stirred with 25 mL of a 5% solution of diethylenetriamine for 2 h. The organic layer was separated, washed with 1 N HCl and 25 mL of saturated aqueous $NaHCO_3$, dried, and concentrated. MPLC separation (1:1 hexane/ether) afforded 0.160 g of **29a**: IR ($CHCl_3$) 1690, 1728 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 0.00 (s, 3 H), 0.01 (s, 3 H), 1.23 (t, J = 7.1 Hz, 3 H), 1.29 (s, 9 H), 1.43–1.54 (m, 2 H), 1.54–1.67 (m, 3 H), 1.71 (s, 3 H), 1.94–2.00 (m, 1 H), 2.40 (dd, J = 6.9, 16.4 Hz, 1 H), 2.50–2.60 (m, 2 H), 2.67 (m, 1 H overlapping dd, J = 5.6, 16.4 Hz, 1 H), 3.00 (dd, J = 8.0, 11.6 Hz, 1 H), 3.43 (dd, J = 5.9, 9.7 Hz, 1 H), 3.57 (dd, J = 4.2, 9.7 Hz, 1 H), 4.10 (AB of ABX_3, J_q = 7.1 Hz, 2 H), 5.50 (br d, J = 9.1 Hz, 1 H). Anal. Calcd for $C_{22}H_{38}O_4Si$: C, 66.96; H, 9.71. Found: C, 67.01; H, 9.85.

***cis*-2-Methyl-*endo*-8-[[(*tert*-butyldiphenylsilyl)oxy]methyl]-*endo*-5-(carbethoxymethyl)bicyclo[5.3.0]dec-2-en-6-one (29b).** Following the procedure described above for the synthesis of **29a** (scaled up ×4), 0.877 g (2.03 mmol) of ketone **28b** was alkylated to give 0.937 g (89% yield) of **29b**: IR ($CHCl_3$) 1701, 1728 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 1.08 (s, 9 H), 1.22 (t, J = 7.1 Hz, 3 H), 1.50–1.72 (m, 2 H), 1.74 (br s, 3 H), 1.95–2.15 (m, 3 H), 2.34 (dd, J = 7.1, 16.4 Hz, 1 H), 2.40–2.60 (m, 2 H), 2.68 (dd, J = 5.6, 16.4 Hz, 1 H), 2.80 (m, 1 H), 3.00 (m, 1 H), 3.14 (dd, J = 7.8, 11.6 Hz, 1 H), 3.56 (m, 1 H), 3.65 (dd, J = 4.5, 9.8 Hz, 1 H), 4.10 (AB of ABX_3, J_q = 7.1 Hz, 2 H), 5.50 (br d, J = 8.0 Hz, 1 H), 7.30–7.45 (m, 6 H), 7.60–7.75 (m, 4 H). Anal. Calcd for $C_{32}H_{42}O_4Si$: C, 74.09; H, 8.16. Found: C, 73.97; H, 8.10.

Acknowledgment. We are grateful to Paul Bruins, Bruce LaBelle, and Carter Green for recording some of the NMR spectra reported herein. We thank the National Institutes of Health (Grant GM26294), the Committee on Research of the University of California, and the University of California at Davis NMR Facility for financial support of this research. Purchase of the NT-360 instrument was made possible by an instrumentation grant from the National Science Foundation. N.E.S. thanks the Camille and Henry Dreyfus Foundation for a Teacher–Scholar Award.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond lengths, and bond angles for **3c** (3 pages). Ordering information is given on any current masthead page.

Mechanism of Intramolecular Photocycloadditions of Cyclooctenones

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The intramolecular photochemical [2 + 2] cycloadditions of a number of 4′-substituted (3′-butenyloxy)-cyclooctenones have been studied. Two classes of substrates were found. One class (phenyl- and vinyl-substituted) forms [2 + 2] adducts in an efficient reaction, while the rest of the compounds form photoproducts slowly and in low yield. The behavior of a carbon analogue shows that rotational relaxation of the cyclooctenone triplet is faster than [2 + 2] cycloaddition. Based on quenching and sensitization studies, it has been suggested that the substituent effect is indicative of an enhanced rate of cyclization to form a 1,4-biradical.

Introduction

Since Corey's initial report[1] of the photochemical enone [2 + 2] cycloaddition, the reaction has been subject to considerable mechanistic scrutiny.[2-7] One of the early observations made on the limitations of the reaction was that enones in flexible systems do not cycloadd successfully. The π,π^* triplet state can relax by rotation about the C_2–C_3 bond,[7] and this rotation about the ethylene linkage allows the T_1 and S_0 surface to cross, the "free rotor effect".[8] In this manner, vibronic coupling allows rapid intersystem crossing to the ground state. An enone–alkene triplet exciplex that undergoes C–C bonding to generate a biradical has been postulated as a key intermediate in the cycloaddition.[4] While exciplex and biradical intermediates are still a matter of some controversy, they do provide a framework in which new results can be discussed without necessarily endorsing their existence. The initial bond formation can occur either α or β to the enone in intermolecular photoannelations.[2,9-12] For intramolecular photoannelations, it is postulated that the biradical is formed from 1,5-closure (the "rule of five"[13]) of the triplet enone to the olefin.

Pulsed laser techniques have provided insight into the enone [2 + 2] cycloaddition. Bonneau has observed transient absorptions at 280 nm assigned to the twisted triplet π,π^* excited state on laser excitation of a number of conjugated enones.[14] The angle of torsion around the double bond, and consequently the triplet energy, varies with the rigidity of the molecule. Constraints to twisting result in higher triplet energies and longer triplet lifetimes, due to the larger gap between the T_1 and S_0 surfaces. Schuster, in collaboration with Bonneau,[15] has integrated the flash and steady-state photochemical behavior of these enones and shown that the excited states involved in the rearrangement[16,17] and cycloaddition reactions are the same

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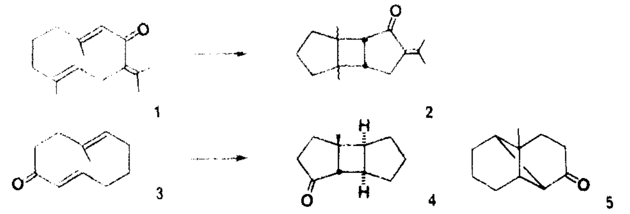
and can be quenched by amines.[18-20]

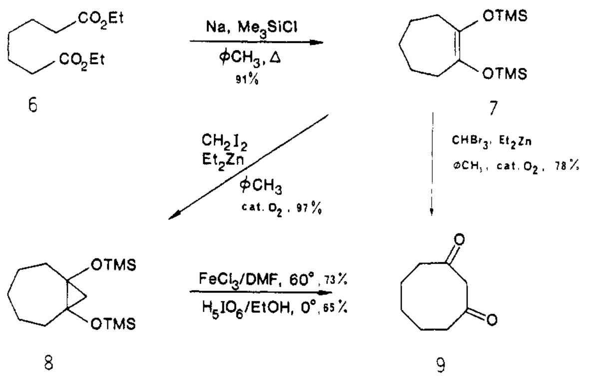
For efficient intermolecular [2 + 2] photocycloaddition, a long-lived enone triplet state is needed. Hence, small-ring enones make good substrates for study. There are few examples of the use of large-ring or acyclic enones. Most have been intramolecular in order that the formation of the triplet exciplex is not diffusion-limited. Two of the early examples of a photoannelation of an acyclic system are Cookson's study of the photochemistry of citral[21] and Brown's synthesis of α-bourbonene.[22] A number of reports on the photochemistry of acyclic dienones have appeared since that time, but many of the results are contradictory.[23-26] Wolff and Agosta conducted an extensive investigation of the intramolecular photochemical reactions of 1,5-hexadien-3-ones, 1-acyl-1,5-hexadienes, and 2-acyl-1,5-hexadienes.[27] They find that for the hexadien-3-ones and the 1-acylhexadienes the initial cyclization occurs between C(1) and C(5) in accordance with the "rule of five". Substitution at C(5) or incorporation of the conjugated double bond into a five- or six-membered ring modifies this behavior and favors 1,6-closure. On the other hand, the 2-acylhexadienes do not show the same substitution or ring dependence and are thought to cyclize C(2) to C(6) initially.

Scheffer has shown that photolysis of isogermacrone (**1**) gives a mixture of $[5.3.0.0^{2,6}]$ adducts (**2**).[28] Similarily, Heathcock has shown that 6-methyl-1,6-cyclodecadien-3-one (**3**) gives a mixture of $[5.3.0.0^{2,6}]$ (**4**) and $[4.4.0.0^{2,7}]$ (**5**) products.[29] The $[4.4.0.0^{2,7}]$ adduct formation can be quenched by the addition of piperylene, thus indicating that it probably results from a triplet state. The other photoadducts must arise from either a singlet or a nonquenchable triplet state. Although Scheffer's and Heathcock's system show photocycloadditions in ten-membered rings, both are heavily biased because of the conformation of the cyclodecane ring.



Previous attempts to use cycloheptenones and cyclooctenones as substrates for the photochemical cycloaddition have been thwarted by the facile rotational relaxation of the triplet excited state. Eaton has shown that *cis*-2-cyclooctenone can be isomerized to the *nonconjugated* trans enone by irradiation at wavelengths greater than 300 nm.[30] Similar results have been obtained for *cis*-2-cycloheptenone. Irradiation in a hydrocarbon matrix at −160 °C generates the trans isomer, which is identified by its IR spectrum.[31,32] Upon warming, dimerization occurs in addition to thermal isomerization to the cis enone. Both trans isomers have been detected by using flash photolysis,[33-35] and both are reactive species that can be trapped in the dark by electron-rich olefins;[1] dienes, giving trans Diels–Alder adducts;[31,32,36] or oxygen and nitrogen nucleophiles.[37-39]

Scheme I



The work described herein was intended to ascertain whether an intramolecular photocycloaddition could compete with rotational relaxation in photoexcited cyclooctenones. A preliminary account has appeared.[40]

Results

Preparation of Substrates. All of the substrates required for this study were prepared from cyclooctane-1,3-dione, which is available by the procedure developed by Saegusa[41] (Scheme I). Diethyl pimelate (**6**) is subjected to the silylacyloin reaction and the resulting alkene is cyclopropanated with diiodomethane and diethylzinc.[42] Compound **8** is obtained in an excellent overall yield of 93%. Notable in the second step is catalysis by molecular oxygen.[43] Oxidative cleavage of **8** using $FeCl_3$ gives **9**, but the workup is inconvenient. A superior method is oxidation with periodic acid, giving the dione in 65% yield. Alternatively, bromocarbene, prepared by the reaction of diethylzinc with bromoform,[45] can be added to **7**, with ring expansion occurring in situ[44] to give the dione **9** in 78% yield.

