Generation of [5.5.*n*] Tricyclic Ring Systems by Radical-Promoted Inter- and Intramolecular [3 + 2] Cycloadditions

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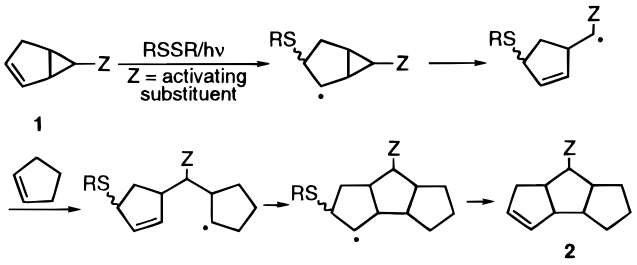
A new method for the synthesis of [5.5.*n*] tricyclic ring systems via radical fragmentation and double cyclization is described. The general process (Scheme 1) involves addition of an alkylthio radical to an alkenylcyclopropane **1** to generate the cyclopropylcarbinyl radical which opens to the homoallylic radical; this radical then adds to an alkene or alkyne radical trap to give a new alkyl radical which then adds back to the thioalkyl allylic system to generate, after loss of the alkylthio radical, the bi- or tricyclic product, **2**, thus making the process analogous to a [3 + 2] cycloaddition. Thus addition of the butylthio radical (generated by photolysis of dibutyl disulfide) to the bicyclo-[3.1.0]hex-2-en-6-yl carboxylate **3** in the presence of an alkene or alkyne—either an acyclic radical trap, e.g., ethyl vinyl ether, isopropenyl acetate, methyl acrylate, or methyl propiolate, or a cyclic one, e.g., cyclopentenone, dihydrofuran, cyclopentenyl acetate, or cyclopentene—affords the desired bi- or tricyclic products **9**−**16** in yields of 54−88%. One can also use 6-vinylbicyclo[3.1.0]hexan-2-one (**4**) as the alkenylcyclopropane unit. Trapping of the radical generated by addition of butylthio radical to **4** with ethyl vinyl ether or cyclopentene affords the bi- and tricyclic products **17** and **18** in 66−68% yields. The products are formed as diastereomeric mixtures in all cases. This cyclization process can also be carried out in an intramolecular fashion, e.g., isomerization of the ketones **25** and **27** or the esters **28**−**30** with butylthio radical to give the tricyclic products **31**−**35** and **41**−**43**. The use of dimethyl-substituted alkenes gives reasonably good diastereoselectivity favoring the cis-syn-cis isomer over the cis-anti-cis isomer, e.g., 7.5:1 for **33** over **34** and 4.2:1 for **41** over **42**. The structures of the diastereomeric products were proven by comparison of the NMR spectra of the saturated analogues, which are known for the unsubstituted series and differ in their symmetry properties for the dimethyl-substituted case. These results indicate that the cyclization of a stabilized 5-hexenyl radical, e.g., **45** in Scheme 8, is reversible and leads to the most stable final product.

Introduction

Both the basic understanding and the synthetic utilization of radical processes have increased dramatically in the last twenty years or so.[3] One of the most powerful methods in today's synthetic arsenal is radical cyclization and/or radical rearrangement−cyclization. A large number of natural products have been prepared using these radical cyclization methods. The initiation of radical cyclizations by fragmentation of a strained ring system beginning with the addition of a sulfur-centered radical to an alkene is a valuable method in organic synthesis.[4] Alkylthiyl radicals can be conveniently generated by photolysis of alkyl disulfides.[5] Normally in the absence of a reducing agent, e.g., any hydride source, longer radical lifetimes are achieved. This methodology has been applied most recently to the synthesis of cyclopentanes through radical reactions of vinylcyclopropanes.[6] To date, the sulfur radical-promoted cyclization of vinylcyclopropanes with alkenes has been designed to produce a single cyclopentane ring. We report herein the application of this methodology to the facile high-yielding preparation of [5.5.*n*] tricyclic ring systems **2** by designing the alkenylcyclopropane precursor as part of a 6-substituted bicyclo[3.1.0]hex-2-ene system of type **1** and by trapping the radical intermediate with cyclic alkenes to give a new alkyl radical which then cyclizes onto the original ring system and terminates with loss of the alkylthiyl radical, an approach that permits the rapid construction of fused-ring compounds of type **2** (Scheme 1).

