, excess) in dry dioxane (20 mL), and the reaction mixture was refluxed for 12 h. The reaction mixture was filtered and washed with ethyl acetate. The filtrate was concentrated in vacuo, diluted with water (15 mL), and extracted with ethyl acetate (3 × 25 mL). The combined extract was washed with brine (1 × 25 mL) and dried. The solvent was removed under vacuum, and the residue was chromatographed on silica gel. Elution with petroleum ether/ethyl acetate (99:1) first gave the compound **21** (1.08 g, 66%) [syn/anti mixture] as a colorless liquid. Further, elution with petroleum ether/ethyl acetate (94:6) furnished the alcohol **22** in minor amounts (0.18 g, 12%) as a colorless liquid.

Data for **21**: IR (neat) ν_{max} 1724 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.68−5.52 (s merged with multiplet, 2H), 4.98 (d, J = 17.2 Hz, 1H), 4.92 (d, J = 9.6 Hz, 1H), 2.98 (dd, J_1 = 6 Hz, J_2 = 2.4 Hz, 1H), 2.62−2.52 (m, 1H), 2.48 (d, J = 2.4 Hz, 1H), 2.18−2.10 (m, 1H), 2.02 (m, 1H), 1.88 (s, 3H), 1.10 (d merged with m, J = 7.2 Hz, total 4H) (data for major isomer). HRMS (EI): found 176.1193 (M^+); calcd for $C_{12}H_{16}O$ 176.1196 (M^+).

Data for **22**: IR (neat) ν_{max} 3371 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$ + CCl_4) δ 5.68 (d, J = 6.6 Hz, 1H), 5.63−5.51 (m, 1H), 4.93−4.81 (m, 4H), 3.96 (s, 1H), 2.83 (m, 2H), 2.55 (m, 1H), 1.94−1.86 (m, 2H), 1.79 (d, J = 1.5 Hz, 3H), 1.20 (ddd, J_1 = 12.3 Hz, J_2 = 5.8 Hz, J_3 = 2.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$ + CCl_4) δ 152.31, 143.77, 142.99, 122.68, 113.04, 107.60, 71.85, 46.58, 45.63, 34.79, 34.32, 19.91. HRMS (ESI): found 177.1286 [M^+ + H]; calcd for $C_{12}H_{17}O$ 177.1279 [M^+ + H].

3-Hydroxymethyl-5-methyl-7-*endo*-vinyl-bicyclo[2.2.2]-oct-5-en-2-one (23). To a solution of the epoxy ketone **20** (2 g, 10.5 mmol) in MeOH−H_2O (6:1, 70 mL) was added zinc (activated 12 g, excess) and NH_4Cl (2.2 g, 40.7 mmol). The reaction mixture was stirred at ambient temperature (~33 °C) for 10 h, filtered on a Celite bed, and washed with ethyl acetate (4 × 5 mL). The filtrate was concentrated under vacuum, diluted with water (10 mL), and extracted with ethyl acetate (4 × 5 mL). The combined extract was washed with brine (10 mL) and dried on anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography. Elution with petroleum ether/ethyl acetate (98:2) gave the ketone **21** as a liquid (0.037 g, 2%). Further elution with petroleum ether/ethyl acetate (90:10) gave the β-keto alcohol **23** as a colorless liquid (syn/anti mixture, 1.51 g, 75%).

Data for **23**: IR (neat) ν_{max} 3426, 1717 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.68 (br s, 1H), 5.58−5.49 (m, 1H), 4.98 (d, J = 17.1 Hz, 1H), 4.91 (d, J = 9.9 Hz, 1H), 3.81−3.75 (m, 1H), 3.63−3.55 (m, 1H), 2.98 (d, J = 6 Hz, 1H), 2.68−2.60 (s merged with m, 3H), 2.21−2.07 (m, 2H), 1.91 (s, 3H), 1.18 (d with structure, J = 12.4 Hz, 1H) (data for the major isomer). HRMS (ESI): found 193.1247 [M^+ + H]; calcd for $C_{12}H_{17}O_2$ 193.1229 [M^+ + H].