All attempts to synthesize vinylogous esters of **9** under Dean–Stark conditions failed. On the basis of a report from a Czechoslovakian group[46] and knowledge that "hard"

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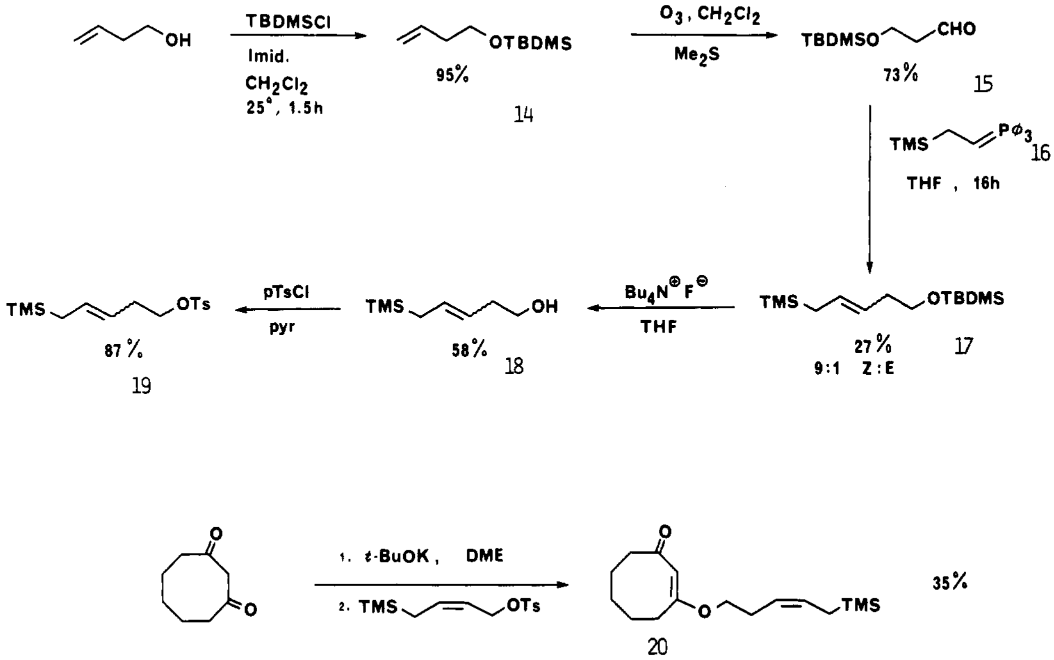
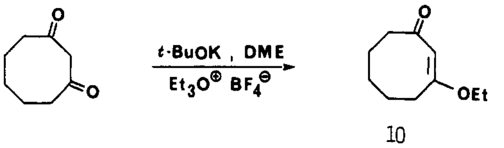
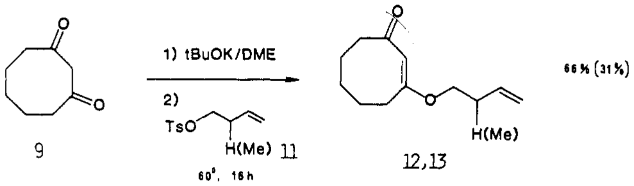
Scheme II



leaving groups and naked enolates give a high percentage of O-alkylation,[47] the alkylation of its potassium enolate was conducted. Chromatography on neutral alumina allows purification of **10** with minimal loss due to hydrolysis of the very sensitive enol ether.



For the vinylogous esters required for the photochemical study, tosylates are used. Compounds **12** and **13** are thus obtained in serviceable yield. Their UV and IR spectra show bands characteristic of normal, conjugated vinylogous esters.



The other vinylogous esters required for this study were prepared from commercially available or known alcohols by tosylation and application of the above alkylation protocol, using either potassium *tert*-butoxide or potassium hexamethyldisilazide as base.

Both *E*- and *Z*-allylic silanes were obtained as described in Scheme II. 3-Buten-1-ol is protected as its *tert*-butyldimethylsilyl ether (**14**). The ether is ozonized to give the protected aldehyde **15**, which is condensed with the ylide derived from [2-(trimethylsilyl)ethyl]triphenylphosphonium bromide,[48] giving the protected allylsilane **17** as a 9:1 mixture of *Z*:*E* isomers. Deprotection, tosylation, and O-alkylation give **20**. The *E* isomer is obtained from the known alcohol of Speckamp and Hiemstra.[49]

An analogue with a methylene group at the 3-position was synthesized to ascertain the effect of the 3-oxygen substituent on the photochemical behavior of these enones. Addition of the Grignard reagent derived from 1-bromo-4-pentene to a solution of vinylogous ester **10** in THF, followed by an acid workup, gives 3-(4-pentenyl)-2-cycloocten-1-one (**21**).

Photochemical Results. In the initial exploratory photolysis, the unsubstituted vinylogous ester **12** was irradiated at 300 nm or 350 nm in hexanes. After 3 days, there was no reaction. The photolysis was performed also in cyclohexane, methylene chloride, acetonitrile, benzene, *tert*-butyl alcohol, and furan, without observable photoaddition. Wolff and Agosta have reported that the photoadditions of a number of acyclic dienones are facilitated by performing the irradiation at elevated temperatures,[27] so the photolysis was performed at −78 °C, 25 °C, and 80 °C, without effect. Acetophenone and benzophenone were tried as triplet sensitizers to no avail. The branched vinylogous ester **13** was also irradiated at 350 nm in cyclohexane, methylene chloride, and furan, and triplet sensitization using acetophenone was attempted. In all cases, no photocyclization is observed.

When **10**, **12**, or **13** is irradiated in furan, no photocyclization or trapping of the trans enone is observed, in contrast to previous reports on *trans*-cycloheptenone and -cyclooctenone.[31,32,36] There are two simple explanations for this observation: either the trans enone in this system is too sterically hindered for trapping to occur or the lifetime is too short for intermolecular trapping. Irradiation of **31** in cyclohexane (room temperature) does not show the change in UV absorption as reported by Eaton.[30] Therefore the lifetime of these trans enones, if formed, must be too short for intermolecular trapping to occur.

Compounds **10** and 3-(3-butenyloxy)-2-cyclohexen-1-one were subjected to a flash photolysis study[35] to investigate the possibility that the trans enones are produced but have a very short lifetime. They were compared to their unsubstituted analogues, 2-cycloocten-1-one and 2-cyclohexen-1-one. These enones were excited by a laser pulse at 355 nm in CH_3CN solution at 60 mM and the transient

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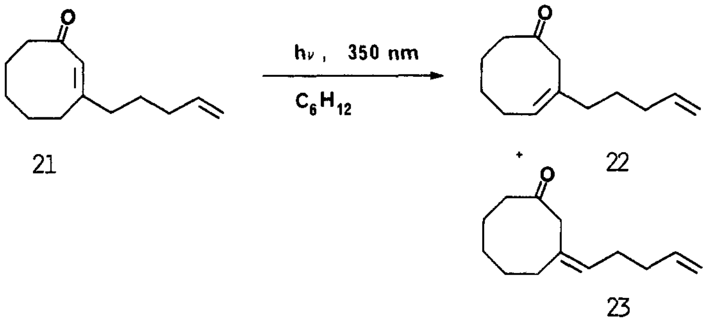


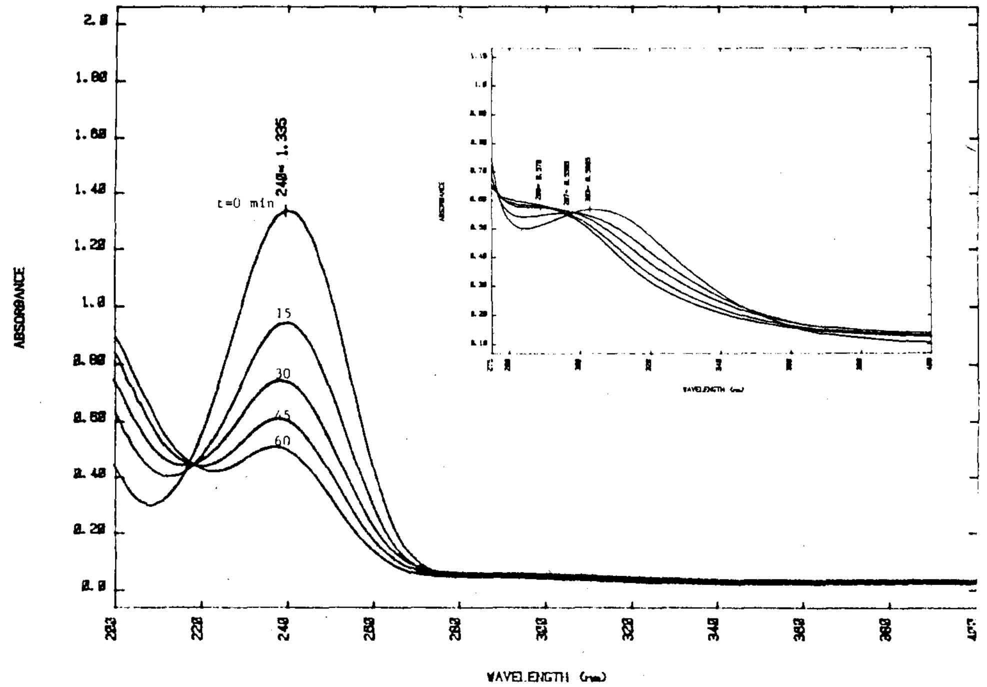


Figure 1. Irradiation of 3-(4-pentenyl)cyclooct-2-en-1-one in cyclohexane and methanol.