Scheme 1



Results and Discussion

We reasoned that the alkenylcyclopropane starting materials should contain an activating substituent in

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(3) For excellent reviews, see: (a) Curran, D. P. Radical Cyclizations and Sequential Radical Reactions. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon; Oxford, 1991; Vol. 4, Chapter 4.2, pp 779−831. (b) Giese, B. *Radicals In Organic Synthesis: Formation of Carbon-Carbon Bonds*; Pergamon Press: Oxford, 1986.

(4) For an example, see: Naito, T.; Honda, Y.; Miyata, O.; Ninomiya, I. *Heterocycles* **1991**, *32*, 2319.

(5) Rao, P. M.; Knight, A. R. *Can. J. Chem.* **1968**, *46*, 2462.

(6) (a) Miura, K.; Fugami, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1988**, *29*, 5135. (b) Miura, K.; Fugami, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1988**, *29*, 1543. (c) Feldman, K. S.; Romanelli, A. L.; Ruckle, R. E.; Miller, R. F. *J. Am. Chem. Soc.* **1988**, *110*, 3300. (d) Feldman, K. S.; Romanelli, A. L.; Ruckle, R. E.; Jean, G. *J. Org. Chem.* **1992**, *57*, 100. (e) Singleton, D. A.; Church, K. M.; Lucero, M. J. *Tetrahedron Lett.* **1990**, *31*, 5551.

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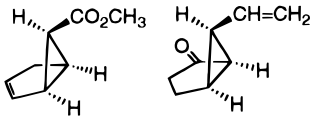
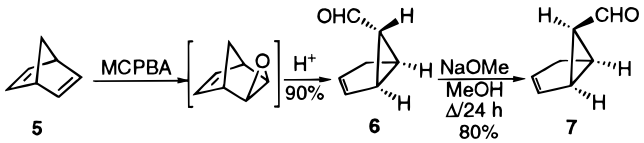
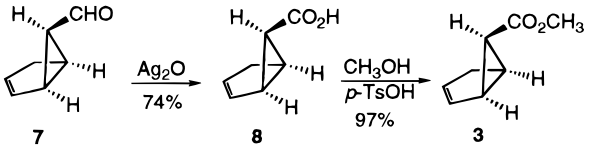
order to increase the ring-opening rate of the cyclopropylcarbinyl radical by stabilizing the resulting butenyl radical. Two known compounds of type **1** were identified which fulfilled this requirement: the ester **3**[7] and the ketone **4**.[8]



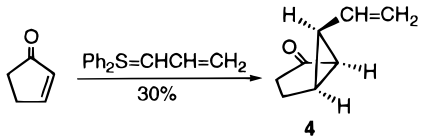
The bicyclo[3.1.0]hexenyl ester **3** was prepared in good yield in three steps from 2,5-bicyclo[2.2.1]heptadiene (**5**) (norbornadiene). The diene was treated with 1 equiv of *m*-CPBA; the initially formed epoxide opened and rearranged under the mildly acidic conditions to give endo-substituted aldehyde **6**.[9] This endo aldehyde **6** readily undergoes reversible Cope rearrangement to 2-oxa-



bicyclo[3.2.1]-3,6-octadiene,[10] and a mixture of the two compounds was clearly visible in the NMR spectrum. To prevent this rearrangement, the crude endo aldehyde **6** was treated with sodium methoxide in refluxing methanol for 24 h to convert it to the exo isomer **7** in 80% yield. Normally it is preferable to go directly from norbornadiene (**5**) to the exo aldehyde **7** without isolation of **6** in 72% isolated yield. This isomer is sterically incapable of performing the Cope rearrangement. The aldehyde **7** was treated with silver oxide to give the acid **8** which was then esterified to give the ester **3**. While we utilized the racemic compound in our studies, the optically active ester **3** may be obtained through chiral resolution of acid **8**.[7]

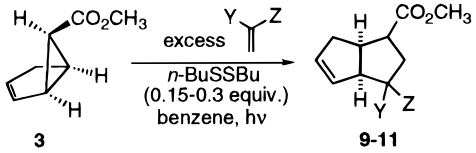


The cyclopropyl ketone **4** was prepared by the reaction of the sulfur ylide (made from *tert*-butyllithium and allylphenylbenzenesulfonium tetrafluoroborate) with cyclopentenone.[8] Only the exo isomer of the desired product is obtained in low yield.