5-Methyl-7-*endo*-vinyl-bicyclo[2.2.2]oct-5-en-2-one (24). To a solution of the β-keto-alcohol **23** (2 g, 10.4 mmol) in acetone (60 mL) at ~5 °C was added freshly prepared Jones' reagent dropwise. After completion of the reaction (TLC, 0.45 h), acetone was removed under vacuum, and the residue was diluted with water (8 mL). The aqueous layer was extracted with ethyl acetate (6 × 10 mL). The extract was combined and dried over anhydrous sodium sulfate, and the solvent was removed under vacuum to give the crude acid, which was subjected to decarboxylation as follows. The carboxylic acid was dissolved in THF−H_2O mixture (1:1, 60 mL) and refluxed for 12 h. The aqueous layer was saturated with sodium chloride, extracted with ether (7 × 10 mL), and dried. The solvent was removed in vacuo, and the residue was chromatographed. Elution with petroleum ether/ethyl acetate (97:3) gave the title compound **24** as a colorless liquid (0.76 g, 45%): IR (neat) ν_{max} 1726 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$ + CCl_4) δ 5.68 (d, J = 5.7 Hz, 1H), 5.61−5.50 (m, 1H), 4.98 (d, J = 16.8 Hz, 1H), 4.91 (d, J = 9.9 Hz, 1H), 2.96 (d, J = 6.6 Hz, 1H), 2.69 (s merged with m, 2H), 1.97 (m, 3H), 1.88 (s, 3H), and 1.29 (br d, J = 12.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$ + CCl_4) δ 211.02, 146.73, 140.97, 118.26, 114.23, 54.43, 39.45, 38.84, 38.03, 31.83, 20.26. HRMS (EI): found 162.1039 (M^+); calcd for $C_{11}H_{14}O$ 162.1046 (M^+).

3-Allyl-3-methyl-7-*endo*-vinyl-bicyclo[2.2.2]oct-5-en-2-one (25). Sodium hydride (0.5 g of 60% w/w suspension in oil, excess) was placed in a dry two-necked flask and washed with dry petroleum ether, and tetrahydrofuran (5 mL) was added. A solution of ketone **18** (0.6 g, 3.70 mmol) in tetrahydrofuran (10 mL) was added slowly to the reaction mixture, and it was refluxed for 1 h. Allyl bromide (1 mL, excess) was then added to the reaction mixture, and the reaction mixture was further refluxed for 8 h. The reaction mixture was then cooled in an ice bath and quenched by careful addition of water, and it was filtered on a Celite pad. The filtrate was then concentrated under vacuum. The residue was diluted with water and extracted with ether (3 × 10 mL). The combined extract was washed with water (10 mL) and brine (10 mL) and dried over anhydrous sodium sulfate. Removal of solvent and column chromatography [petroleum ether/ethyl acetate, (99:1)] of the residue on silica gel gave an inseparable mixture of alkylated products as a syn/anti mixture (0.59 g, 79%) that was further chromatographed on silver nitrate-impregnated silica gel. Elution with petroleum ether/ethyl acetate (99:1) first gave the mixture of the syn/anti isomers followed by the pure syn isomer **25** (0.486 g, 65%) as a colorless liquid: IR (neat) ν_{max} 1718 cm^{-1}; UV (MeOH) λ_{max} 296.4 (w), 217.6 (s) nm; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.55 (superimposed dd, J_1 = J_2 = 7.2 Hz, 1H), 6.02 (superimposed dd, J_1 = J_2 = 7.2 Hz, 1H), 5.85−5.70 (m, 1H), 5.64−5.50 (m, 1H), and 5.1−4.90 (m, 4H), 3.11 (d with structure, J = 6.2 Hz, 1H), 2.76−2.64 (m, 2H), 2.26−2.12 (m, 2H), 2.08−1.99 (m, 1H), 1.19 (ddd, J_1 = 13.4, J_2 = 6.1, J_3 = 2.5 Hz, 1H), and 1.09 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.88, 140.74, 138.12, 133.64, 124.05, 117.92, 114.09, 55.04, 46.10, 43.33, 41.04, 39.14, 28.34, 21.21. HRMS (EI): found 202.1357 (M^+); calcd for $C_{14}H_{18}O$ 202.1352 (M^+).

3-Allyl-3,5-dimethyl-7-*endo*-vinyl-bicyclo[2.2.2]oct-5-en-2-one (26). Sodium hydride (0.250 g of 60% w/w suspension in oil, excess) was placed in a dry two-necked flask and washed with dry petroleum ether, and tetrahydrofuran (2 mL) was added to it. A solution of ketone **21** (0.3 g, 1.70 mmol) in