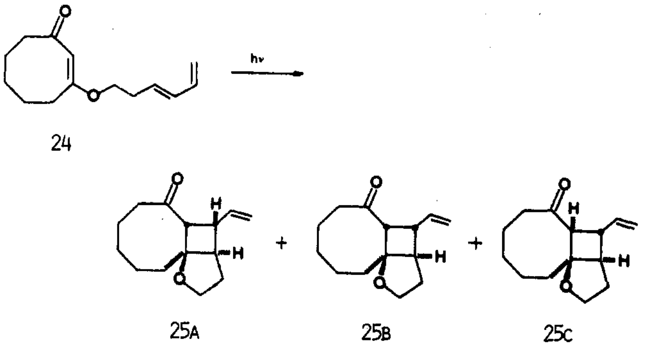
UV absorption recorded. The transient Bonneau previously observed and assigned as a twisted triplet, π,π^* state[14] was seen for cyclohexenone, and the long-lived transient that was observed and assigned as its trans isomer was seen by using *cis*-cyclooctenone.[34] However, when 3-ethoxy- or 3-(butenyloxy)-2-cyclohexenone is flashed, a corresponding short-lived transient is not observed ($\tau <$ 8 ns). Moreover, the long-lived absorption expected of a trans enone is not observed when **10** is flashed.

The photochemical behavior of the carbon analogue **21** is markedly different (Figure 1). The trans isomer is rapidly formed on irradiation at 350 nm in cyclohexane at room temperature. After 60 min a photostationary state is reached with a 1:8 ratio of cis:trans isomers. On prolonged irradiation, a 1.6:1 mixture of **22** and **23** is produced. Similar results are observed at 300 nm, and the reaction exhibits no solvent or sensitizer effect. The β,γ enones appear not be be derived from a singlet-state photodeconjugation[51] but to arise from the strained trans enone. In another experiment **21** was irradiated for 60 min to produce a 47:6:47 ratio of trans:cis:β,γ. Storage of the reaction mixture in the dark at 0 °C for 48 h gives an isomeric composition of 15:6:79. Photolysis in methanol produces a 65:12:23 ratio of trans:cis:β,γ enones. Extended irradiation gives a 1:2 ratio of **22**:**23** as the exclusive products. No products corresponding to the addition of methanol are isolated.

Table I. Solvent Dependence of Product Ratio for Photolysis of 24

solvent	25a	25b	25c	yield, %
cyclohexane	22	31	29	76
acetone	23	38	18	88
CH_2Cl_2	29	35		98

The possibility that internal Diels–Alder trapping of the trans enone could be accomplished was examined through photolysis of **24** at 350 nm in cyclohexane. Three photoadducts (76%) **25a**/**b**/**c** are produced in the ratio (**a**:**b**:**c**) 22:31:29. A small solvent effect is observed (Table I). No products resulting from the intramolecular Diels–Alder trapping of the trans enone are found, and there is no wavelength dependence.



Irradiation of **26** gives a mixture of three diastereomeric

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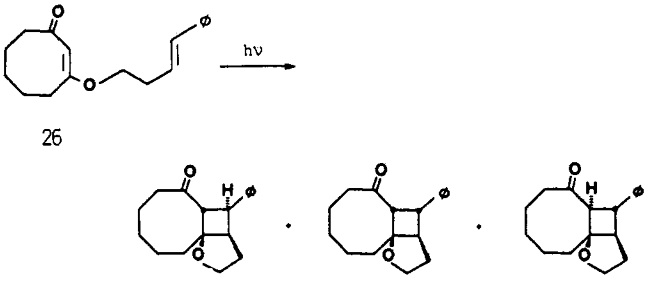
Table II. Solvent Dependence of the Product Ratio for Photolysis of 26

solvent	27a	27b	27c	yield, %
cyclohexane	1	4	3	43[a]
benzene	1	13	7	90
acetone	1	13		81
CH_2Cl_2		2	1	38[a]

[a] After chromatography.

products **27a/b/c** in a 1:4:3 ratio (**a**:**b**:**c**). Here again a solvent effect is observed (Table II).



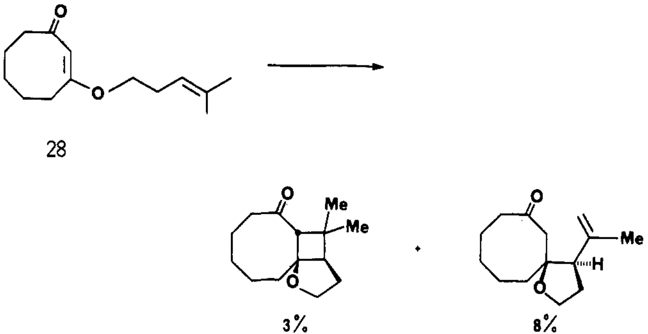
26

27A

27B

27C

The irradiation of the dimethyl derivative **28** for 7 days leads to **29** and **30** in 3% and 8% yields, respectively.

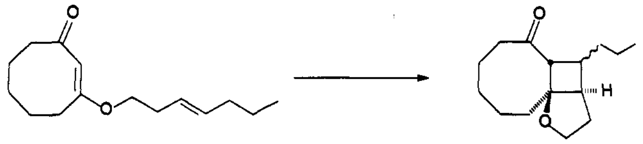


28

29

30

Irradiation of the propyl derivative **31** for 7 days gives in 5.5% yield a mixture of two compounds **32a/b** in a 1:2 diastereomeric ratio. Irradiation of **33** followed by chromatography gives in 60% yield a mixture of five diastereomeric photoadducts, characterized as **34a/b**, **34c/d**, and **34e** and produced in the ratio 22:16:31:7:11.



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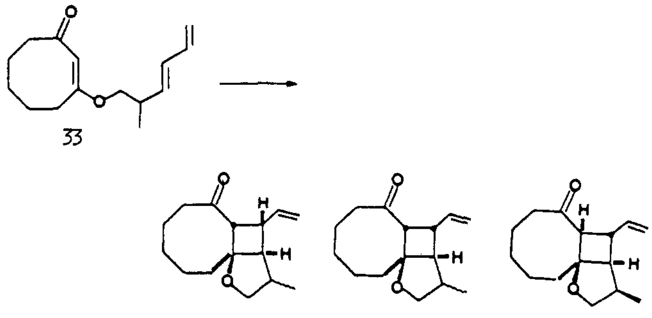
32



33

34A,B

34C,D

34E

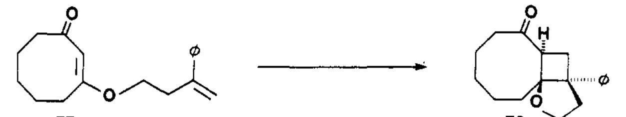
Table III. Quantum Yield Determination

enone	Φ_d[a]	Φ_p[b]
24	0.28	0.19
33	0.29	0.22

[a] Quantum yield for disappearance of enone. [b] Quantum yield for appearance of photoadducts.

The quantum yields for the photolysis of the two dienyl enones **24** and **33** were measured as 0.01 M solutions in cyclohexane by using the valerophenone–acetophenone chemical actinometer[52] (Table III).

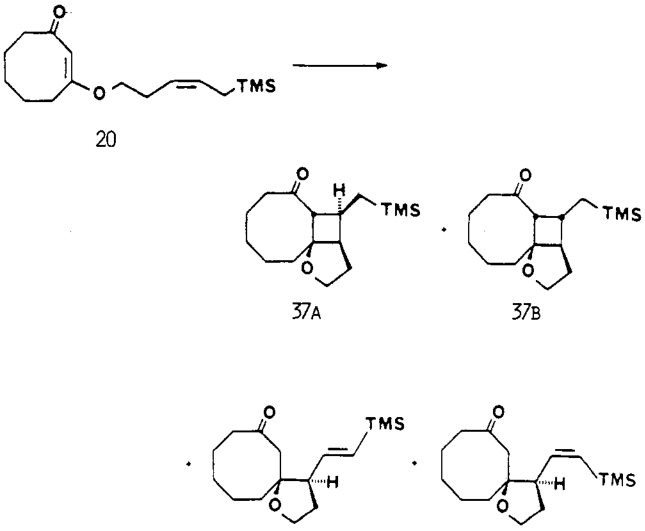
To investigate the effect of substitution at the 3′-position of the butenyl side chain, **35** was examined. Photolysis at 350 nm for 90 h gives **36** in 31% yield.



35

36

Photolysis of the (*Z*)-allylsilane **20** at 350 nm for 7 days gives two chromatographic fractions. The first fraction (14%) consists of a 2:1 mixture of **37a** and **37b**. The second fraction (17%) consists of a 10:6:3 mixture of starting enone and **38a** and **38b**, respectively. Extended photolysis of the *E* isomer gives in 2% yield adducts **37a** and **37b** in a 3:2 ratio and in 26% yield photo–ene adducts **38a** and **38b** in a 1:1 ratio.



20

37A

37B

38A

38B

Epimerization of Photoadducts. Because little is known about the thermodynamics of the 8/4 ring junction, a number of epimerization experiments were performed. On stirring in methanol with 5 mol % sodium methoxide, photoadduct **25b** epimerizes to give a 25:1 mixture of diastereomers **25c**:**25b**. Diastereomer **25a**, on the other hand, does not epimerize, but does exchange with deuteriated solvent. The phenyl compound **27b** on treatment with 1.2 equiv of sodium methoxide epimerizes to give exclusively diastereomer **27c**. As with the vinyl series, diastereomer **27a** does not epimerize but does undergo exchange.

A series of molecular mechanics calculations using MM2 were conducted to evaluate the thermodynamic preference of the 8/4 ring junction. The unsubstituted oxatricyclo[6.5.0.0^{8,12}]tridecan-2-one system was investigated initially. A number of possible conformations of the two rings were examined for both the cis and trans ring junctions. The two conformations for each junction that have the lowest final steric energy are shown in Figure 2. Obviously, there

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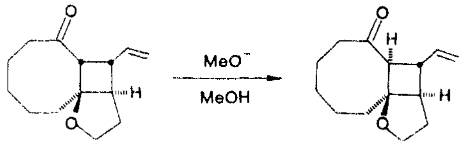
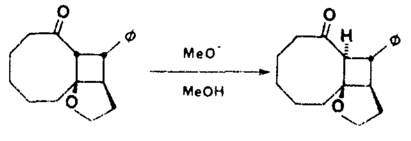
[52] Wagner, P. J.; Kempainen, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 7495.



