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Unusual endoperoxide isomerizations: a convenient entry into 2-vinyl-2-cyclopentenones from saturated fulvene endoperoxides[1]

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Abstract

An unusual peroxide base promoted isomerization was uncovered. Saturated endoperoxides derived from fulvenes give rise to 2-vinyl-2-cyclopentenones upon treatment with DBU in CH_2Cl_2 in a one-pot reaction. This methodology was applied to a convenient synthesis of dihydrojasmone. Moreover, functional groups placed on the side chain at C-6 participate in the base catalyzed isomerizations via conjugate attack at the enone moiety to give 2-cyclopentenones carrying oxygen heterocycles at C2.

1. Introduction

Endoperoxides, readily available in most cases from 1,3-dienes by way of a Diels-Alder reaction with singlet oxygen[1] are sensitive to thermal, photochemical, and reductive conditions.[2] In particular, base-catalyzed rearrangements, also known as Kornblum- De la Mare reactions are well-known.[3] Treatment of bridged bicyclic endoperoxides typically result in the formation of hydroxy ketones. The mechanism of these reactions have been thoroughly studied. In particular, the base-catalyzed disproportionation of 2,3-dioxabicyclo[2.2.1]heptane (**1**) to 3-hydroyxcyclopentanone (**3**) and levulinaldehyde (**5**) by amine catalysis has been reported by Salomon and Zagorski in an elegant study.[4] Isotope labeling studies show that the most likely mechanism for the disproportionation involves initial abstraction of the bridgehead proton in the rate-determining step (Scheme 1).

Previously, we studied the singlet oxygenations of fulvenes and low-temperature diazene reduction of the unstable endoperoxides[5] and reported on some novel mechanisms encountered during the thermal isomerizations of saturated fulvene endoperoxide, e.g., **23**, **32**, **42** and **46**.[6, 7] We have explored the synthetic utility of the allene oxides/cyclopropanones[8] to prepare functionalized cyclopentenones derived from saturated fulvene endoperoxides, e.g., **6**→**7**→**8**[9] and also disclosed the first aliphatic examples of [3,4]-sigmatropic shifts on suitably substituted cyclopropanones derived from the corresponding endoperoxides by thermolysis (**9**→**10**→**11**) (Scheme 2) .[10]

[1]This paper is dedicated to my teacher, friend and associate, Professor Armin de Meijere, on the occasion of his choice

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2. Results and Discussion

We here report a new and synthetically useful facet of base-catalyzed endoperoxide isomerizations that we observed on saturated fulvene endoperoxides. The outcome of these reactions has proved particular to the nature of the base. Thus, treatment of fulvene endoperoxides with triethylamine at 0°-r.t. in CH_2Cl_2 results in the formation of the corresponding hydroxyketone as expected.[5] However, the use of the stronger base, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), gave 2-vinyl-2-cyclopentenones, e.g., **14**, in high yields (Scheme 3).

The mechanism presumably commences with initial proton abstraction at the bridgehead. However, the resulting hydroxyketone is prone to further proton abstraction at the allylic position. The timing of the proton elimination is subject to discussion and further studies, and two alternative mechanisms may be advanced for the dehydration step. One possible dehydration pathway would involve deprotonation of the γ-H, enolate formation, followed by hydroxide elimination (presumably via initial protonation by BH^+), an E1Cb mechanism (Scheme 4). However, the fact that the reaction proceeds in CH_2Cl_2, an aprotic solvent that does not encourage ionic species, points to a concerted 1,4-elimination (E2). Regardless of the mechanism of the dehydration step, the resulting compounds from this tandem isomerization-dehydration process are 2-vinylcyclopentenones, a substance class for which there are very few synthetic methods.[11-15] The ease with which the 2-vinylcyclopentenones can be constructed from the readily available fulvenes in a one-pot reaction makes this approach particularly attractive. Table 1 depicts some selected systems we have prepared so far.

In one case, where the starting fulvene carried a 6-vinyl group, the reaction with DBU led to a mixture of the expected hydrox ketone **47** (50%) and a mixture of the two isomers **48** and **49** (9%). It appears that the protons at the remote methyl group are just acidic enough to permit abstraction, resulting in the formation of a highly conjugated system (Scheme 5).

In another example, we subjected the hydroxy ketone **52**, obtained from **51** by treatment with DBU to reaction with catalytic trifluoroacetic acid, in hopes of affecting dehydration. The product from this reaction was the alcohol **53**, obviously stemming from a process involving dehydration, double bond shift and rehydration.

The presence of functionality on side chain of the exocyclic double bond was tested in the case of **37** (entry 6). The treatment of the endoperoxide **35** with DBU delivered a 3:2 mixture of the dehydration products **36** and **37** (Scheme 7). Obviously the hydroxyl group in the side chain did not suffer elimination. The two products were identified in the mixture by means of their ^1H and ^{13}C NMR spectra.

When the hydroxyl group was placed at C-3 on the side chain of the exocyclic double bond in the starting fulvene (entry 7), treatment of the saturated endoperoxides **42** with DBU furnished the tetrahydrofuran derivative **40** exclusively. Compound **40** appears to be a suitable precursor of the hypotensive drug oudenone,[16] and this approach is currently being explored (Scheme 8).

Finally, the fulvene endoperoxide-DBU isomerization-dehydration methodology was implemented in a short synthesis of the naturally occurring fragrant compound dihydrojasmone.[17] Starting with fulvene **22** (entry 2), readily available from valeraldehyde in 77% yield was photooxygenated in CH_2Cl_2 at −78 °C, followed by diazene reduction, generated in situ from azodicarboxylate and acetic acid at low temperatures, endoperoxide **23** was obtained which without isolation was treated with DBU to give the cyclopentenone **24** in 83% yield. The conversion of **24** to dihydrojasmone was achieved by the well-documented protocol [18, 19] involving methyllithium addition to the carbonyl group and

subsequent treatment with PCC in CH_2Cl_2 to furnish **56** in 50% overall yield from **24** (Scheme 9).