tetrahydrofuran (5 mL) was added slowly to the reaction mixture, and the reaction mixture was refluxed for 1 h. Allyl bromide (0.5 mL, excess) was then added to the reaction mixture, and the reaction mixture was further refluxed for 7 h. The reaction mixture was worked up as described above, and the product obtained was chromatographed on silver nitrate-impregnated silica gel. Elution with petroleum ether/ethyl acetate, (99:1) first gave a mixture of syn/anti isomers. Continued elution furnished the syn isomer **26** (0.228 g, 62%) as a colorless liquid: IR (neat) ν_{max} 1719 cm^{-1}; UV (MeOH) λ_{max} 299 (w), 226 (s) nm; ^1H NMR (300 MHz, $CDCl_3$) δ 5.90−5.69 (m, 3H), 5.12−4.80 (m, 4H), 2.97 (dd, J_1 = 7 Hz, J_2 = 3 Hz, 1H), 2.54−2.44 (m, 2H), 2.24 (d of part of an AB system, J_{AB} = 14 Hz, J = 8 Hz, 1H), 2.07 (d of part of an AB system, J_{AB} = 14 Hz, J = 8 Hz, 1H), 1.90 (d, J = 1.5 Hz, 3H), 1.82−1.69 (m, 2H), 1.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 216.45, 147.12, 140.55, 134.03, 120.54, 118.17, 115.11, 54.32, 47.31, 46.46, 43.16, 42.05, 26.60, 21.33, 19.46. HRMS (ESI): found 216.1503 (M^+); calcd for $C_{15}H_{20}O$ 216.1508 (M^+).

3,3-Dimethyl-7-*endo*-vinyl-bicyclo[2.2.2]oct-5-en-2-one (27). Sodium hydride (0.3 g of 60% w/w suspension in oil, excess) was placed in a dry two-necked flask and washed with dry petroleum ether, and tetrahydrofuran (2 mL) was added. A solution of ketone **18** (0.3 g, 1.85 mmol) in tetrahydrofuran (6 mL) was added slowly to the reaction mixture, and it was refluxed for 1 h. Methyl iodide (1.5 mL, excess) was then added to the reaction mixture, and the reaction mixture was further refluxed for 8 h. It was then worked up as described above, and the product thus obtained was chromatographed on silica gel. Elution with petroleum ether/ethyl acetate (99:1) furnished the alkylated product **27** (0.257 g, 79%) as a colorless liquid: IR (neat) ν_{max} 1724 cm^{-1}; UV (MeOH) λ_{max} 296.2 (w), 217.8 (s) nm; ^1H NMR (400 MHz, $CDCl_3$) δ 6.56 (superimposed dd, J_1 = J_2 = 7.2 Hz, 1H), 6.02 (superimposed dd, J_1 = J_2 = 7.2 Hz, 1H), 5.61−5.51 (m, 1H), 4.99 (d, J = 17.2 Hz, 1H), 4.92 (d, J = 10 Hz, 1H), 3.08 (d, J = 6 Hz, 1H), 2.69 (m, 1H), 2.58 (br s, 1H), 2.26 (m, 1H), 1.19 (ddd, J_1 = 13 Hz, J_2 = 5.8 Hz, J_3 = 2 Hz, 1H), 1.11 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 216.38, 141.09, 139.21, 124.21, 114.22, 55.00, 44.40, 43.31, 38.47, 28.66, 27.60, 24.45; mass (*m/z*) 176 (M^+). HRMS (ESI): found 177.1281 [M^+ + H]; calcd for $C_{12}H_{17}O$ 177.1279 [M^+ + H].

3-Methyl-3-prop-2-ynyl-7-*endo*-vinyl-bicyclo[2.2.2]oct-5-en-2-one (28). A solution of ketone **18** (0.6 g, 3.70 mmol) in tetrahydrofuran (10 mL) was added to a suspension of sodium hydride (0.5 g of 60% w/w suspension in oil, excess, washed with dry pentane) in THF (5 mL), and the reaction mixture was refluxed for 1 h. Propargyl bromide (0.6 mL, excess) was then added to the reaction mixture, and the reaction mixture was further refluxed for 10 h. The reaction mixture was worked up as described previously, and the resulting product was chromatographed on silica gel. Elution with petroleum ether/ethyl acetate, (98:2) gave propargylated products **28** and **29** as a mixture of syn/anti isomers (0.44 g, 60%). Repeated chromatography of the mixture on silica gel (100−200 mesh) furnished the major syn isomer **28** as a colorless liquid: IR (neat) ν_{max} 1724 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.59 (superimposed dd, J_1 = J_2 = 7 Hz, 1H), 6.03 (superimposed dd, J_1 = J_2 = 7 Hz, 1H), 5.62−5.50 (m, 1H), 5.0 (d, J = 15.8 Hz, 1H), 4.93 (d, J = 9.7 Hz, 1H), 3.12 (d, J = 6.1 Hz, 1H), 3.0 (s with structure, 1H), 2.72 (m, 1H), 2.39 (d of a part of an AB system, J_1 = 17 Hz, J_2 = 2.4 Hz, 1H), 2.24 (m, 1H), 2.14 (part of an AB system, J_{AB} = 17 Hz, 1H), 2.05 (d, J = 2.4 Hz, 1H), 1.23 (s merged with m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.96, 140.69, 138.72, 124.80, 114.398, 80.56, 71.33, 54.76, 45.24, 40.52, 38.51, 29.01, 28.26, 21.11. HRMS (EI): found 200.1201 (M^+); calcd for $C_{14}H_{16}O$ 200.1195 (M^+).