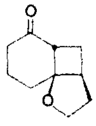
25B 25C



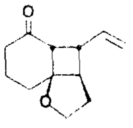
27B 27C

is no inherent preference for a particular stereochemistry. A methyl group was added at C-13 on the cyclobutane both syn and anti to the THF ring. As shown in Figure 2, when the methyl group is syn to the THF ring, the cis ring junction is favored by 3.7 kcal mol^{-1}. However, when the methyl group is anti to the THF ring, the trans ring junction is favored by 1.9 kcal mol^{-1}. These energies are consistent with the observed behavior.

Stereochemical Assignments. The structural assignments for the cycloadducts rest on simple decoupling experiments, NOE difference spectroscopy, and lanthanide-induced shift studies in ^{1}H NMR. These results were compared to two model compounds **39** and **40**, which for



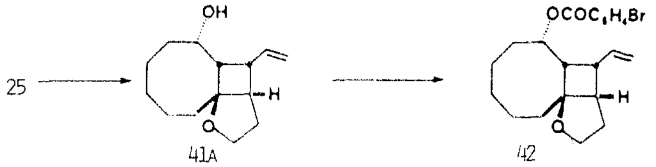
39



40

thermodynamic reasons have unambiguous stereochemistry. In general, cis-fused 8/4 adducts have a large NOE between the methine α to the carbonyl and one proton adjacent to the ether function. The trans-fused adducts show large downfield shifts of this ethereal proton with increasing concentration of shift reagent.[50] Finally, these assignments were supported by an X-ray crystal structure of a derivative.

Reduction of a mixture of vinyl photoadducts **25a** and **25b** with L-Selectride (Aldrich) in THF gives a mixture **41a/b** whose stereochemistry was determined by NOEDS.



41A 42

Hydride addition occurs exclusively from the exo face of the 8/4 ring system. Alcohol **41a** was converted by treatment with methyllithium and *p*-bromobenzoyl chloride into its *p*-bromobenzoate derivative (**42**) whose structure was determined by X-ray crystallography (Figure 3).

Discussion

Irradiation of vinylogous esters **10**, **12**, and **13** in furan does not give any products derived from trapping of the *trans*-cyclooctenone, and irradiation of the dienyl vinylogous ester **24** gives no [4 + 2] adducts. These results are striking in light of earlier reports that *trans*-cyclooctenone can be easily trapped by electron-rich olefins,[1] dienes,[32,36] and alcohols.[37-39] In the carbon analogue **21**, the trans isomer is formed very rapidly, so rotational relaxation of the cyclooctenone triplet state must be faster than [2 + 2] cycloaddition. Our results indicate that a long-lived *trans*-cyclooctenone is not formed in the case of **10**. Substitution of an oxygen atom on the 3-position of the chromophore therefore must have resulted in preferential relaxation to the conjugated cis enone. Because the carbon analogue **21** *is* isomerized to the nonphotoactive trans enone, it cannot undergo [2 + 2] cycloaddition under these conditions.

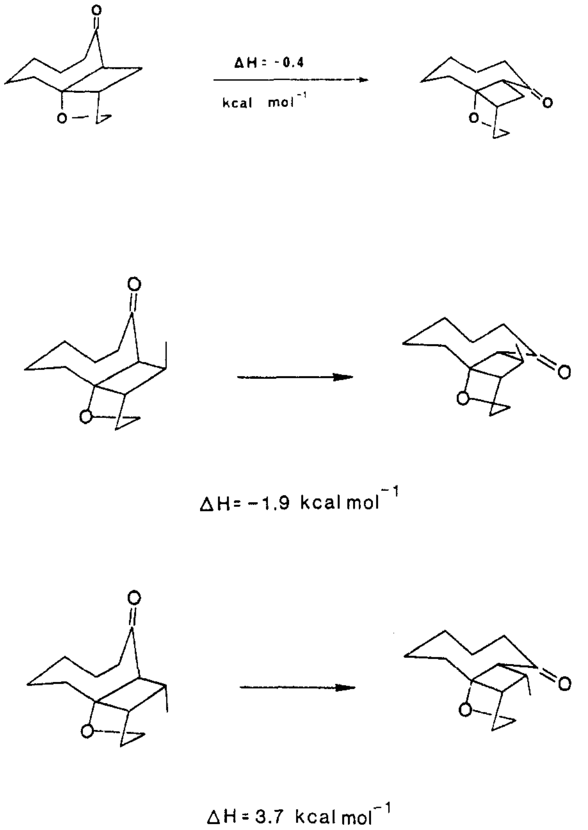


Figure 2. MM2 results for tricyclo[6.5.0.0^{8,12}]tridecan-2-one system.

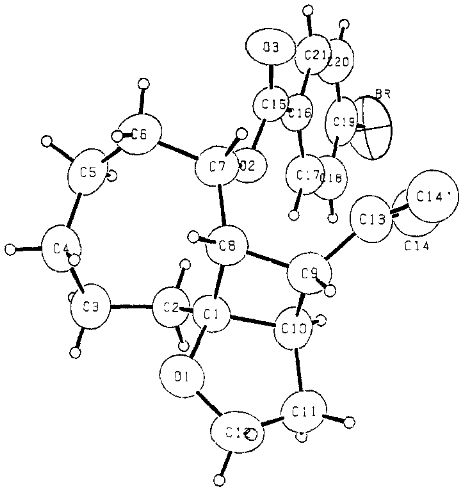


Figure 3. ORTEP view of X-ray structure of compound **42**.

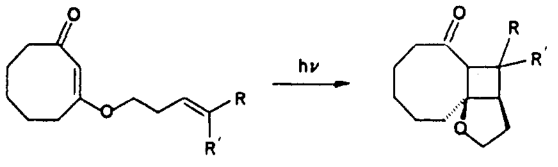
Origin of Observed Photoadducts. For the vinyl and phenyl series three photoadducts are seen, two of which have the cis 8/4 ring junction, the other having a trans junction. Because of previous data on the regiochemistry of [2 + 2] reactions and stereochemistry of [4 + 2] reactions of the trans enone, it would be expected that internal cycloadducts of the trans enone would have a trans ring junction. Therefore, the two cis adducts *must* have arisen from a photochemical reaction. While it is conceivable that photochemical or thermal epimerization of the cis isomers might be the source of the trans isomer, control experiments eliminate this possibility.[50] The lack of a wavelength dependence of the product ratio for the photoaddition suggests a single reactive excited state. Triplet sensitization using acetone gives the same three adducts (Table I), but the ratio varies slightly. The difference in product ratio is most likely a consequence of triplet-sensitized isomerization of the diene (vide infra). The reaction is not quenched by 1,3-cyclohexadiene, suggesting that the cycloaddition involves a nonquenchable triplet state.

An Alternative Mechanism. The generally accepted mechanism for the photochemical addition of an olefin to an enone was described earlier. However, the nature of the olefins that undergo efficient photoaddition, either a diene or a styrene, raises another possible reaction mechanism. The triplet energies of these two groupings (E_t = 59 and 60 kcal mol^{-1}, respectively) lie below the triplet energy of an enone ($E_t \cong 70$ kcal mol^{-1}).[53] Hence, triplet energy transfer is exothermic and therefore a possibility. The photoadducts could be derived from attack of the triplet diene or styrene on the ground-state enone. To investigate this possibility, the triplet diene or styrene was generated independently to see if it would add to the ground-state enone. Acetone was used as a triplet sensitizer in the photolyses of enones **24** and **26** (Tables I and II).

Triplet sensitization by acetone does not affect greatly the photoaddition of **24**, but a slight effect is observed with **26**. Irradiation in acetone leads to the formation of only photoadducts **27a** and **27b**, rather than the mixture of three adducts, and also causes isomerization of the pendant olefin in the starting material. In the case of **24**, a photostationary state corresponding to a cis to trans diene ratio of 1.8:1 is reached after 1 h. This result demonstrates that the triplet diene is indeed produced, but the rate of cycloaddition is not changed significantly. Isomerization of the diene shows that the rate of rotational relaxation of the triplet diene must be at least comparable to that of intramolecular addition to the ground-state enone. On the other hand, no isomerization is observed when the photolysis is performed in cyclohexane (at 350 nm, where absorption by the diene is negligible; at 300 nm a cis/trans ratio of 5:1 is seen after 1 h). In order to explain this lack of isomerization, the rate of addition of the triplet diene to the ground-state enone would have to be much faster than the rate of rotational relaxation. Because these conclusions are contradictory, they suggest that sensitization by the enone is insignificant.

Similar results are found by monitoring the isomerization of the styrene-substituted enone **26** in benzene and acetone, irradiating at 350 nm. Some isomerization occurs even in benzene because of appreciable absorption of the styrene chromophore at 295 nm (ε 700), but the rate is different from that in acetone. In acetone, the photostationary state (cis:trans = 1.8:1) has been reached in 1 h. As a comparison, the isomerization of β-methylstyrene was monitored under the same conditions, showing almost identical behavior with **26**. A potential but less likely explanation for the difference in behavior under the two conditions is the production of distinct excited states.

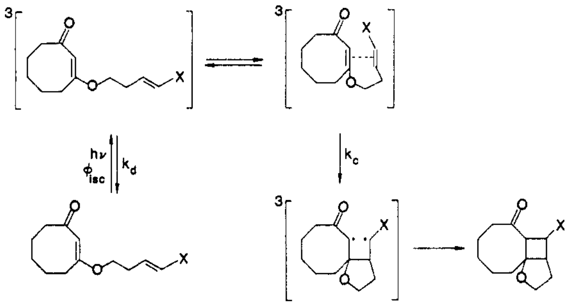
Table IV. Photochemical Yields in Cyclohexane



R	R′	time	yield (%)
H	H		0
CH=CH$_2$	H	5 h	76
C$_6$H$_5$	H	6 h	43[a]
CH$_3$	CH$_3$	7 days	13[b]
C$_3$H$_7$	H	7 days	6
H	CH$_2$Si(CH$_3$)$_3$	7 days	22[b]
CH$_2$Si(CH$_3$)$_3$	H	11 days	28[b]

[a] After HPLC. [b] Both [2 + 2] and ene products.