Compound **30** (entry 4) can also be obtained in this manner in a very short sequence from the readily available fulvene. The former represents an important precursor of certain prostaglandins and related compounds. These aspects are currently being explored.

It is noteworthy, that the respective unsaturated fulvene endoperoxides do not suffer dehydration after base-catalyzed isomerization with DBU, presumably owing to the unstable nature of the products (cyclopentadienones). Endoperoxide **57**, derived from 6,6-dimethylfulvene for instance, gave a mixture of the hydroxyketones **58** and **59** in a ratio of 5:1 (Scheme 10).[20]

Compound **58** is the expected primary isomerization product, however, **59** is a secondary product that most likely forms by further isomerization of **58** by a mechanism outlined in Scheme 11.

It is interesting to note, that the base-catalyzed decomposition of unsaturated fulvene endoperoxides appears to be entirely analogous to those of the saturated counterparts, except for the dehydration step in the latter. Intermediates **16** (Scheme 2) and **61** (Scheme 11) differ only in the nature of the leaving groups (alcohol, versus epoxide). The epoxide suffers ring opening to the allyllic alcohol, whereas the hydroxyl group is eliminated in **16**.

3. Conclusion

In summary, we have uncovered a new useful facet of base-catalyzed endoperoxide rearrangements that result in a Kornblum-De la Mare isomerization followed by dehydration to give 2-vinyl-2-cyclopentenones which are highly desirable synthetic intermediates. In cases where there are oxygen nucleophiles on the side chain, conjugate attack at the β-carbon of the exocyclic double bond occurs to give 2-cyclopentenones that carry a heterocycle at C2. Implementation of this methodology in the synthesis of a variety of targets is underway.

4. Experimental

^1H and ^{13}C NMR spectra were recorded on a General Electric QE-Plus 300 MHz and Bruker Avance DRX 300 MHz spectrometers, using $CDCl_3$ as solvent and TMS as internal standard, unless specified otherwise. IR spectra were obtained on a Nicolet Avance 370 DTGS FT-IR spectrometer. Column chromatographic separations were carried out with Davison 6–200 Mesh silica gel. For preparative TLC, Merck silica gel (grade 60 PF254) was used. All reactions were conducted under an atmosphere of dry nitrogen or argon. Fulvenes were stored under argon in the freezer at −30 °C. Non-deuterated solvents were dried and distilled prior to use. All fulvenes in this study were prepared according to published procedures.[20, 21] Signal multiplicities in the NMR spectra are reported as follows: s-singlet, d-doublet, t-triplet, dd-doublet of doublets, dt-doublet of triplets, q-quartet, quin-quintuplet, sext-sextet, m-multiplet, br-broad.

Spectroscopic data for the synthesis of those fulvenes not found in literature are described below.

Fulvene **25** was prepared from **38** (*vide infra*) by stirring with acetic anhydride in the presence of pyridine for 48 hours followed by aqueous work-up in 86% yield. ^1H NMR ($CDCl_3$, TMS): δ 6.55 (m, 1H, 6.46 (m, 2H), 6.37 (t, J= 8.0 Hz, 1H), 6.12 (dt, 1H), 4.95 (m, 1H), 2.55 (m, 2H), 2.02 (s, 3H), 1.8 (m, 2H), 1.55 (m, 2H), 1.33 (m, 2H), 0.9 (t, J= 7.2 Hz, 3H); ^{13}C NMR

($CDCl_3$, TMS): δ 170.8, 146.2, 141.5, 133.4, 131.1, 125.6, 118.9, 73.5, 36.3, 33.9, 27.1, 21.2, 18.7, 14.0 ppm; *Anal*. Calcd for $C_{14}H_{20}O_2$: C 76.33; H 9.15. Found: C 76.28; H 9.13.

Fulvene **28** (78%). ^{1}H NMR ($CDCl_3$, TMS): δ 6.6-6.4 (m, 4H), 6.2 (m, 1H), 4.1 (q, J= 7.5 Hz, 2 H), 2.54 (q, J= 7.5 Hz, 2H), 2.30 (t, J= 7.2 Hz, 2H), 1.65 (m, 2H), 1.50 (m, 2H), 1.4 (m, 2H), 1.25 (t, J= 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, TMS): δ 173.7, 146.1, 142.8, 133.1, 130.8, 125.6, 119.1, 60.2, 34.2, 30.9, 29.1, 28.8, 24.8, 14.3 ppm; *Anal*. Calcd for $C_{14}H_{20}O_2$: C 76.33; H 9.15. Found: C 76.31; H 9.15.

Fulvene **38** (49% yield): ^{1}H NMR ($CDCl_3$, TMS): δ 6.53 (m, 2H), 6.45 (m, 1H), 6.40 (t, J= 7.5 Hz, 1H), 6.2 (m, 1H), 3.63 (m, 1H), 2.65 (q, J= 7.5 Hz, 2H), 1.67 (m, 2H), 1. 44 (m, 2H), 1.30 (m, 4H), 0.9 (t, J= 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, TMS): δ 146. 2, 142.6, 1332, 130.8, 125.6, 119.1, 71.3, 37.6, 36.9, 31.9, 27.5, 25.3, 22.7, 14.1 ppm. *Anal*. Calcd for $C_{12}H_{18}O$: C 80.85; H 10.18. Found: C 80.82; H 10.23.