3-Methyl-3-(2-oxo-propyl)-7-*endo*-vinyl-bicyclo[2.2.2]-oct-5-en-2-one (30). A solution of the syn/anti mixture **28** and **29** (0.120 g, 0.6 mmol) in methanol (6 mL) was added to a suspension of HgO (0.024 g) in 4% H_2SO_4 (2 mL), and the reaction mixture was heated at 60 °C for 12 h. The reaction mixture was then poured into water (5 mL) and extracted with ethyl acetate (3 × 10 mL). The organic layer was washed with brine (10 mL) and dried. The solvent was removed under reduced pressure, and the residue was chromatographed on silica gel. Elution with petroleum ether/ethyl acetate (90:10) gave a mixture of the syn/anti isomers (0.105 g, 81%) in the ratio of 85:15. This mixture was further subjected to column chromatography on silver nitrate-impregnated silica gel. Elution with petroleum ether/ethyl acetate (94:6) first gave a mixture of the syn/anti isomers. Continued elution with the same solvent furnished the desired syn isomer **30** (0.085 g, 66%) as a colorless liquid: IR (neat) ν_{max} 1715 cm^{-1}; UV (MeOH) λ_{max} 296.6 (w), 214.4 (s) nm; ^1H NMR (300 MHz, $CDCl_3$ + CCl_4) δ 6.50 (superimposed dd, J_1 = J_2 = 7.2 Hz, 1H), 6.04 (superimposed dd, J_1 = J_2 = 7.2 Hz, 1H), 5.58−5.46 (m, 1H), 4.98 (d, J = 16.5 Hz, 1H), and 4.92 (d, J = 10.8 Hz, 1H), 3.28 (m, 1H), 3.08 (d, J = 6.6 Hz, 1H), 2.65 (part of AB system merged with a multiplet, J_{AB} = 16.5 Hz, 2H), 2.38 (part of an AB system, J_{AB} = 16.5, 1H), 2.25−2.22 (m, 1H), 2.06 (s, 3H), 1.25−1.20 (m merged to a singlet, 4H); ^{13}C NMR (75 MHz, $CDCl_3$ + CCl_4) δ 213.50, 206.23, 140.73, 138.93, 125.13, 114.49, 54.50, 50.29, 45.30, 40.02, 38.38, 31.89, 28.33, and 20.94. HRMS (ESI): found 219.1372 [M^+ + H]; calcd for $C_{14}H_{19}O_2$ 219.1380 [M^+ + H].

1-Chloromethyl-1-hydroxy-4a,5,8,8a-tetrahydro-1*H*-naphthalen-2-one (13a). The adduct **12a** (0.5 g, 2.35 mmol) was heated in *o*-dichlorobenzene (8 mL) at 170 °C for 12 h. The reaction mixture was chromatographed on silica gel. Elution with petroleum ether first gave *o*-dichlorobenzene. Further elution with petroleum ether/ethyl acetate (97:3) furnished the enone **13a** (0.495 g, ∼100%) as a colorless liquid: IR (neat) ν_{max} 3480, 1682 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$ + CCl_4) δ 6.73 (m of d, J = 10 Hz, 1H), 6.06 (dd, J_1 = 10 Hz, J_2 = 3.7 Hz, 1H), 5.69 (m, 2H), 3.80 (part of an AB system, J_{AB} = 11.7 Hz, 1H), 3.71 (s, 1H), 3.57 (part of an AB system, J_{AB} = 11.7 Hz, 1H), 3.03 (br m, 1H), 2.74−2.73 (m, 1H), 2.52 (d with structure, J = 17.7 Hz, 1H), 2.32−2.16 (m, 2H), 1.70−1.61 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$ + CCl_4) δ 198.4, 156.2, 126.9, 126.7, 124.3, 78.6, 48.7, 39.1, 33.5, 30.2, 21.7. HRMS (EI): found 212.0596 (M^+); calcd for $C_{11}H_{13}O_2Cl$ 212.0599 (M^+).