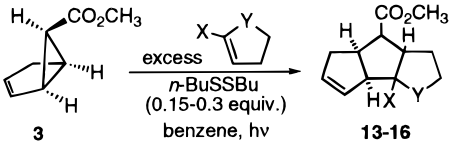
For our first test of the sulfur radical-promoted cyclization, a degassed benzene solution containing

Table 1. Cyclization Products from Alkylthiyl Radical-Promoted Ring Opening and Trapping with Simple Alkenes



alkene substituents (Y, Z)	compd	yield, %
OEt, H	**9**	88
$OCOCH_3$, CH_3	**10**	87
CO_2CH_3, H	**11**	54

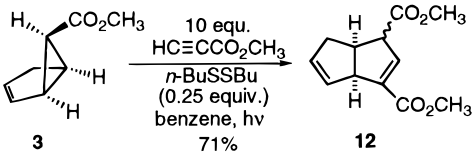
Table 2. Cyclization Products from Alkylthiyl Radical-Promoted Ring Opening and Trapping with Cyclic Alkenes



alkene substituents (X, Y)	compd	yield, %
H, C= O	**13**	83
H, O	**14**	83
$OCOCH_3$, CH_2	**15**	70[a]
H, CH_2	**16**	66[a]

[a] Based on recovered **3**.

cyclopropyl ester **3**, an alkene or alkyne trapping agent, and catalytic *n*-butyl disulfide was photolyzed using a medium-pressure mercury lamp. Table 1 shows the results of the reaction with various simple alkene traps. The desired cyclization product was obtained in high yield with most alkenes and with the single alkyne studied. In most cases, a mixture of four diastereomers was obtained. Compound **12**, generated from trapping of methyl propiolate, was obtained as a 1:1 mixture of two diastereomers. The tricyclic products that resulted from trapping with cyclic alkenes were obtained as four diastereomers, two with cis-syn-cis and two with cis-anti-cis ring junctions (Table 2). On the basis of Beckwith's studies of tin-mediated radical cyclizations yielding (5,5) and (5,6) ring systems,[11] we expected the cis ring fusions.

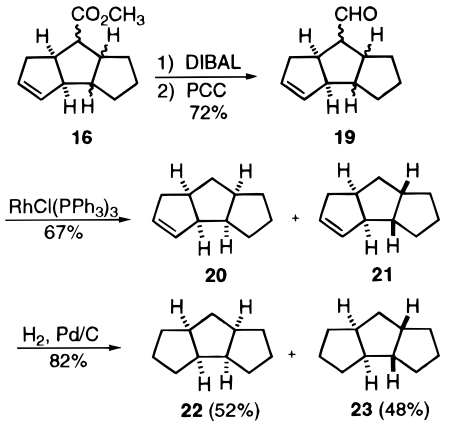


Many of the reactions were complete within 48 h, although up to 2 weeks of photolysis was required when less reactive alkenes were used as radical traps. However, with the two cyclic alkenes, 1-(acetyloxy)cyclopentene and cyclopentene, the reaction was incomplete even after 2 weeks. The yields reported are based on recovered starting material.