Fulvene **50** (39% yield): ^{1}H NMR (($CDCl_3$, TMS): δ 675 (m, 2H), 6.5-6.2 (m, 5 H), 5.4 (m, 2H), 2.3 (m, 2H), 2.2 (m, 2H), 2.05 (m, 2H), 1.0 (t, J= 7.5 Hz, 3H) ppm. *Anal*. Calcd for $C_{14}H_{18}$: C 90.26; H 9.74. Found: C 90.25; H 9.73.

Typical procedure for the preparation of the saturated endoperoxides

A solution of 6,6-dimethylfulvene (1.06 g, 10 mmol) and 5 mg of TPP (meso-tetraphenylporphyrin) in 200 mL CH_2Cl_2 was cooled to −78 in a flat Dewar containing dry ice-acteone. The mixture was stirred while being irradiated with a 250 W high-pressure sodium lamp for 3 hours under an oxygen atmosphere (a ballon filled with oxygen served this purpose). Then the lamp was turned off, 8.7 g (45 mmol) of potassium azodicarboxylate was added to the mixture in small portions, a pressure-equalizing dropping funnel fitted with a drying tube containing drierite was attached to the flask. A solution of 5.1 g (85 mmol) of acetic acid in 20 mL CH_2Cl_2 was added dropwise to the stirred slurry at −78 °C, and the mixture was slowly warmed up to −35 °C and stirred at this temperature for 1h. The mixture was then slowly warmed up to 0 °C for an additional 30 minutes. Then the salt was filtered by suction, the filtercake washed with cold CH_2Cl_2, while keeping the filter flask in an ice bath. The filtrate was washed with saturated aqueous $NaHCO_3$, dried over $MgSO_4$, filtered into a 250 mL round-bottomed flask. An aliquote was concentrated at reduced pressure (caution: saturated fulvene endoperoxides -when neat- are potentially explosive!), and dissolved in $CDCl_3$ for NMR spectroscopy. The product was practically pure according to its ^{1}H NMR spectrum.[5] For the DBU-catalyzed isomerizations, the endoperoxides need not be isolated.

Typical procedure for the DBU-catalyzed isomerizations

Three drops of DBU were added to a solution of endoperoxide **57**, obtained as described above, in 250 mL CH_2Cl_2 at 0 °C, and the solution was stirred at room temperature for 12–15 hours. Then the mixture was concentrated at reduced pressure, and the residue chromatographed on SiO_2, eluting with hexane/ether (3:1).

2-Isopropenyl-2-cyclopentenone (**21**): ^{1}H NMR ($CDCl_3$, TMS): δ 7.5 ((t, J= 3.0 Hz, 1H), 6. 07 (s, 1H), 5.16 (s, 1H), 2.60 (m, 2H), 2.47 (m, 2H), 1.94 (s, 3H); ^{13}C NMR ($CDCl_3$, TMS): δ 208.5, 158.5, 143.7, 135.1, 117.3, 36.7, 26.3, 22.0 ppm. FT-IR (film): 2973, 2927, 2855, 1710, 1453, 1387, 1262, 1177, 1038, 913, 802 cm^{-1}. *Anal*. Calcd for C8H10O: C 78.65; H 8.25. Found: C 78.61; H 8.24.

(*E*)-(2)-Pent-1-enyl-2-cyclopentenone (**24**): ^{1}H NMR ($CDCl_3$, TMS): δ 7.4 (t, J= 3.0 Hz, 1H), 6.6 (dt, J= 16.0, 7.0 Hz, 1H), 6.1 (d, J= 16.0 Hz, 1H), 2.6 (m, 2H), 2.45 (m, 2H), 2.1 (q, J= 7.0 Hz, 2H), 1.50 (sextet, J= 7.0 Hz, 2H), 0.94 (t, J= 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, TMS): δ

208.3, 156.5, 141.2, 135.7, 119.8, 35.57, 35.52, 26.2, 22.2, 13.7 ppm. Anal. Calcd for $C_{10}H_{14}O$: C 79.96; H 9.39. Found: C 79.95; H 9.38.

(*E*)-1-(5-Oxocylopent-1-enyl)hept-1-en-4yl acetate (**27**): ^{1}H NMR ($CDCl_3$, TMS): δ 7.3 (br s, 1H), 6.45 (dt, J= 15.6, 7.2 Hz, 1H), 6.0 (d, J= 15.6 Hz, 1H), 4.85 (quin, J= 6.0 Hz, 1H), 2.5 (m, 2H), 2.35 (m, 2H), 2.26 (m, 2H), 1.94 (s, 3H), 1.45 (m, 2H), 1.24 (m, 2H), 0.82 (t, J= 7.2, 3H); ^{13}C NMR ($CDCl_3$, TMS): δ 207.8, 170.4, 157.4, 157.2, 140.6, 129.9, 122.3, 72.9, 38.0, 35.3, 26.0, 20.1, 18.3, 13.7, 13.5 ppm. *Anal*. Calcd for $C_{14}H_{23}O_3$: C 70.20; H 9.69. Found: C 70. 17; H 9.66.

(E)-Ethyl 7-(5-oxocyclopent-1-enyl)hept-6-enoate (**30**): ^{1}H NMR ($CDCl_3$, TMS): δ 7.3 (t, J= 3Hz, 1H), 6.5 (dt, J= 16.0, 7.2 Hz, 1H), 4.0 (q, J= 7.2 Hz, 2H), 2.5 (m, 2H), 2.35 (m, 2H), 2.2 (m, 2H), 2.05 (m, 2H), 1.60 (m, 2H), 1.35 (m, 2H), 1.7 (t, J= 7.2 Hz, 3H);. ^{13} C NMR ($CDCl_3$, TMS): δ 208.4, 173.6, 157.0, 141.0, 135.1, 120.1, 60.2, 35.6, 34.1, 33.1, 28.4, 26.3, 24.5, 14.2 ppm. *Anal*. Calcd for $C_{14}H_{20}O_3$: C 70.20; H 9.69.Found: C 70.19; H 9.66.