1-Chloromethyl-1-hydroxy-4a-methyl-4a,5,8,8a-tetrahydro-1*H*-naphthalen-2-one (13b). A solution of the adduct **12b** (0.532 g, 2.35 mmol) in *o*-dichlorobenzene (8 mL) was heated at 180 °C for 25 h, after which the reaction mixture was chromatographed on silica gel. Elution with petroleum ether followed by petroleum ether/ethyl acetate (98:2) gave the *o*-dichlorobenzene and unreacted starting material (0.106 g, 20%), respectively. Further elution with petroleum ether/ethyl acetate (97:3) furnished the enone **13b** (0.399 g, 75%) as a solid which was recrystallized from petroleum ether/ethyl acetate (97:3): mp 96−97 °C; IR (film) ν_{max} 3478, 1680 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$ + CCl_4) δ 6.87 (d, J = 10 Hz, 1H), 6.02 (d, J = 10 Hz, 1H), 5.75 (m, 1H), 5.70 (m, 1H), 3.89 (part of an AB system, J_{AB} = 10.5 Hz, 1H), 3.48 (part of an AB system, J_{AB} = 10.5 Hz, 1H), 2.78 (br m, 1H), 2.47−2.37 (m, 2H), 2.22 (superimposed dd, J_1 = J_2 = 14.7 Hz, 2H), 1.97 (d with structure, J = 14.7 Hz, 1H), 1.25 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$ + CCl_4) δ 196.21, 160.82, 125.61, 125.30, 124.03, 45.45, 38.84, 36.43, 34.48, 27.33, 22.43. Analysis found: C, 63.64; H, 6.95%. Calcd for $C_{12}H_{15}O_2Cl$: C, 63.57; H, 6.62%. Mass (*m/z*) 226 (M^+).

1-Chloromethyl-1-hydroxy-3,4a-dimethyl-4a,5,8,8a-tetrahydro-1*H*-naphthalen-2-one (13c). Heating a solution of the adduct **12c** (0.565 g, 2.35 mmol) in *o*-dichlorobenzene (8 mL) at 165 °C for 8 h followed by chromatography [petroleum ether/ethyl acetate (98:2)] furnished the enone **13c** (0.559 g, ∼100%) as a solid that was recrystallized from petroleum ether/ethyl acetate (98:2): mp 57−59 °C; IR (film) ν_{max} 3468, 1669 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.66 (s, 1H), 5.79 (m, 1H), 5.75 (m, 1H), 3.92 (part of an AB system, J_{AB} = 10.8 Hz, 1H), 3.53 (part of an AB system, J_{AB} = 10.8 Hz, 1H), 2.80 (m,

1H), 2.42 (s merged with m, 2H), 2.20 (m, 1H), 2.15 (s, 1H), 2.0 (m, 1H), 1.84 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.63, 156.75, 131.83, 125.67, 124.57, 46.29, 38.82, 36.68, 33.75, 27.50, 22.45, 15.84. HRMS (EI): found 240.0905 (M^+); calcd for $C_{13}H_{17}O_2Cl$ 240.0917 (M^+).

1-Hydroxy-1,3-dimethyl-4a,5,8,8a-tetrahydro-1*H*-naphthalen-2-one (16). A solution of the adduct **15** (0.450 g, 2.35 mmol) in *o*-dichlorobenzene (8 mL) was heated at 140 °C for 8 h, after which it was chromatographed on silica gel. Elution with petroleum ether first gave *o*-dichlorobenzene. Further elution with petroleum ether/ethyl acetate (98:2) furnished the enone **16** (0.445 g, ~100%) as a colorless liquid: IR (neat) ν_{max} 3500, 1673 cm^{-1}; ^{1}H NMR(300 MHz, $CDCl_3$) δ 6.41 (d, J = 1.5 Hz, 1H), 5.74−5.63 (m, 2H), 3.63 (s, 1H), 2.99 (m, 1H), 2.42−2.12 (clusters of m, 4H), 1.81 (s with structure, 3H), 1.63−1.51 (m, 1H), 1.38 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.20, 150.54, 132.69, 126.86, 124.53, 76.58, 43.07, 32.90, 30.66, 24.32, 22.28, 15.59. HRMS (EI): found 192.1140 (M^+); calcd for $C_{12}H_{16}O_2$ 192.1150 (M^+).

4a-Methyl-4a,5,8,8a-tetrahydro-1*H*-naphthalen-2-one (31). A solution of the compound **24** (0.1 g, 0.61 mmol) in diphenyl ether (5 mL) was heated at 195 °C in a sealed tube for 10 h, after which it was chromatographed on silica gel. Elution with petroleum ether first gave diphenyl ether. Further elution with petroleum ether/ethyl acetate (98:2) furnished the rearranged product **31** (0.045 g, 45%) as a colorless liquid: IR (neat) ν_{max} 1680 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.81 (d, J = 10 Hz, 1H), 5.87 (d, J = 10 Hz, 1H), 5.74−5.62 (m, 2H), 2.44−2.31 (m, 3H), 2.13−1.94 (m, 3H), 1.87−1.79 (m, 1H), 1.17 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.61, 161.28, 127.54, 124.69, 124.38, 41.32, 37.45, 34.60, 34.43, 28.56, 25.66. HRMS (ESI): found 163.1130 [M^+ + H]; calcd for $C_{11}H_{15}O$ 163.1123 [M^+ + H].