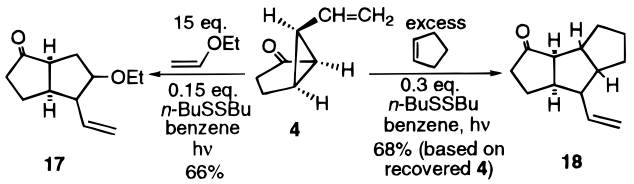
The cyclization of the cyclopropyl ketone **4** was performed with ethyl vinyl ether and cyclopentene. Both alkenes were trapped successfully, although the reaction with cyclopentene was only 40% complete after 2 weeks

(7) Garin, D. L.; Cooke, D. J. *J. Chem. Soc., Chem. Commun.* **1972**, 33.
(8) Hudlicky, T.; Koszyk, F. J.; Kutchan, T. M.; Sheth, J. P. *J. Org. Chem.* **1980**, *45*, 5020.
(9) Meinwald, J.; Labana, S. S.; Chadha, M. S. *J. Am. Chem. Soc.* **1963**, *85*, 582.
(10) Grigg, R.; Shelton, G. *J. Chem. Soc., Chem. Commun.* **1971**, 1247.
(11) Beckwith, A. L. J.; Phillipou, G.; Serelis, A. K. *Tetrahedron Lett.* **1981**, *22*, 2811.

Scheme 2



of photolysis. Products **17** and **18** were obtained as mixtures of four diastereomers.

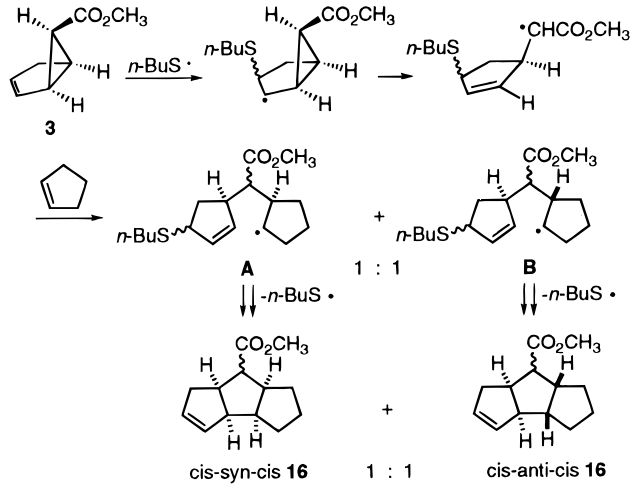


The structure and stereochemistry of the products was proven by transformation of the cyclopentene adduct **16** to the known triquinanes[12] **22** and **23** (Scheme 2). The ester **16**, obtained as a mixture of four diastereomers, was reduced to the corresponding alcohol with DIBAL and then oxidized to the aldehyde **19** with PCC in 72% yield for the two steps. The aldehyde **19** was then decarbonylated with Wilkinson's catalyst, tris(triphenylphosphine)rhodium(I) chloride, to provide the two alkenes **20** and **21** in 67% yield. After catalytic hydrogenation over Pd on carbon, a 52:48 mixture of the cis-syn-cis (**22**) and cis-anti-cis (**23**) triquinanes was obtained. These two products were distinguished by comparison with the published ^{13}C NMR spectra.[12]

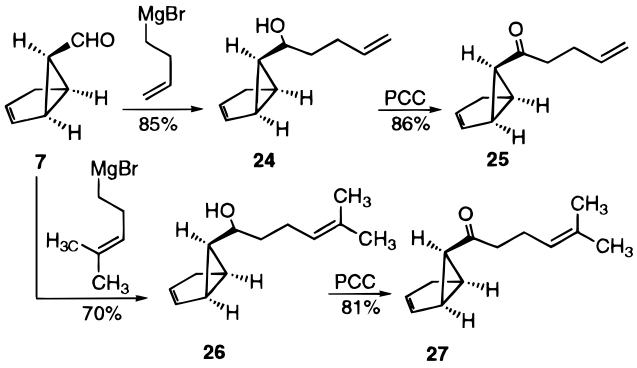
Nearly equal amounts of the two cis-fused adducts were obtained, indicating that the intermolecular trapping of the radical generated from ring opening of **3** with alkenes occurs with little or no stereocontrol. However, the subsequent cyclization occurs with good stereocontrol (caused by the preference for a cis ring fusion),[11] generating **16** as two pairs of cis-fused triquinanes in nearly equal amounts (Scheme 3).