2-Cycloheptenylcyclopent-2-one (**33**): ^{1}H NMR ($CDCl_3$, TMS): δ 7.4 (t, J= 3.0 Hz, 1H), 6.7 (t, J= 6.6 Hz, 1H), 2.56 (m, 2H), 2.45 (m, 2H), 2.37 (m, 2H), 2.25 (m, 2H), 1.8 (m, 2H), 1.55 (m, 4H); ^{13}C NMR ($CDCl_3$, TMS): δ 208.2, 155.5, 145.0, 135.8, 133, 36.0, 32.2, 31.1, 28.4, 26.4, 26.3, 25.3 ppm. *Anal*. Calcd for C_{12} $H_{16}O$: C 81.77; H 9.15. Found: C 81.77; H 9.14.

(*E*)-5-(3-Hydroxybutan-2-ylidene)cyclopent-2-enone (**36**): ^{1}H NMR ($CDCl_3$, TMS): δ 7.54 (m, 1H), 6.30 (m, 1H), 5.2 (br s, 1H, OH), 5.05 (q, J= 7.0 Hz, 1H), 3.2 (s, 2H), 1.32 (d, J= 7.0 Hz, 3H) ppm.

2-(3-Hydroxybut-1-en-2-yl)cyclopent-2-enone (**37**):): ^{1}H NMR ($CDCl_3$, TMS): δ 7.7 (t, J= 3.0 Hz, 1H), 5.65 (s, 1H), 5.4 (s, 1H), 4.5 (q, J= 6.6, 1H), 3.9 (br s, 1H, OH), 2.7 (m, 2H), 2.5 (m, 2H), 1.26 (d, J= 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, TMS, **36**+**37**): δ 209.1, 197.4, 160.7, 156.0, 156.4, 143.5, 142.5, 137.0, 128.5, 114.7, 68.9, 68.2, 35.2, 35.0, 26.3, 22.0, 21.0, 18.2 ppm.

2-(5-Propyltetrahydrofuran-2-yl)cyclopent-2-enone (**40,** both epimers): ^{1}H NMR ($CDCl_3$, TMS): δ 7. 5 (t, J= 2.7 Hz, 1H), 4.7 and 4.61 (m, 1H), 4.1 and 3.8 (m, 1H), 2.6 (m, 2H), 2.42 (m, 2H), 2.3-1.9 (m, 2H), 1.2–1.8 (m, 6 H), 0.9 (m, 3H); ^{13}C NMR ($CDCl_3$, TMS): δ 208.7, 208.5, 157.8, 157.5, 148.4, 148.2, 79.7, 79.4, 74.1, 73.8, 38.25, 38.16, 35.6, 32.0, 31.9, 31.4, 26.63, 26.6, 19.5, 14.3 ppm. *Anal*. Calcd for $C_{12}H_{18}O_2$: C 74.19; H 9.34. Found: C 74.14; H 933.

(*E*)-(2-Buta-1,3-dienyl)cyclopent-2-enone (**43**): ^{1}H NMR ($CDCl_3$, TMS): δ 7.5 (t, J= 3..0 Hz, 1H), 7.16 (dd, J= 17.0, 10.5 Hz, 1H), 6.2–6.5 (m, 2H), 5.35 (d, J= 17.0 Hz, 1H), 5.17 (d, J= 10.5 Hz, 1H), 2.6 (m, 2H), 2.46 (m, 2H); ^{13}C NMR ($CDCl_3$, TMS): δ 208.6, 159.0, 141.6, 138.0, 134.3, 123.0, 120.0, 36.3, 27.2 ppm. HRMS *m/z* calcd for $C_9H_{10}O$: 134.0732. Found: 134.0733.

(*5E*, 7*E*)-4-Oxonona-5,7-dienal (**44**): ^{1}H NMR ($CDCl_3$, TMS): δ 9.8 (s, 1H), 7.35 (m, 1H), 6.4 (t, J= 11.1 Hz, 1H), 6.1 (m, 1H), 5.9 (d, J= 11.1 Hz, 1H), 2.75 (m, AA'BB' pattern, 4H), 1.8 (dd, J= 6.6, 1.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, TMS): δ 201.3, 198.7, 144.2, 141.5, 130.9, 127.8, 38.3, 33.2, 19.5 ppm. HRMS *m/z* calcd for C $_8H_{10}O_2$: 138.0681. Found: 138.0677.

(*E*)-3-Hydroxy-2-((E)-2-methylbut-2-enylidene)cyclopentanone (**47**): ^{1}H NMR ($CDCl_3$, TMS): δ 7.0 (s, 1H), 6.2 (q, J= 7.2 Hz, 1H), 5.2 (d, J= 4.8 Hz, 1H), 2.6 (m, 2H), 3.3 (br s, 1H, OH), 2.23 (m, 2H), 2.0 (s, 3H), 1.8 (d, J=7.2, 3H) ppm. *Anal*. Calcd for $C_{10}H_{14}O_2$: C 72.26; H 8.49. Found: C 72.35; H 8.50.

(*E*) and (Z)-2-(2-Methylbuta-1,3-dienyl)cyclopent-2-enone and (**48** and **49**): ^{1}H NMR ($CDCl_3$, TMS): δ 7.6 (t, J= 3.0 Hz, 1H), 7.5 (t, J= 3.0 Hz, 1H), 6.8 (dd, J= 17.1, 10.8 Hz, 1H), 6.5 (dd, J= 17.4, 10.8 Hz, 1H), 6.2 (s, 1H), 6.13 (s, 1H), 5.4 (dd, J= 17.4, 10.8, 1H), 5.2 (dd, J= 17.1, 10.8 Hz, 1H), 2.7 (m, 2H), 2.4 (m, 2H), 1.97 (s, 3H), 1.95 (s, 3H) ppm.