Scheme III



On the basis of these results, triplet energy transfer to the diene or styrene is insignificant. Quenching by dienes occurs near or at the diffusion limit (10^{10} s^{-1}) when energy transfer is exothermic ($\Delta E > 5$ kcal mol^{-1}). However, in these enones there is no evidence that the triplet is being quenched. This is surprising since the quenching is intramolecular and therefore not diffusion-limited. Intramolecular energy transfer, both singlet and triplet, has been shown to be a very facile process. A good example of this phenomenon is the photochemical behavior of 4,4-diaryl-2-cyclohexenones studied by Zimmerman.[54] Intramolecular triplet transfer between a benzoyl group (E_t = 74 kcal mol^{-1}) and a styryl group (E_t = 60 kcal mol^{-1}) has been measured over a range of separations.[55] The measured rates are all greater than 10^{10} s^{-1}. One potential explanation for the behavior observed here is that the greater freedom of the cyclooctenone triplet to twist reduces its energy to the point that transfer is no longer sufficiently exothermic.

Substituent Effects. The results collected in Table IV show a pronounced substituent effect. Substituents on the terminal methylene that can stabilize adjacent radical character result in a greater amount of cyclization. A mechanism may be postulated to account for the results (Scheme III). Since dimerization is not observed, self-quenching can be ruled out. Initial bond formation is postulated to occur β to the enone, between carbons 2 and 6 of the heptadiene, following the "rule of five".[56,57] Excitation of the enone chromophore does not cause isom-

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[53] Murov, S. L. *Handbook of Photochemistry*; Dekker: New York, 1973.

[54] Zimmerman, H. E.; Jian-hua, X.; King, R. K.; Caufield, C. E. *J. Am. Chem. Soc.* **1985**, *107*, 7724.

[55] Cowan, D. O.; Baum, A. A. *J. Am. Chem. Soc.* **1971**, *93*, 1153.

[56] Becker, D.; Nasler, M.; Hirsh, S.; Ramun, J. *J. Chem. Soc., Chem. Commun.* **1983**, 371.

[57] Matlin, A. R.; George, C. F.; Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 3385.

erization of the olefin in this instance, and the lack of stereochemical scrambling in the recovered starting material demonstrates that reversion of the putative 1,4-biradical intermediate to the ground-state enone and olefin does not occur.

One anomaly that needs to be addressed is the photochemical behavior of the 3′-phenyl substituted enone **35**. On photolysis, the single diastereomer **36** is produced with a trans 8/4 ring junction. The origin of this product has not been established, but it was demonstrated earlier that the trans enone is probably not formed. In addition, it was shown that energy transfer to the styrene group does not occur, so the adduct must be derived from addition of the triplet enone to the olefin. However, the structure of this adduct is inconsistent with the proposed mechanism. A biradical intermediate analogous to that in Scheme III does not benefit from stabilization by the phenyl substituent, yet cyclization is seen. Initial bond formation likely occurs α to the enone between carbons 1 and 7 of the heptadiene, generating a benzylic radical. Evidence supporting 1,7-closure has been reported by Wolff and Agosta.[57] Examination of models suggests that such a closure would indeed result in trans stereochemistry.

It is evident that stabilization of the 1,4-biradical intermediate can lead to enhanced yields and rates of photoaddition. This enhancement is very dramatic, from no cycloaddition for the unsubstituted case to 70–80% for the vinyl and phenyl cases. The stabilization afforded to a radical upon substitution with a vinyl or phenyl group must strongly affect the reaction efficiency. Potential sources of inefficiency are therefore important to consider.

In de Mayo and Wagner's early findings,[4–6] the major source of efficiency was proposed to be partitioning of the biradical between closure to adduct and reversion to enone. As demonstrated here and in Becker's work,[56] in these intramolecular cycloadditions biradical formation is irreversible. Two other possibilities could be the triplet enone or the exciplex. The work of de Mayo on intermolecular reactions concluded that relaxation of the exciplex to the ground state is not important. We speculate that in these intramolecular cycloadditions, exciplex formation is reversible. Therefore the efficiency of the photoaddition will be determined by the relative rates of closure of the putative exciplex and of relaxation of the triplet enone, $k_c/(k_c + k_d)$.

The next question to be answered is whether the change in stability of the biradical (thermodynamic) can alter its rate of formation (kinetic). Beckwith and others have shown that for 1,5-radical cyclizations, the stability of the resultant radical does affect the rate of closure.[58] This rate is more than doubled upon substitution of two methyl groups on C6, in which a tertiary rather than a primary radical is formed. From these results, it is highly likely that the rate of closure of the postulated exciplex in these systems is affected by the stability of the resulting biradical.

Experimental Section

General. Unless otherwise noted, all materials were obtained from commercial suppliers. Ether, tetrahydrofuran (THF), and 1,2-dimethoxyethane (DME) were distilled from sodium/benzophenone under nitrogen immediately prior to use. All other solvents were distilled from calcium hydride and stored over molecular sieves under a nitrogen atmosphere. All reactions were performed under a nitrogen atmosphere in oven-dried glassware. Flash chromatography was performed on EM Reagents 0.042–0.063-mm grade silica gel (Kieselgel 60), or Woelm N neutral alumina Activity III, using the solvent system specified. Thin-layer chromatography was performed on EM Reagents silica gel 60 F-254 precoated plates using the same solvent system unless otherwise specified. Melting points were obtained on a Haake-Buchler capillary melting point apparatus and are uncorrected. IR spectra were determined on a Perkin-Elmer 1310 infrared spectrophotometer. UV spectra were obtained on a Hewlett-Packard 8450A ultraviolet/visible spectrophotometer; reported as λ_{max} in nm (ϵ). ^{1}H NMR spectra were determined on the following spectrometers: Varian XL-100, Nicolet NMC-300, or Varian XL-400. Tetramethylsilane or chloroform was used as an internal standard and the chemical shifts are reported as ppm on the δ scale. Data are reported as follows: chemical shift (number of hydrogens, multiplicity, coupling constants in hertz). ^{13}C NMR were measured at 99.7 MHz on the Varian XL-400 instrument using $CDCl_3$ as internal reference. Low-resolution mass spectral data were obtained on a Hewlett-Packard 5970 or 5990 gas chromatograph/mass spectrometer and are reported as m/z (relative intensity). High resolution mass spectra were obtained through the NIH regional Mass Spectrometry Facility at the University of California, San Francisco. Elemental analyses were performed by the Microanalytical Laboratory, Department of Chemistry, Stanford University, Stanford, CA. Gas chromatography was performed on either a Perkin-Elmer Sigma 3B or a Hewlett-Packard 5890A gas chromatograph, equipped with a Hewlett-Packard 3390A reporting integrator, on a J&W Scientific SE54 15 m × 0.25 mm capillary column. Unless otherwise stated, the following temperature program was used: initial temperature = 100 °C, final temperature = 200 °C, ramp rate = 10°/min, final time = 5 min. High-pressure liquid chromatography (HPLC) was performed on a semipreparative scale on a DuPont Instruments 870 system equipped with 21-mm Zorbax Sil column, or on a preparative scale on a Waters Associates PrepLC/system 500. Photolyses were conducted as indicated either in a Southern New England Ultraviolet RPR-100 Rayonet photochemical reactor, equipped with a merry-go-round apparatus, or on a preparative scale on a Hanovia medium-pressure mercury vapor lamp in an immersion well.

(*Z*)-1,2-Bis(trimethylsiloxy)cycloheptene (7). To a suspension of 21.5 g (935 mmol) of sodium in 350 mL of toluene at room temperature was added 100 mL (85.6 g, 785 mmol) of chlorotrimethylsilane. The resulting solution was stirred at 40 °C while 40.3 g (187 mmol) of diethyl pimelate in 60.0 mL of toluene was added over a period of 16 h. The reaction was then heated at reflux for 4 days. After cooling, the deep purple solution was filtered and the residue washed with 2 × 100 mL portions of toluene. The combined organic extract was concentrated in vacuo to yield 48.51 g (96%) of a pale yellow liquid: bp 104–106 °C (4 Torr); ^{1}H NMR ($CDCl_3$) δ 0.20 (18 H, s), 1.44–1.69 (6 H, m), 2.08–2.29 (4 H, m); IR (thin film) 1670, 1440, 1250, 1240, 1200 cm^{-1}. Anal. $C_{13}H_{28}O_2Si_2$: C, H.

1,7-Bis(trimethylsiloxy)bicyclo[5.1.0]octane (8). A solution of 1,2-bis(trimethylsiloxy)cycloheptene (9.48 g, 34.8 mmol) and diiodomethane (7.60 mL, 94.3 mmol) in toluene (50 mL) was cooled in an ice/salt bath under a nitrogen atmosphere. To this was added a 1.6 M solution of diethylzinc in toluene (60.0 mL, 96.0 mmol) over a period of 30 min. The reaction was stirred for 1 h and then at room temperature for 16 h. After quenching into cold, saturated aqueous NH_4Cl (100 mL), the aqueous layer was extracted with toluene (3 × 100 mL). The combined organic layers were washed with saturated NH_4Cl and brine and then dried over $MgSO_4$. Filtration and removal of solvents in vacuo yielded 9.65 g (97%) of a yellow oil: bp 104–106 °C (4 Torr); ^{1}H NMR ($CDCl_3$) δ 0.20 (18 H, s), 0.75 (1 H, d, J = 7.0), 0.90 (1 H, d, J = 7.0), 1.20–1.80 (6 H, m), 2.00–2.40 (4 H, m); IR (thin film) 3080, 2920, 2850, 1450, 1240, 830 cm^{-1}. Anal. $C_{13}H_{28}O_2Si_2$: C, H.

Cyclooctane-1,3-dione (9). Anhydrous $FeCl_3$ (2.15 g, 13.3 mmol) was added to a solution of 1,7-bis(trimethylsiloxy)bicyclo[5.1.0]octane (0.92 g, 3.20 mmol) in dry DMF (3.0 mL) under a nitrogen atmosphere at room temperature. The dark brown suspension was stirred at 60 °C overnight (16 h). After cooling, the reaction was quenched into 10% aqueous HCl (25 mL) and extracted with $CHCl_3$ (4 × 25 mL). The combined organic layers were washed with 10% HCl (2 × 20 mL) and brine and then dried over $MgSO_4$. Filtraton and removal of the solvents in vacuo

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(58) Beckwith, A. L. J.; Blair, I. A.; Phillipou, G. *Tetrahedron Lett.* 1974, 2251.

afforded 0.459 g of crude product. The product was taken up in 30 mL ether and extracted with 3% aqueous KOH solution (3 × 20 mL). The aqueous layer was acidified with concentrated HCl, saturated with NaCl, and back-extracted with $CHCl_3$ (3 × 25 mL). Drying of the organic layer over $MgSO_4$ followed by filtration and removal of the solvents in vacuo gave 0.30 g (73%) of a colorless oil that was Kugelrohr distilled, bp 88 °C (3 Torr): ^1H NMR ($CDCl_3$) δ 1.5–1.9 (6 H, m), 2.3–2.6 (4 H, m), 3.5 (2 H, s); IR (thin film) 2920, 2850, 1650, 1380, 1250, 1090, 730, 650 cm^{-1}.