We next studied the ring opening and trapping of a nonstabilized alkenylcyclopropane substrate. A solution of 3,7,7-trimethylbicyclo[4.1.0]hept-2-ene (2-carene), *n*-butyl disulfide, and ethyl vinyl ether was photolyzed for 4 days. Only unreacted starting material was recovered. As predicted, the rate of cyclopropylcarbinyl ring opening is significantly reduced by the inability to form an acyclic radical stabilized with an electron-withdrawing group. The rate of phenylthio-substituted cyclopropylcarbinyl radical reversion to alkylthiyl radical and vinylcyclopropane has been estimated[13] to be on the order of 10^8 s^{-1}, comparable to the ring-opening rate of a dimethyl-

Scheme 3



Scheme 4



substituted cyclopropylcarbinyl radical.[14] Addition of a stabilizing substituent such as an ester or phenyl group to a cyclopropylcarbinyl radical increases its ring-opening rate by a factor of 800−3000.[15] The presence of a stabilizing substituent is essential to induce the cyclopropylcarbinyl radical to open at a reasonable rate to allow intermolecular trapping of the acyclic radical intermediate.

While the tandem radical fragmentation−cyclization was successful, the lack of stereoselectivity was disappointing. We therefore turned to intramolecular tandem radical reactions hoping that the stereoselectivity of the reactions might be improved by tethering the alkenylcyclopropane system to the alkene trap. We therefore prepared several keto- and ester-substituted cyclopropyl alkenes as substrates. The two keto-substituted cyclopropanes **25** and **27** were prepared by a two-step route involving initially the Grignard addition of the organometallic reagent prepared from magnesium and 4-bromo-1-butene and 5-bromo-2-methyl-2-pentene to the aldehyde **7** to give the alcohols **24** and **26** in 85% and 70% yields respectively (Scheme 4). The intermediate alcohols were then oxidized with PCC to afford the ketones **25** and **27** in yields of 86% and 81%, respectively.

The three cyclopropyl esters **28**−**30** were also prepared by esterification of the acid **8** with allyl alcohol, 2-methyl-3-buten-2-ol, and 3-methyl-2-buten-1-ol (Scheme 5).

Each substrate was treated with catalytic *n*-butyl disulfide and photolyzed. Both keto-substituted cyclo-

(12) (a) Wu, T.-C.; Houk, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 5308. (b) Kakiuchi, K.; Takeuchi, H.; Tobe, Y.; Odaira, Y. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1613.

(13) Wagner, P. J.; Sedon, J. H.; Lindstrom, M. J. *J. Am. Chem. Soc.* **1978**, *100*, 2579.

(14) Newcomb, M.; Glenn, A. G.; Williams, W. G. *J. Org. Chem.* **1989**, *54*, 2675.

(15) (a) Newcomb, M.; Choi, S.-Y. *Tetrahedron Lett.* **1993**, *34*, 6363. (b) Newcomb, M.; Johnson, C. C.; Manek, M. B.; Varick, T. R. *J. Am. Chem. Soc.* **1992**, *114*, 10915.

Scheme 5

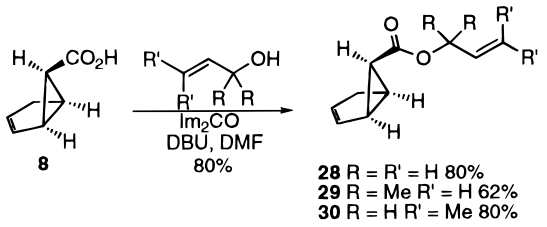
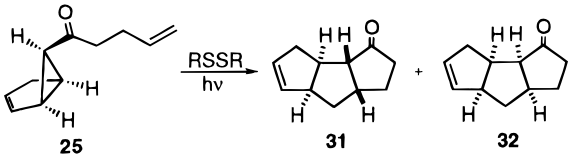
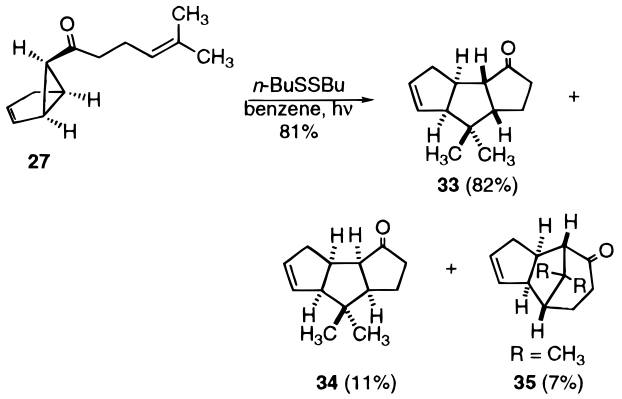