(*E*)-3-Hydroxy-2-((2*E*, 6*Z*)-octa-2,6-dienylidene)cyclopentanone (**52**): ^{1}H NMR ($CDCl_3$, TMS): δ 7.0 (d, J= 11.4 Hz, 1H), 6.5 (m, 1H), 6.3 (m, 1H), 5.3 (m, 2H), 5.1 (m, 1H), 2.6 (m, 2H), 1.9–2.4 (m, 8H), 0.9 (t, J= 7.5 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, TMS): δ 206.8, 149.4, 137.3, 137.2, 133.5, 128.0, 126.8, 70.2, 36.4, 34.3, 31.0, 26.9, 21.2, 15.0 ppm. *Anal*. Calcd for $C_{14}H_{20}O_2$: C 76.33; H 9.15. Found: C 76.36; H 9.12.

2-((1*E*, 6*Z*)-3-Hydroxyocta-1,6-dienyl)cyclopent-2-enone (**53**): ^{1}H NMR ($CDCl_3$, TMS): δ 7.5 (t, J= 3.0 Hz, 1H), 6.8 (dd, J= 16.0, 8.0 HZ, 1H), 6.4 (d, J= 16 Hz, 1H), 5.4 (m, 2H), 5.3 (m, 1H), 2.64 (m, 2H), 2.5 (m, 2H), 1.7–2.2 (m, 6H), 0.9 (t, J= 7.5 Hz, 3H). *Anal*. Calcd for $C_{14}H_{20}O_2$: C 76.33; H 9.15. Found: C 76.29; H 9.14.

(E)-1-Methyl-2-(pent-1-enyl)cyclopent-2-enol (**54**). To a stirred solution of 1.00 g (6.66 mmol) of **24** in 50 mL of dry ether at −78 °C was added dropwise through a syringe 5.23 mL of an ethereal solution of methyllithium (1.4 M). The reaction mixture was allowed to warm up to room temperature and stirred for 1 hour. A saturated aqueous solution of NH_4Cl solution (10 mL) was added dropwise, the layers separated and the aqueous layers extracted twice with 10-mL portions of ether. The combined organic layers were washed twice with 10 mL of brine each, and the organic layer dried over anhydrous $MgSO_4$. The solvent was removed at reduced pressure and the residue chromatographed on SiO_2 (3:1 hexanes/EtOAc), providing 0.8 g (72% yield) of **54**. ^{1}H NMR ($CDCl_3$, TMS): δ 6.15 (dt, J= 16.2, 6.6 Hz, 1H), 5.95 (d, J= 16.2 Hz, 1H), 5.6 (narrow m, 1H), 2.4-1.9 (m, 6H), 1.45 (sext, J= 7.2 Hz, 2H), 1.40 (s, 3H), 0.91 (t, J= 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, TMS) δ 146.6, 132.1, 127.5, 123.2, 83.2, 42.5, 35.5, 28.5, 25.8, 22.5, 13.7 ppm.

(*E*)-3-Methyl-(2-pent-1-enyl)cyclopent-2-enone (**55**). A solution of 1.0 g (6 mmol) of the tertiary alcohol **54** in 5 mL of CH_2Cl_2 was added dropwise to a stirred suspension of 2.58 g (12.0 mmol) of pyridinium chlorochromate (PCC) in 20 mL CH_2Cl_2 at 0 °C. The mixture was stirred at room temperature for 1 hour, and was diluted with 25 mL of ether. The ethereal solution was decanted from the solid, which was washed with three 20 mL portions of ether. The combined ethereal phases were washed successively with two 25 mL portions of 5% NaOH, 5% HCl, and two 10 mL portions of saturated aqueous $NaHCO_3$, and dried over $MgSO_4$. The solvent was removed at reduced pressure and the residue purified by column chromatography on SiO_2, eluting with 3:1 hexanes/EtOAc, to give 0.74 (69%) of 55 as a pale yellow oil. ^{1}H NMR ($CDCl_3$, TMS): δ 6.7 (dt, J= 16.0, 7.2 Hz, 1H), 6.06 (d, J= 16 Hz, 1H), 2.55 (m, 2H), 2.35 (m, 2H), 2.12 (s, 3H), 2.0 (m, 2H), 1.5 (m, 2H), 0.9 (t, J= 7.2 Hz, 3H). These data are almost identical to those reported for **55**.[13]

4-Hydroxy-2-(propen-1-en-2-yl)cyclopent-2-one (**59**). ^{1}H NMR ($CDCl_3$, TMS): 7.3 (d, 1H), 6.1 (s, 1H), 5.2 (s, 1H), 4.9 (m, 1H), 3.4 (br, OH), 2.9 (dd, B part of an ABX system, ^{2}J= 18.6 Hz, 1H), 2.38 (d, ^{2}J= 18.6 Hz, 1H), 1.93 (s, 3H); ^{13}C NMR ($CDCl_3$, TMS): δ 204.9, 156.2, 144.3, 134.4, 119.9, 68.0, 48.9, 22.5 ppm.

3-Methyl-2-pentylcyclopent-2-enone (dihydrojasmone, **56**). Ketone **55** (0.5g, 3.0 mmol) was dissolved in 10 mL of methanol, 2% PtO_2 was added, and the mixture was hydrogenated at atmospheric pressure at room temperature. Hydrogenation was interrupted after the uptake of one equivalent of H_2, and the catalyst filtered off, the residue concentrated at reduced pressure to give **56** in quantitative yield. Its physical and spectroscopic data were identical in all respects with the reported values in literature.