Alternative Procedure. A solution of periodic acid (0.390 g, 1.71 mmol) in absolute ethanol (3 mL) was cooled to −10 °C. To this was added a solution of 1,7-bis(trimethylsiloxy)bicyclo[5.1.0]octane (0.474 g, 1.66 mmol) in ethanol (3 mL). An orange color formed immediately. The reaction was stirred at −10 °C for 30 min, by which time the color had discharged. Following dilution with 30 mL of chloroform, the solution was washed with H_2O, 5% aqueous Na_2SO_3, and brine and then dried over $MgSO_4$. Filtration and removal of the solvents in vacuo gave 0.239 g of crude material, which was Kugelrohr distilled to give 0.153 g (65%).

3-Ethoxy-2-cycloocten-1-one (10). A solution of cyclooctane-1,3-dione (152 mg, 1.09 mmol) in 3.0 mL of DME was added to a suspension of potassium *tert*-butoxide (140 mg, 1.25 mmol) in 1.0 mL of DME at 0 °C. The orange suspension was stirred for 60 min; then a 1.2 M solution of triethyloxonium tetrafluoroborate in CH_2Cl_2 (1.1 mL, 1.32 mmol) was added. Stirring was continued for a further 30 min, by which time the color had discharged; then 5 mL of ether was added and the suspension filtered through a plug of alumina. Removal of the solvents in vacuo gave 132 mg (72%) of crude product. Flash chromatography through alumina using 50% ether/hexanes as eluent afforded 79.1 mg (43%) of the title compound (R_f 0.22): ^1H NMR ($CDCl_3$) δ 1.32 (3 H, t, J = 7.0), 1.40–1.90 (6 H, m), 2.80 (4 H, m), 3.80 (2 H, q, J = 7.0), 5.56 (1 H, s); IR (thinfilm) 2980, 2920, 1630, 1600, 1380, 1230 cm^{-1}; UV (cyclohexane) λ_{max} 245 nm (ϵ 12600), tail to 340 (106 at 320 nm); HRMS, m/z 168.1150 (M^+, calcd for $C_{10}H_{16}O_2$, 168.1150).

3-(3-Butenyloxy)-2-cycloocten-1-one (12). To a suspension of 370 mg (3.30 mmol) of potassium *tert*-butoxide in 2.0 mL of dry DME at −10 °C was added 387 mg (2.77 mmol) of cyclooctane-1,3-dione in 2.0 mL of dry DME. The resulting orange suspension was stirred for 40 min; then a solution of 780 mg (3.45 mmol) of 3-butenyl toluenesulfonate in 2.0 mL of dry DME was added. The reaction mixture was then heated at 60 °C for 24 h. After cooling, 25 mL of dry ether was added, the solution was filtered through a plug of alumina, and the solvents were removed in vacuo, to give 683 mg of crude product. Flash chromatography through alumina using 1:2 ether/hexanes as eluent afforded 353 mg (66%) of the title compound (R_f 0.15). Anal. $C_{12}H_{18}O_2$: C, H.

3-[(2-Methyl-3-butenyl)oxy]-2-cycloocten-1-one (13). The procedure described for **12** afforded 31% of the title compound: HRMS, m/z 208.1458 (M^+, calcd for $C_{13}H_{20}O_2$, 208.1463).

3-[(*E*)-3,5-Hexadienyloxy]-2-cycloocten-1-one (24). The procedure described for **12** afforded 12% of recovered tosylate and 133 mg (57%) of the title compound. Anal. $C_{14}H_{20}O_2$: C, H.

3-[((*E*)-4-Phenyl-3-butenyl)oxy]-2-cycloocten-1-one (26). The procedure described for **12** afforded 9.5 mg of recovered tosylate and 86.7 mg (60%) of the title compound: HRMS, m/z 270.1626 (M^+, calcd for $C_{18}H_{22}O_2$, 270.1620).

3-[(*E*)-3-Heptenyloxy]-2-cycloocten-1-one (31). To a stirring solution of cyclooctane-1,3-dione (693 mg, 4.95 mmol) in DME (15 mL) at 0 °C was added a 0.5 M solution of potassium hexamethyldisilazide (KHMDS) in toluene (9.9 mL, 4.95 mmol). The resulting orange suspension was stirred for 30 min; then a solution of 3-heptenyl toluenesulfonate (438 mg, 1.63 mmol) was added. The reaction was heated at 60 °C overnight (16 h), cooled, diluted with THF (20 mL), filtered through a plug of alumina, and washed through with THF (2 × 20 mL). The solvents were removed in vacuo to give 777 mg of crude product. Flash chromatography through alumina using 1:3 ether/hexanes as eluent yielded 83.8 mg of recovered tosylate and 283 mg (75%) of the title compound: HRMS, m/z 236.1774 (M^+, calcd for $C_{15}H_{24}O_2$, 236.1776).

4-Methyl-3-pentenyl Toluenesulfonate. Following the method of Wenkert,[59] dichloro[1,3-bis(diphenylphosphino)propane]nickel(II) (64.6 mg, 0.12 mmol) was dissolved in benzene (1.5 mL) and a 3.0 M solution of methylmagnesium bromide in ether (80 μL, 0.24 mmol) was added to reduce the catalyst. After stirring for 15 min, a further portion of methylmagnesium bromide (0.40 mL, 1.20 mmol) was added. The ether was removed by heating the resultant solution at 60 °C for 30 min; then benzene (1.0 mL) was added followed by 2-methyl-4,5-dihydrofuran (100 μL, 1.10 mmol). The reaction was heated at reflux for 24 h, cooled, and quenched into saturated aqueous NH_4Cl (10 mL). The product was extracted into ether (2 × 10 mL), dried over $MgSO_4$, filtered, and concentrated at atmospheric pressure. The crude product was dissolved in pyridine (0.5 mL) and added to a solution of p-toluenesulfonyl chloride (223 mg, 1.17 mmol) in pyridine (0.5 mL) at 0 °C. The reaction was stirred for 3 h and then placed in a refrigerator overnight. Following a quench into ice-cold 10% aqueous HCl, the product was extracted into ether (2 × 10 mL). The combined organic layers were washed successively with 5% aqueous $CuSO_4$ (5 mL), saturated aqueous $NaHCO_3$ (5 mL), and brine (5 mL) and then dried over $MgSO_4$. Filtration and removal of the solvents in vacuo gave 163 mg (58%) of the title compound: ^1H NMR ($CDCl_3$) δ 1.56 (3 H, br s), 1.66 (3 H, br s), 2.34 (2 H, q, J = 7.0), 2.45 (3 H, s), 3.98 (2 H, t, J = 7.0), 4.96 (1 H, br t, J = 7.2), 7.33 (2 H, d, J = 8.0), 7.79 (2 H, d, J = 8.0); IR (thin film) 2980, 2920, 1600, 1360, 1190, 1180, 960, 820, 660 cm^{-1}.

3-[(4-Methyl-3-pentenyl)oxy]-2-cycloocten-1-one (28). The procedure used for **31** afforded 56.6 mg (82%) of the title compound: HRMS, m/z 222.1619 (M^+, calcd for $C_{14}H_{22}O_2$, 222.1620).

3-[(3-Phenyl-3-butenyl)oxy]-2-cycloocten-1-one (35). The procedure described for **12** afforded 57.5 mg (22%) of recovered tosylate, 42.9 mg (16%) of recovered dione, and 134 mg (57%) of the title compound: HRMS, m/z 270.1617 (M^+, calcd for $C_{18}H_{22}O_2$, 270.1619).

(3-*tert*-Butyldimethylsiloxy)propanal (15). 3-Buten-1-ol (5.02 g, 69.7 mmol) was added to a solution of *tert*-butyldimethylchlorosilane (10.8 g, 71.7 mmol) and imidazole (4.79 g, 70.4 mmol) in 70 mL of CH_2Cl_2. The reaction was stirred for 90 min at room temperature, diluted with 150 mL of ether, washed successively with H_2O, 10% HCl, and brine, and then dried over $MgSO_4$. Removal of the solvents in vacuo gave 12.28 g (95%) of **1-(*tert*-butyldimethylsiloxy)-3-butene (14)**. A stream of ozone was bubbled through a solution of 1-(*tert*-butyldimethylsiloxy)-3-butene (10.12 g, 54.4 mmol) in 150 mL of MeOH at −35 °C until a pale blue color developed. Oxygen was allowed to bubble through the solution for 15 min to remove excess ozone. Dimethyl sulfide (10.0 mL) was added and the solution stirred as it warmed to room temperature over 3 h. The solvents were removed in vacuo to give 7.5 g (73%) of crude product. The crude residue was fractionally distilled through a Vigreux column to give 1.28 g of a mixture of product and *tert*-butyldimethylsilanol (bp 70–90 °C, 23 Torr), followed by 5.54 g (54%) of the title compound (bp 95 °C, 23 Torr): HRMS, m/z 187.1146 ($M^+ - H$, calcd for $C_9H_{19}O_2Si$, 187.1145), 132.0974 ($M^+ - C_4H_8$, calcd for $C_5H_{12}O_2Si$, 132.0974).