1-Allyl-1-methyl-4a,5,8,8a-tetrahydro-1*H*-naphthalen-2-one (32). A solution of the compound **25** (0.200 g, 0.99 mmol) in *o*-dichlorobenzene (5 mL) was refluxed at 180 °C for 30 h, after which the reaction mixture was chromatographed on silica gel. Elution with petroleum ether followed by petroleum ether/ethyl acetate (98:2) gave *o*-dichlorobenzene and some unreacted starting material **25** (0.02 g, 10%), respectively. Further elution with petroleum ether/ethyl acetate (96:4) furnished the rearranged product **32** (0.09 g, 45%) as a colorless liquid: IR (neat) ν_{max} 1674 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$ + CCl_4) δ 6.51 (d with structure, J = 9.9 Hz, 1H), 5.87 (dd, J_1 = 9.9 Hz, J_2 = 2.7 Hz, 1H), 5.82−5.71 (m, 2H), 5.71−5.59 (m, 1H), 5.08 (m, 2H), 3.09 (s with structure, 1H), 2.45−2.37 (m, 2H), 2.17−2.04 (clusters of m, 4H), 1.78 (m, 1H), 1.06 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$ + CCl_4) δ 202.26, 152.20, 133.75, 129.08, 127.32, 124.95, 118.32, 49.15, 40.30, 39.62, 31.20, 30.76, 23.88, 18.62. HRMS (EI): found 202.1349 (M^+); calcd for $C_{14}H_{18}O$ 202.1352 (M^+).

1-Allyl-1,4a-dimethyl-4a,5,8,8a-tetrahydro-1*H*-naphthalen-2-one (33). A solution of the compound **26** (0.08 g, 0.37 mmol) in diphenyl ether (4 mL) was heated at 195 °C in a sealed tube for 10 h, after which it was brought to room temperature and chromatographed on silica gel. Elution with petroleum ether first gave diphenyl ether. Further elution with petroleum ether/ethyl acetate (98:2) furnished the rearranged product **33** (0.036 g, 45%) as a colorless liquid: IR (neat) ν_{max} 1670 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 (d, J = 10 Hz, 1H), 5.89 (d, J = 10 Hz, 1H), 5.80−5.74 (m, 1H), 5.70−5.63 (m, 1H), 5.60−5.48 (m, 1H), 5.20−5.00 (m, 2H), 2.80 (dd, J_1 = 13 Hz, J_2 = 5.5 Hz, 1H), 2.30−2.20 (m, 1H), 2.20−2.02 (overlapped m, 4H), 1.99−1.90 (m, 1H), 1.15 (s, 3H), 1.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.90, 159.16, 135.09, 126.03, 125.78, 123.25, 117.54, 48.88, 41.83, 38.71, 34.89, 34.27, 28.82, 22.20, 20.71. HRMS (ESI): found 217.1574 (M^+ + H); calcd for $C_{15}H_{21}O$ 217.1589 (M^+ + H).

1-Methyl-1-prop-2-ynyl-4a,5,8,8a-tetrahydro-1*H*-naphthalen-2-one (34). A solution of the compound **28** (0.075 g, 0.37 mmol) in diphenyl ether (3 mL) was heated at 195 °C for 10 h, after which it was chromatographed on silica gel. Elution with petroleum ether first gave diphenyl ether. Further elution with petroleum ether/ethyl acetate (97:3) furnished the rearranged product **34** (0.038 g, 50%) as a colorless liquid: IR (neat) ν_{max} 1673 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.57 (d, J = 9.9 Hz, 1H), 5.87 (d with structure, J = 9.9 Hz, 1H), 5.71 (m, 1H), 5.65 (m, 1H), 3.06 (s, 1H), 2.60 (part of an AB system, J_{AB} = 17.4 Hz, 1H), 2.43 (m, 2H), 2.13 (part of an AB system partly merged with a multiplet, J_{AB} = 17.4 Hz, 3H), 1.99 (s, 1H), 1.76 (m, 1H), 1.19 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$ + CCl_4) δ 201.48, 153.00, 128.70, 127.09, 125.03, 80.13, 71.44, 48.61, 38.84, 31.43, 30.69, 26.27, 23.55, 18.72. HRMS (ESI): found 223.1092 [M^+ + Na]; calcd for $C_{14}H_{16}ONa$ 223.1093 [M^+ + Na].