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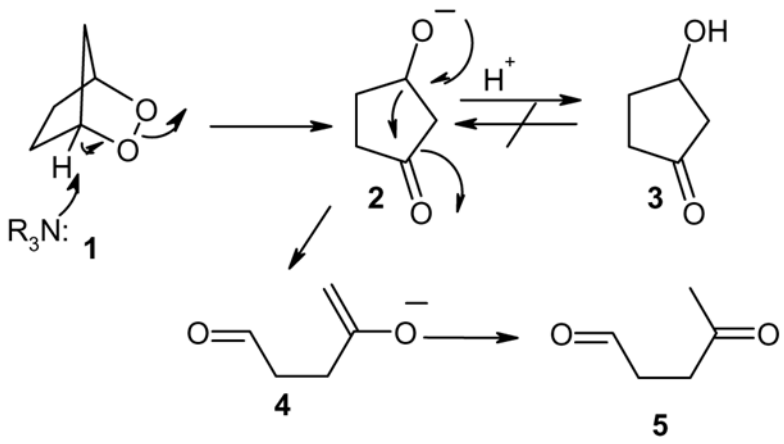
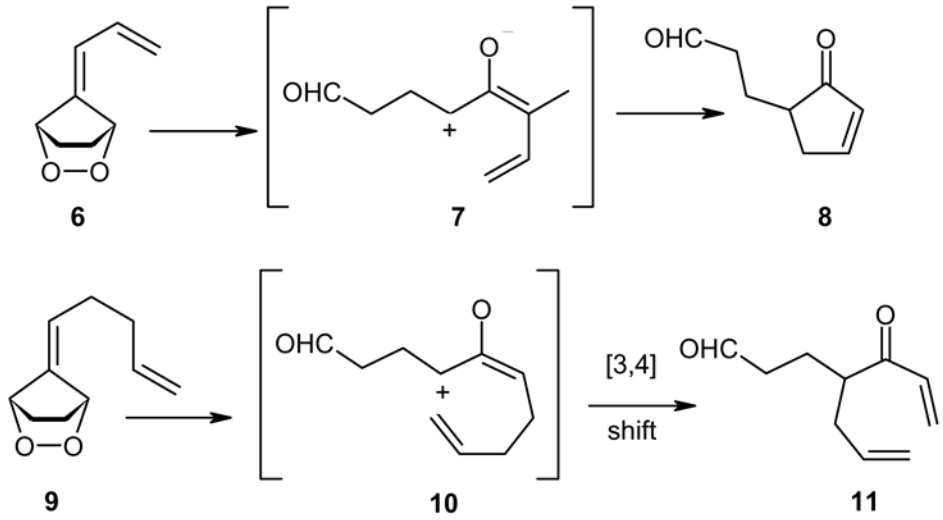
References

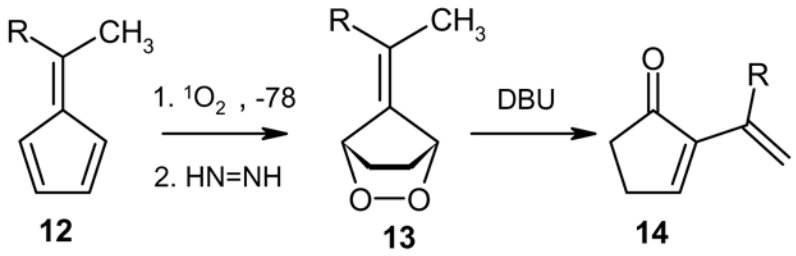
1. Wasserman, HH.; Murray, RW., editors. Singlet Oxygen. Academic Press; New York: 1979.
2. Balci M. Chem Rev 1981;81:91–108.
3. Kornblum N, De La Mare HE. JAmChemSoc 1951;73:880.
4. Zagorski MG, Salomon RG. J AmChemSoc 1980;102:2501.
5. Adam W, Erden I. Angew Chem 1978;90:223.Angew Chem Int Ed Engl 1978;17:210.
6. Erden I, Amputch M. Tetrahedron Lett 1987;28:3779.
7. Erden I, Drummond J, Alstad R, Xu F. Tetrahedron Lett 1993;34:1255.
8. Erden I, Drummond J, Alstad R, Xu F. Tetrahedron Lett 1993;34:2291.
9. Erden I, Xu F, Drummond J, Alstad R. J Org Chem 1993;58:3611.
10. Erden I, Xu F, Cao W. Angew Chem 1997;109:1557.Angew Chem Int Ed Engl 1997;36:1516.
11. Ishihara H, Inomata K, Mukaiyama T. Chem Lett 1975:531.
12. Funel JA, Prunet J. J Org Chem 2004;69:4555. [PubMed: 15202921]
13. Shimada J, Hashimoto K, Kim BH, Nakamura E, Kuwajima I. J Am ChemSoc 1984;106:1759.Nakamura E, Shimada J, Kuwajima I. J Chem Soc, Chem Comm 1983;9:498.
14. Stetter H, Leinen HT. ChemBer 1983;116:254.
15. Johnson CR, Adams JP, Braun MP, Senayake CBW. Tetrahedron Lett 1992;33:919.
16. For a recent synthesis of oudenone, see Flynn BL, Silveira Claudio C, de Meijere A. Synlett 1995:812.
17. For a review on Jasmonoids, see Ho T-L. Syn Commun 1974;4:265.
18. Dauben WG, Michno DM. J Org Chem 1977;42:682.
19. Seo J, Fain H, Blanc JB, Montgomery J. J Org Chem 1999;64:6060.
20. Though 2(*3H*)-oxepinones are the sole products from thermal isomerizations of unsaturated fulvene endoperoxides in aprotic, non-nucleophilic solvents, , **57** has been reported to give rise to considerable amounts of **58** in methanol; see refs. [23] and [24].
21. Stone KJ, Little RD. J Org Chem 1984;49:1849.
22. Erden I, Xu F, Sadoun A, Smith W, Sheff G, Ossun M. J Org Chem 1995;60:813.
23. Harada N, Suzuki S, Uda H, Ueno H. J Am Chem Soc 1971;94:1777.Harada N, Uda H, Ueno H, Utsumi S. Chem Lett 1973:1173.
24. a) Skorianetz W, Schulte-Elte KH, Ohloff G. Angew Chem 1972;84:3111.Angew Chem Int Ed Engl 1972;11:330. b) Skoriantez W, Schulte-Elte KH, Ohloff G. Helv Chim Acta 1971;54:1913.