5-(*tert*-Butyldimethylsiloxy)-1-(trimethylsilyl)-2-pentene (17). Following the method of Fleming,[48] a 1.0 M solution of n-BuLi in hexanes (5.60 mL, 5.60 mmol) was added to a stirring suspension of methyltriphenylphosphonium bromide (1.83 g, 5.13 mmol) in 10.0 mL of THF at 0 °C over a period of 30 min. The suspension was warmed to 25 °C and stirred for 1 h to give an orange solution. After cooling to 0 °C, iodomethyltrimethylsilane (0.76 mL, 5.12 mmol) was added dropwise over 5 min. The reaction was then warmed slowly to 25 °C and stirring was continued for a further 1 h before cooling to −78 °C. A 1.6 M solution of n-BuLi in hexanes (3.50 mL, 5.60 mmol) was added, and the suspension was then warmed slowly to 25 °C and stirred for 1 h to give a deep red solution. After cooling to −78 °C, a solution of 3-(*tert*-butyldimethylsiloxy)propanal (0.92 g, 4.89 mmol) in 2.0 mL of THF was added over 10 min. The reaction was allowed to warm to 25 °C overnight, then was quenched into saturated aqueous NH_4Cl (25 mL) and extracted with ether (3 × 50 mL), and finally the organics were dried over $MgSO_4$. Removal of the solvents in vacuo gave 1.65 g of crude product. Flash chroma-

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(59) Wenkert, E.; Michelotti, E. L.; Swindell, C. S.; Tingoli, M. *J. Org. Chem.* 1984, *49*, 4894.

Table V. Solvent Dependence of Product Ratio for Photolysis of 21

solvent	yield (%) 23	yield (%) 22
cyclohexane	57	35
carbon tetrachloride	23	43
acetone	43	38
methanol	66	33

tography through silica using 1:5 ether/hexanes as eluent afforded 0.36 g (27%) of the title compound as a 9:1 mixture of *Z* and *E* isomers **a**/**b**: HRMS, *m*/*z* 215.1288 ($M^+ - C_4H_9$, calcd for $C_{10}H_{23}OSi_2$, 215.1288).

3-[[(*Z*)-5-(Trimethylsilyl)-3-pentenyl]oxy]-2-cycloocten-1-one (20). The procedure described for **12** afforded 28.7 mg (24%) of recovered tosylate and 35.5 mg (35%) of the title compound: HRMS, *m*/*z* 280.1856 (M^+, calcd for $C_{16}H_{28}O_2Si$, 280.1859).

3-[[(*E*)-5-(Trimethylsilyl)-3-pentenyl]oxy]-2-cycloocten-1-one. The procedure described for **12** afforded 14.9 mg of recovered tosylate and 82.9 mg (45%) of the title compound: ^1H NMR ($CDCl_3$) δ −0.03 (9 H, s), 1.42 (2 H, dd, *J* = 8.1, 1.1), 1.55–1.80 (6 H, m), 2.38 (2 H, dq, *J* = 6.9, 1.1), 2.76 (2 H, t, *J* = 7.3), 2.78 (2 H, t, *J* = 7.2), 3.72 (2 H, t, *J* = 6.8), 5.21 (1 H, dtt, *J* = 15.3, 8.2, 1.2), 5.50 (1 H, dtt, *J* = 15.3, 8.2, 1.4), 5.58 (1 H, s); IR (thin film) 3020, 2960, 1640, 1605, 1230, 1130, 860 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 201.2, 172.3, 129.6, 123.2, 108.6, 68.4, 41.5, 33.0, 32.1, 23.7, 23.3, 23.1, 22.8, −2.0; UV (cyclohexane) λ_{max} 245 nm (ϵ 14 100), 315 (70); HRMS, *m*/*z* 280.1856 (M^+, calcd for $C_{16}H_{28}O_2Si$, 280.1859).

3-[((*E*)-2-Methyl-3,5-hexadienyl)oxy]-2-cycloocten-1-one (30). The procedure described for **12** afforded 170 mg (55%) of recovered tosylate and 57.3 mg (33%) of the title compound. Anal. $C_{15}H_{22}O_2$: C, H.

3-(4-Pentenyl)-2-cycloocten-1-one (21). 3-Ethoxy-2-cycloocten-1-one (81.1 mg, 0.483 mmol) was dissolved in 2.0 mL of THF and cooled to 0 °C while being stirred under a nitrogen atmosphere. To this was added a 1.0 M solution of 4-pentenylmagnesium bromide in THF (0.97 mL, 0.97 mmol). The reaction was allowed to warm to room temperature overnight; then 0.5 mL of 10% aqueous HCl was added and stirring was continued for 30 min. Following dilution with 15 mL of ether and separation of the organic layer, the organics were washed with saturated brine and then dried over $MgSO_4$. Removal of the solvents in vacuo gave 115 mg of crude product. Flash chromatography through silica gel using 10% ethyl acetate/hexanes as eluent afforded 41.8 mg (45%) of the title compound (R_f 0.20): HRMS, *m*/*z* 192.1510 (M^+, calcd for $C_{13}H_{20}O$, 192.1514).

General Procedure for Photochemical Cycloadditions. A 0.01 M solution of enone in cyclohexane was degassed by the freeze–pump–thaw or positive displacement (with nitrogen or argon) methods in a base-washed quartz tube. The irradiation was performed in a Rayonet photoreactor at 350 nm (or 300 nm as indicated).

Photolysis of 3-(4-Pentenyl)-2-cycloocten-1-one (21) (Table V). Irradiation of 6.0 mg, 0.031 mmol, for 17 h and removal of solvents in vacuo gave 4.5 mg (75%) of crude product. GC and ^1H NMR analysis showed the presence of two compounds. HPLC using 10% ether/hexane as eluent afforded a separation of two β,γ enones: 3-(4-pentenyl)-3-cycloocten-1-one (**22**) and 3-(4-pentenylidene)cyclooctanone (**23**): IR (thin film) 3080, 2920, 2860, 1700, 1640, 1450, 915 cm^{-1}.

Preparative Photolyses of 3-[(*E*)-3,5-Hexadienyloxy]-2-cycloocten-1-one (24) (Table VI). Irradiation of 89.4 mg, 0.41 mmol, for 26 h and removal of solvents in vacuo gave 78.7 mg (88%) of crude product. GC analysis showed the presence of three products (retention time, yield: 7.55 min, 39%; 7.98 min, 29%; 8.09 min, 31%). Flash chromatography through silica gel using 2% ethyl acetate/benzene as eluent afforded 1.4 mg (1.6%) of the ring-expanded product (1R*,2R*)-2-ethenyl-11-oxabicyclo[8.3.0]tridec-9-en-4-one (**25d**), 6.0 mg (6.7%) of (1R*,8R*,12R*,13S*)-13-ethenyl-9-oxatricyclo[6.5.0.0^{8,12}]tridecan-2-one (**25a**), 7.8 mg (8.7%) of (1R*,8R*,12R*,13R*)-13-ethenyl-9-oxatricyclo[6.5.0.0^{8,12}]tridecan-2-one (**25b**), and 19.5 mg (21.8%) of a mixed fraction.

Table VI. Wavelength Dependence of Product Ratio for Photolysis of 24

wavelength, nm	25a	25b	25c
350	22	31	29
300	21	32	25
254	20	29	27

Preparative Photolyses of 3-[((*E*)-4-Phenyl-3-butenyl)oxy]-2-cycloocten-1-one (26). Irradiation of 40.0 mg, 0.15 mmol, for 26 h and removal of solvents in vacuo gave 47.0 mg of crude product. Flash chromatography through silica gel using 2% ethyl acetate/hexanes as eluent yielded 0.6 mg (1.5%) of the ring-expanded product (1R*,2S*)-2-phenyl-11-oxabicyclo[8.3.0]tridec-9-en-4-one (**27d**), 9.0 mg (22.5%) of a 3:1 mixture of (1S*,8R*,12R*,13R*)-13-phenyl-9-oxatricyclo[6.5.0.0^{8,12}]tridecan-2-one (**27c**) and (1R*,8R*,12R*,13S*)-13-phenyl-9-oxatricyclo[6.5.0.0^{8,12}]tridecan-2-one (**27a**), respectively, 8.3 mg (20.7%) of (1R*,8R*,12R*,13R*)-13-phenyl-9-oxatricyclo[6.5.0.0^{8,12}]tridecan-2-one (**27b**), and 5.6 mg of recovered starting material: IR (thin film) 3040, 2940, 2780, 1695, 1610, 1455, 1370, 1185, 1040, 760, 705 cm^{-1}.

Photolysis of 3-[(4-Methyl-3-pentenyl)oxy]-2-cycloocten-1-one (28). Irradiation of 13.7 mg, 0.06 mmol, for 7 days and removal of solvents in vacuo gave 7.4 mg of crude product. GC analysis showed the presence of three compounds. Flash chromatography through silica gel using 50% ether/hexanes as eluent afforded 0.3 mg (2.2%) of (1R*,8R*,12R*)-13,13-dimethyl-9-oxatricyclo[6.5.0.0^{8,12}]tridecan-2-one (**29**) and 1.4 mg (8%) of the photo–ene product (5S*,4R*)-4-(1-methylethenyl)-1-oxaspiro[4.7]dodecan-7-one (**30**).

Photolysis of 3-[(*E*)-3-Heptenyloxy]-2-cycloocten-1-one (31). Irradiation of 20.0 mg, 0.08 mmol, for 7 days and removal of solvents in vacuo gave 20.0 mg (100%) of crude residue. Flash chromatography through alumina using 2% ethyl acetate/benzene as eluent afforded 1.1 mg (5.5%) of a mixture of cycloadducts (1R*,8R*,12R*)-13-propyl-9-oxatricyclo[6.5.0.0^{8,12}]tridecan-2-one (**32a**/**b**) and 5.9 mg (29.5%) of recovered starting material: IR (thin film) 2960, 2940, 2880, 1700, 1455, 1360, 1155, 1040 cm^{-1}; HRMS, *m*/*z* 236.1780 (M^+, calcd for $C_{15}H_{24}O_2$, 236.1776).

Photolysis of 3-[((*E*)-2-Methyl-3,5-hexadienyl)oxy]-2-cycloocten-1-one (33). Irradiation of 21.6 mg, 0.092 mmol, for 5 h and removal of solvents in vacuo gave the crude product. Flash chromatography through silica gel using 25% ether/hexanes as eluent afforded 12.9 mg (60%) of a mixture of photoadducts. GC analysis showed the presence of five major compounds (retention time, yield; 8.70 min, 11%; 9.07 min, 16%; 9.23 min, 22%; 9.29 min, 31%; 9.49 min, 7%). A partial separation was achieved on repeated chromatography on silica gel using 25% ether/hexanes, giving 0.9 mg of cycloadduct **34a**, 3.4 mg of a mixture of adducts **34a**,**b**,**c**,**e**, and 8.6 mg of a mixture of **34b**,**c**,**d**,**e**. ^1H NMR analysis on the partially purified compounds allowed the identification of the following diastereomers: (1R*,8R*,12R*,13S*)-13-ethenyl-11-methyl-9-oxatricyclo[6.5.0.0^{8,12}]tridecan-2-one (**34a**/**b**), (1R*,8R*,12R*,13R*)-13-ethenyl-11-methyl-9-oxatricyclo[6.5.0.0^{8,12}]tridecan-2-one (**34c**/**d**), and (1S*,8R*,12R*,13R*)-13-ethenyl-11-methyl-9-oxatricyclo[6.5.0.0^{8,12}]tridecan-2-one (**34e**). Anal. $C_{15}H_{22}O_2$: C, H.