1-Methyl-1-(2-oxo-propyl)-4a,5,8,8a-tetrahydro-1*H*-naphthalen-2-one (35). A solution of the diketone **30** (0.16 g, 0.73 mmol) in *o*-dichlorobenzene (4 mL) was refluxed at 180 °C for 30 h. Chromatography of the reaction mixture on silica gel and elution with petroleum ether first gave *o*-dichlorobenzene. Further elution with petroleum ether/ethyl acetate (94:6) gave some unreacted starting material (0.012 g, 8%). Continued elution with petroleum ether/ethyl acetate (92:8) furnished the rearranged product **35** (0.105 g, 66%) as a solid, which was recrystallized from petroleum ether/ethyl acetate (94:6): mp 73−74 °C; IR (film) ν_{max} 1713, 1675 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.65 (m of d, J = 10.2 Hz, 1H), 5.95 (dd, J_1 = 10.2 Hz, J_2 = 2.5 Hz, 1H), 5.80−5.72 (m, 1H), 5.68−5.6 (m, 1H), 3.02 (br m, 1H), 2.74 (part of an AB system, J_{AB} = 15 Hz, 1H), 2.62−2.40 (m merged with a part of an AB system, J_{AB} = 15 Hz, total 3H), 2.22−2.04 (s merged with a m, total 5H), 1.78−1.60 (m merged with the signal due to H_2O present in $CDCl_3$, 1H), 1.2 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.82, 202.41, 153.82, 128.60, 126.78, 125.10, 48.92, 47.68, 37.96, 32.37, 31.99, 30.47, 23.73, 18.72. Analysis found: C, 76.84; H, 8.33%. Calcd for $C_{14}H_{18}O_2$: C, 77.06; H, 8.25%. Mass (m/z) 218 (M^+).

Crystal data: $C_{14}H_{18}O_2$, M = 218.28, $\bar{P}1$ Triclinic, Z = 2, λ = 0.70930°, a = 6.6080(11) Å, b = 8.3730(5) Å, c = 12.3070(8) Å, U = 603.00(11) Å^3, T = 293(2) K, D_c = 1.198 Mg m^{-3}, μ = 0.078 mm^{-1}, $F(000)$ = 236, size = 0.30 mm × 0.20 mm × 0.15 mm. Reflections collected/unique = 1572/1572 [R(int) = 0.0000]. Final R indices [$I > 2\sigma(I)$]: R1 = 0.0523, wR2 = 0.1167, R indices (all data): R1 = 0.0969, wR2 = 0.1392.

2,6-Dimethyl-2-hydroxy-7-vinyl-tricyclo[3.3.0.0^{4,6}]octa-3-one (36). A solution of **15** (0.085 g, 0.44 mmol) in degassed acetone (110 mL, solvent as well as sensitizer) was irradiated with a mercury vapor lamp (125 W) in a Pyrex immersion well for 1 h under nitrogen. Acetone was removed under vacuum, and the residue was chromatographed. Elution with petroleum ether/ethyl acetate (97:3) gave some unreacted starting material (0.010 g, 12%). Further elution with petroleum ether/ethyl acetate (96:4) yielded the photoproduct **36** (0.029 g, 35%) as a solid: mp 63−64 °C; IR (film) ν_{max} 3470, 1722 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 (m, 1H), 5.0 (m, 2H), 2.65 (superimposed dd, J_1 = J_2 = 5.8 Hz, 1H), 2.4 (m, 2H), 2.2 (dd, J_1 = 12.6 Hz, J_2 = 6.2 Hz, 1H), 1.9 (d, J = 4.8 Hz, 1H), 1.75 (m, 2H), 1.30 (s, 3H), 1.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.75, 139.67, 115.90, 81.37, 47.96, 46.71, 43.37, 39.84, 39.01, 27.10, 19.65. HRMS (EI): found 192.1150 (M^+); calcd for $C_{12}H_{16}O_2$ 192.11502 (M^+).

2-Allyl-2-methyl-7-vinyl-tricyclo[3.3.0.0^{4,6}]octa-3-one (37). A solution of **25** (0.080 g, 0.39 mmol) in degassed acetone (110 mL, solvent as well as sensitizer) was irradiated as described above for 1.5 h. Acetone was removed under vacuum, and the residue was chromatographed. Elution with petroleum ether/ethyl acetate (99:1) gave some unreacted starting material (0.014 g, 18%). Further elution with petroleum ether/ethyl acetate (98:2) afforded the product **37** (0.036 g, 45%) as a colorless liquid: IR (neat) ν_{max} 1724 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$ + CCl_4) δ 5.84−5.64 (m, 2H), 5.10−4.93 (m, 4H), 2.63 (m, 1H), 2.57 (m, 1H), 2.33 (m, 1H), 2.11 (d, J = 7.2 Hz, 2H), 2.03−1.98 (m, 1H), 1.88−1.75 (m, 3H), 0.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$ + CCl_4) δ 216.72, 141.07, 133.41, 118.54,

114.46, 54.76, 47.55, 44.94, 43.18, 42.64, 35.92, 34.36, 15.35. HRMS (EI): found 202.1361 (M^+); calcd for $C_{14}H_{18}O$ 202.1352 (M^+).