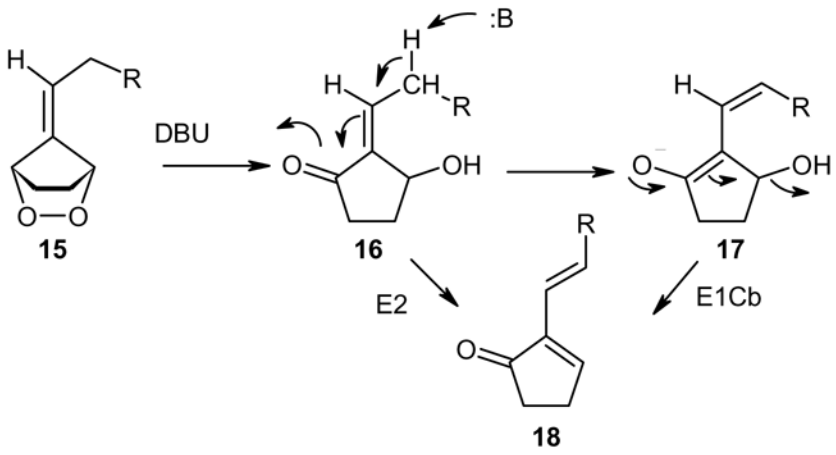
Scheme 1.



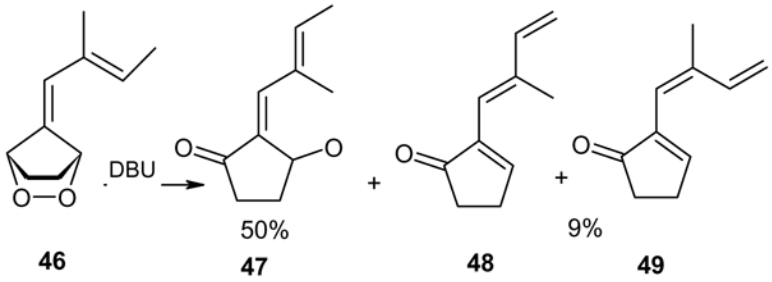
Scheme 2.



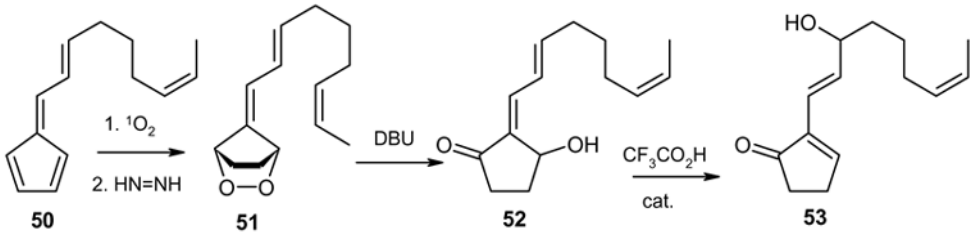
Scheme 3.



Scheme 4.



Scheme 5.



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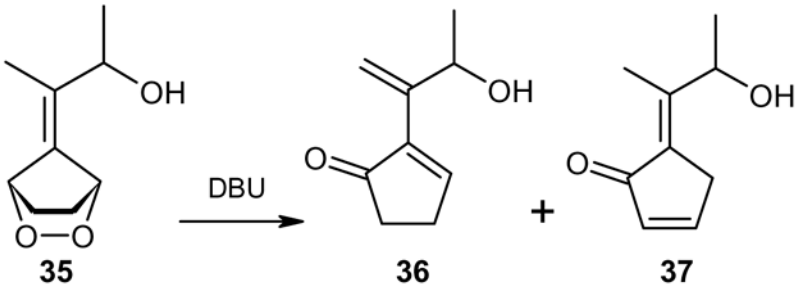

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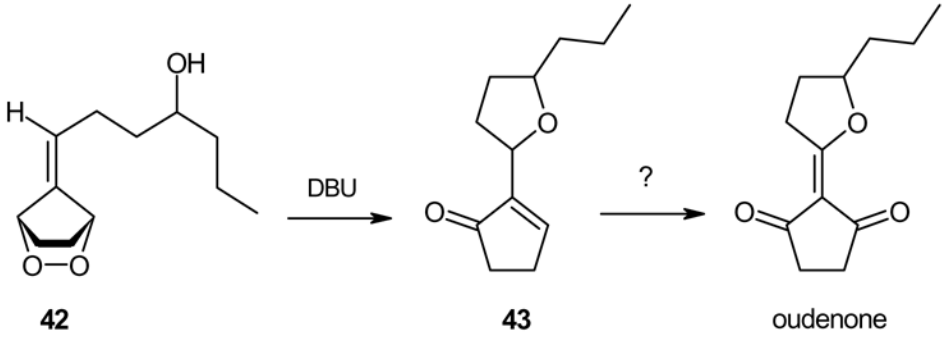
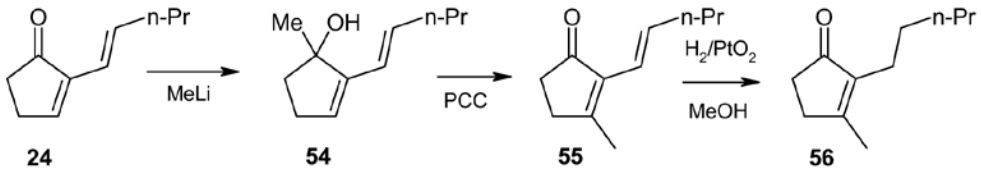
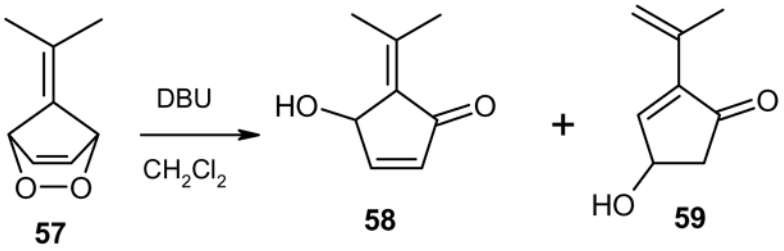