Photolysis of 3-[(3-Phenyl-3-butenyl)oxy]-2-cycloocten-1-one (35). Irradiation of 23.9 mg, 0.089 mmol, for 90 h and removal of solvents in vacuo gave 41.0 mg of crude product. Flash chromatography through silica gel using 50% ether/hexanes as eluent afforded 7.3 mg (31%) of (1S*,8R*,12S*)-12-phenyl-9-oxatricyclo[6.5.0.0^{8,12}]tridecan-2-one (**36**): HRMS, *m*/*z* 270.1617 (M^+, calcd for $C_{18}H_{22}O_2$, 270.1619).

Photolysis of 3-[((*Z*)-5-(Trimethylsilyl)-3-pentenyl)oxy]-2-cycloocten-1-one (20). Irradiation of 21.8 mg, 0.078 mmol, for 7 days and removal of solvents in vacuo gave 29.9 mg of crude material. Flash chromatography through silica gel using 20% ether/hexanes as eluent afforded 3.0 mg (14%) of a mixture of (1R*,8R*,12R*,13S*)-13-[(trimethylsilyl)methyl]-9-oxatricyclo[6.5.0.0^{8,12}]tridecan-2-one (**37a**) and (1R*,8R*,12R*,13R*)-13-[(trimethylsilyl)methyl]-9-oxatricyclo[6.5.0.0^{8,12}]tridecan-2-one (**37b**) and 3.7 mg (17%) of a mixture of starting material, (4R*,5S*)-4-[(*E*)-2-(trimethylsilyl)ethenyl]-1-oxaspiro[4.7]dodecan-7-one (**38a**), and (4R*,5S*)-4-[(*Z*)-2-(trimethylsilyl)-

ethenyl]-1-oxaspiro[4.7]dodecan-7-one (**38b**). GC and ^{1}H NMR analysis of the mixture of [2 + 2] adducts showed a 2:1 ratio of **37a**:**37b**. A similar analysis of the second fraction showed a 5:3:1.5 ratio of enone:**38a**:**38b**.

Photolysis of 3-[[(*E*)-5-(Trimethylsilyl)-3-pentenyl]oxy]-2-cycloocten-1-one. Irradiation of 75.4 mg, 0.269 mmol, was conducted for 11 days. Flash chromatography through silica gel using 20% ether/hexanes as eluent afforded 1.7 mg (2%) of a mixture of **37a** and **37b** and 19.5 mg (26%) of a mixture of **38a** and **38b**. GC and ^{1}H NMR analysis of the mixture of [2 + 2] adducts showed a 3:2 ratio of **37a**:**37b**. The second fraction showed a 1:1 ratio of **38a**:**38b**.

3-(3-Butenyloxy)-2-cyclohexen-1-one. Cyclohexane-1,3-dione (5.05 g, 43.7 mmol), 3-buten-1-ol (3.60 mL, 3.02 g, 41.8 mmol), and *p*-toluenesulfonic acid (0.41 g, 2.16 mmol) were heated at reflux in benzene (120 mL) in a Dean–Stark apparatus for 3 h. After cooling, the solvents were removed in vacuo. The crude residue was taken up in ether (100 mL), washed with 10% aqueous $NaHCO_3$ solution (20 mL) and brine (20 mL), and then dried over $MgSO_4$. Filtration and removal of the solvents in vacuo afforded 6.78 g (94%) of the title compound: ^{1}H NMR ($CDCl_3$) δ 1.90 (2 H, q, $J = 5.7$), 2.29 (6 H, m), 3.80 (2 H, t, $J = 6.6$), 5.01 (1 H, dq, $J = 9.8, 1.0$), 5.04 (1 H, dq, $J = 17.8, 10.0$), 5.29 (1 H, s), 5.72 (1 H, ddt, $J = 17.4, 9.7, 6.5$); IR (thin film) 3065, 2935, 2875, 1635, 1590, 1360, 1210, 1170, 920, 725 cm^{-1}; UV (cyclohexane) λ_{max} 237 nm (ϵ 17 800), 309 (40). Anal. $C_{10}H_{14}O_2$: C, H.

Photolysis of 3-(3-Butenyloxy)-2-cyclohexen-1-one. A solution of 3-(3-butenyloxy)-2-cyclohexen-1-one (4.06 g, 24.5 mmol) in cyclohexane (450 mL) was irradiated in an immersion well by using a Hanovia lamp through a Pyrex filter (300 nm). The solution was deoxygenated by bubbling nitrogen throughout the irradiation. Irradiation was maintained for 16 h, after which time the solvents were removed in vacuo to yield 3.92 g (97%) of (1*R**,5*S**,7*R**)-2-oxatricyclo[5.4.0.0^{1,5}]undecan-8-one (**39**).[60] GC analysis showed the product to be 82% pure. An analytical sample was prepared by Kugelrohr distillation (88 °C, 2.2 Torr). Anal. $C_{10}H_{14}O_2$: C, H.

3-[(*E*)-3,5-Hexadienyloxy]-2-cyclohexen-1-one. Cyclohexane-1,3-dione (148 mg, 1.32 mmol), (*E*)-3,5-hexadien-1-ol (57.6 mg, 0.59 mmol), and *p*-toluenesulfonic acid (2.0 mg, 0.01 mmol) were heated at reflux in benzene (10.0 mL) with azeotropic removal of water for 6 h. After cooling, the reaction was diluted with ether (25 mL), washed with 3% aqueous KOH solution (10 mL) and then with brine (10 mL), and finally dried over $MgSO_4$. Filtration and removal of the solvents in vacuo afforded 156 mg of crude product. Flash chromatography through silica gel using 1:2 ether/hexanes as eluent gave 110 mg (97%) of the title compound: ^{1}H NMR ($CDCl_3$) δ 1.98 (2 H, q, $J = 6$), 2.20–2.60 (6 H, m), 3.86 (2 H, t, $J = 7$), 5.03 (1 H, d, $J = 9$), 5.13 (1 H, d, $J = 16$), 5.33 (1 H, s), 5.66 (1 H, dt, $J = 15, 7$), 6.12 (1 H, dd, $J = 14, 10$), 6.32 (1 H, dt, $J = 16, 10$); IR (thin film) 3095, 2960, 2900, 1655, 1607, 1370, 1190, 1140, 1010 cm^{-1}; UV (cyclohexane) λ_{max} 225 nm (ϵ 40 900), 234 (40 500), 289 (64), 299 (63). Anal. $C_{12}H_{16}O_2$: C, H.

Photolysis of 3-[(*E*)-3,5-Hexadienyloxy]-2-cyclohexen-1-one. A solution of 3-[(*E*)-3,5-hexadienyloxy]-2-cyclohexen-1-one (12.2 mg, 0.06 mmol) in cyclohexane (6.40 mL) was degassed by the freeze–pump–thaw method in a base-washed quartz tube. The solution was irradiated in a Rayonet photoreactor at 350 nm at 25 °C for 7 h, and solvents were removed in vacuo. Flash chromatography through silica gel using 1:1 ether/hexanes as eluent afforded 6.1 mg (50%) of (1*R**,5*S**,6*R**,7*R**)-6-ethenyl-2-oxatricyclo[5.4.0.0^{1,5}]undecan-8-one (**40**). Anal. $C_{12}H_{16}O_2$: C, H.

(1*S,2*S**,8*R**,12*R**,13*R*/*S*)-13-Ethenyl-9-oxatricyclo[6.5.0.0^{8,12}]tridecan-2-ol (41a/b).** A 74-mg crude mixture of photoadducts **25a/b** was dissolved in 3.0 mL of THF and cooled to −78 °C. To this stirred solution was added a 1.0 M solution of L-Selectride in THF (0.40 mL, 0.40 mmol). The reaction was stirred for 3 h and then quenched by the addition of 1.0 mL of 15% aqueous NaOH, followed by 1.0 mL of 30% aqueous H_2O_2. The solution was allowed to warm to room temperature, stirred for 30 min, and diluted with 20 mL of ether. The aqueous layer was extracted with ether. The combined organic layer was washed with brine and dried over $MgSO_4$. Removal of the solvents in vacuo gave 71.6 mg of crude product. Flash chromatography through silica gel using 20% ether/hexanes as eluent afforded 23.8 mg (32.5%) of the title compounds: IR (thin film) 3460, 3080, 2940, 2860, 1635, 1460, 1040, 920 cm^{-1}.

(1*S,2*S**,8*R**,12*R**,13*S**)-13-Ethenyl-9-oxatricyclo[6.5.0.0^{8,12}]tridecan-2-ol *p*-Bromobenzoate (42).** A 1.4 M solution of MeLi in hexanes (40.0 μL, 0.056 mmol) was added to a stirring solution of **41a** in 1.5 mL of THF. After 30 min, a solution of *p*-bromobenzoyl chloride (30.4 mg) in 0.5 mL of THF was added. The reaction was stirred for 2 days, diluted with 20 mL of ether, washed with 5 mL of H_2O, 5 mL of 10% NaOH, and 5 mL of brine, and then dried over $MgSO_4$. Removal of the solvents in vacuo gave 14.7 mg (96%) of crude ester. Flash chromatography through silica gel using 10% ether/hexanes as eluent afforded 5.6 mg (37%) of the title compound (R_f 0.16), which was recrystallized from pentane at −10 °C: mp 102.4–104.2 °C.

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Supplementary Material Available: Description of solution of the X-ray structure of **42** and spectral data for compounds **12–15**, **17**, and **20–42** (25 pages); tables of calculated and observed structure factors (15 pages). Ordering information is given on any current masthead page.

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[60] Tamura, Y.; Ishibashi, H.; Kita, Y.; Ikeda, M. *J. Chem. Soc., Chem. Commun.* **1973**, 101.