2-Allyl-2,5-dimethyl-7-vinyl-tricyclo[3.3.0.0^{4,6}]octa-3-one (38). A solution of **26** (0.080 g, 0.37 mmol) in degassed acetone (110 mL, solvent as well as sensitizer) was irradiated as described above. Removal of solvent followed by chromatography [petroleum ether/ethyl acetate (99:1)] first gave some unreacted starting material (0.009 g, 12%). Further elution with petroleum ether/ethyl acetate (98:2) afforded the product **38** (0.04 g, 50%) as a colorless liquid: IR (neat) ν_{max} 1718 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86−5.68 (m, 2H), 5.17−4.93 (m, 4H), 2.40−2.33 (m partially merged with d, 1H), 2.30 (d, J = 6.1 Hz, 1H), 2.16 (m merged with d, J = 7.3 Hz, 2H), 1.96 (d, J = 9.7 Hz, 1H), 1.90−1.76 (m, 2H), 1.50 (s merged with m, total 4H), 0.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 218.90, 140.10, 133.47, 118.82, 115.60, 56.21, 52.94, 45.24, 44.98, 44.94, 43.08, 41.63, 38.68, 18.92, 16.73. HRMS (EI): found 216.1507 (M^+); calcd for $C_{15}H_{20}O$ 216.1509 (M^+).

2,2-Dimethyl-7-vinyl-tricyclo[3.3.0.0^{4,6}]octa-3-one (39). A solution of **27** (0.070 g, 0.39 mmol) in degassed acetone (110 mL, solvent as well as sensitizer) was irradiated as described above (1.25 h). Removal of solvent followed by chromatography [petroleum ether/ethyl acetate (99:1)] first gave some unreacted starting material (0.01 g, 15%). Further elution with petroleum ether/ethyl acetate (98:2) gave the photoproduct **39** (0.024 g, 35%) as a colorless liquid: IR (neat) ν_{max} 1724 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.8 (m, 1H), 5.0 (d, J = 17.2 Hz, 1H), 4.9 (d, J = 10 Hz, 1H), 2.7 (m, 1H), 2.44 (superimposed dd, $J_1 = J_2$ = 5.6 Hz, 1H), 2.35 (m, 1H), 2.05 (m, 1H), 1.9 (m, 1H), 1.85−1.70 (m, 2H), 1.09 (s, 3H), 0.9 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 219.33, 141.34, 114.33, 51.62, 50.46, 42.81, 35.90, 35.59, 34.32, 28.73, 17.38. HRMS (ESI): found 177.1281 [M^+ + H]; calcd for $C_{12}H_{17}O$ 177.1279 [M^+ + H].

2-Acetonyl-2-methyl-7-vinyl-tricyclo[3.3.0.0^{4,6}]octa-3-one (40). A solution of **30** (0.075 g, 0.34 mmol) in degassed acetone (110 mL, solvent as well as sensitizer) was irradiated as described above. Acetone was removed under vacuum, and the residue was chromatographed. Elution with petroleum ether/ethyl acetate (98:2) first gave some unreacted starting material (0.011 g, 15%). Further elution with petroleum ether/ethyl acetate (97:3) furnished the product **40** (0.03 g, 40%) as a colorless liquid: IR (neat) ν_{max} 1717 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.83−5.77 (m, 1H), 5.01 (d, J = 16.8 Hz, 1H), 4.96 (d, J = 10.8 Hz, 1H), 2.99 (m, 1H), 2.66 (m, 1H), 2.52 (part of AB system, J_{AB} = 15.6 Hz, 1H), 2.39 (part of AB system, J_{AB} = 15.6 Hz, 1H), 2.33 (m, 1H), 2.12 (s, 3H), 2.05 (m, 1H), 1.88 (m, 1H), 1.85−1.78 (m, 2H), and 0.95 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 217.35, 206.40, 140.97, 114.26, 54.15, 50.91, 46.44, 42.94, 42.46, 36.20, 35.89, 34.38, 32.04, 15.04. HRMS (ESI): found 219.1371 (M^+ + H); calcd for $C_{14}H_{19}O_2$ 219.1380 (M^+ + H).

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Supporting Information Available: General procedure for the preparation of silver nitrate-impregnated silica gel, ^{13}C NMR spectra of compounds **12a**−**c**, **13a**−**c**, **15**-**17**, **19**, **20**, **22**, **24**−**28**, **30**−**40**, ^{1}H NMR spectra of compounds **18**, **21**, **23**, and crystallographic data for compound **35**. This material is available free of charge via the Internet at http://pubs.acs.org.

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