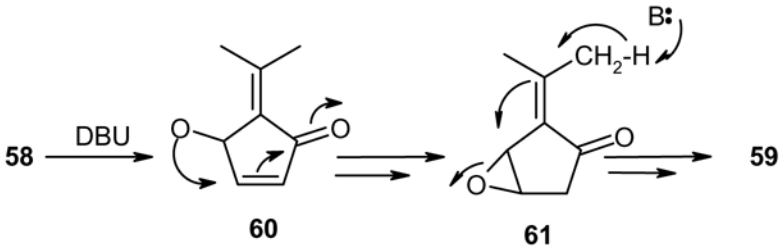
Scheme 8.



Scheme 9.



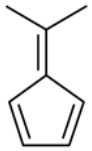
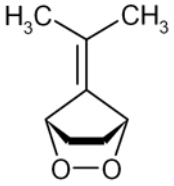
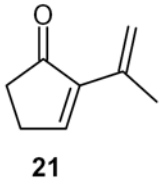
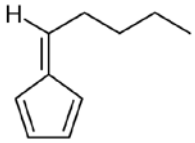
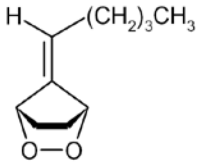
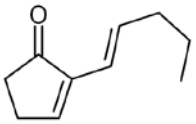
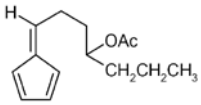
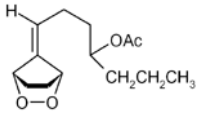
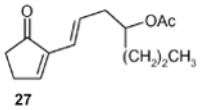
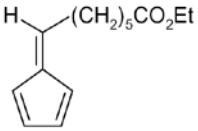
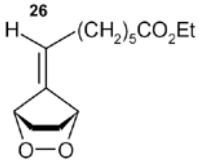
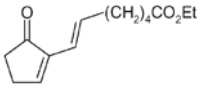
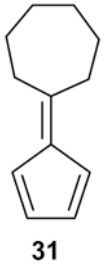
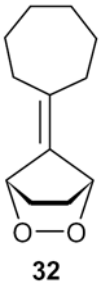
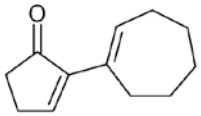
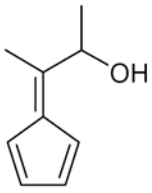
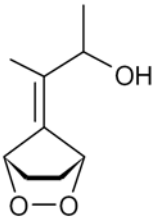
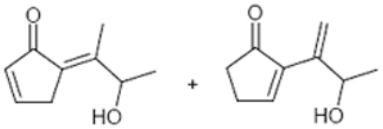
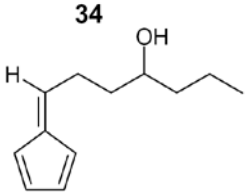
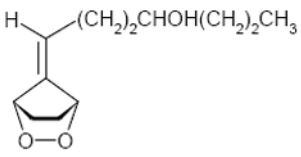
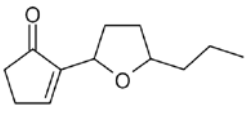
Scheme 10.

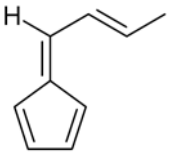
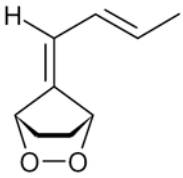
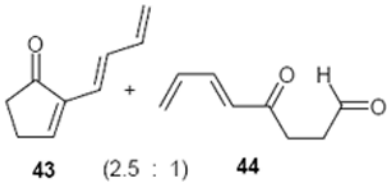
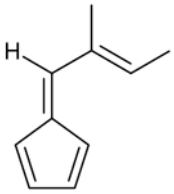
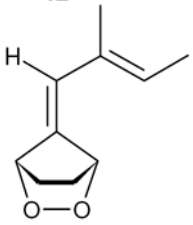
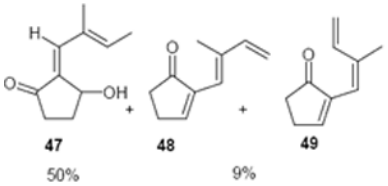


Scheme 11.

Table 1

DBU-catalyzed isomerizations/dehydrations of fulvene endoperoxides

Entry	Fulvene	Endoperoxide	Cyclopentenone	Yield
1	 **19**	 **20**	 **21**	76%
2	 **22**	 **23**	 **24**	83%
3	 **25**	 **26**	 **27**	81%
4	 **28**	 **29**	 **30**	69%
5	 **31**	 **32**	 **33**	82%
6	 **34**	 **35**	 **36** (1.7:1) **37**	66%
7	 **38**	 **39**	 **40**	68%

Entry	Fulvene	Endoperoxide	Cyclopentenone	Yield
8	 **41**	 **42**	 **43** (2.5 : 1) **44**	66%
9	 **45**	 **46**	 **47** 50% **48** **49** 9%	59%