Table 3. Solvent Effect on Diastereomeric Ratio and Reaction Time for the Cyclization of 25



solvent	reaction time	product ratio (31:32)
benzene	7−12 days	65:35
DMSO	6 weeks	82:18

propanes cyclized upon photolysis, and some stereoselectivity was observed in these reactions. Ketone **25** afforded the cyclization product as two diastereomers, **31** and **32**. The major isomer was proven to be the cis-anti-cis compound **31** (see below). The effect of varying the

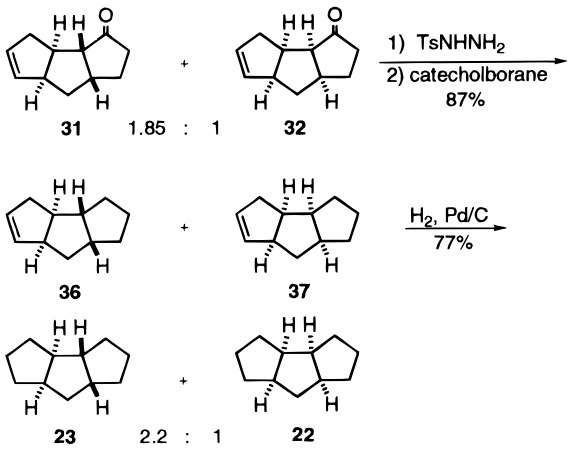


solvent and the disulfide catalyst utilized in the cyclization of **25** was also studied (Table 3). The reaction was run under the same conditions in degassed DMSO and benzene. The cyclization proceeded over three times more slowly in DMSO. However, the diastereomeric ratio was improved; the cis-anti-cis product **31** comprised 82% of the product from the cyclization in DMSO, compared to the 65% obtained in benzene. This is an intriguing result, since radical reactions typically are not subject to solvent effects. However, the long reaction times required to complete the cyclization discouraged us from pursuing this observed solvent effect further.

Cyclization of the keto substrate **27**, in which the keto-substituted cyclopropane was tethered to a trisubstituted alkene, afforded the desired adduct (81%) as a mixture of three isomers **33**−**35**. The stereoselectivity of this reaction was even higher than that in the reaction of **25**. The cis-anti-cis isomer **33** was preferentially formed as 82% of the product mixture. The second isomer (11%) was identified as the cis-syn-cis isomer **34**, while the minor product (7%) was tentatively identified as **35**.

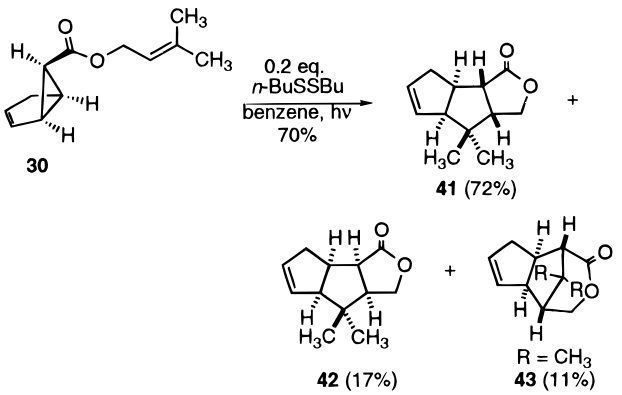
The stereochemistry of the major isomers in both keto-substituted adducts was determined by conversion of the products to the corresponding unsubstituted triquinanes (Scheme 6). The mixture of diastereomeric ketones **31**

Scheme 6

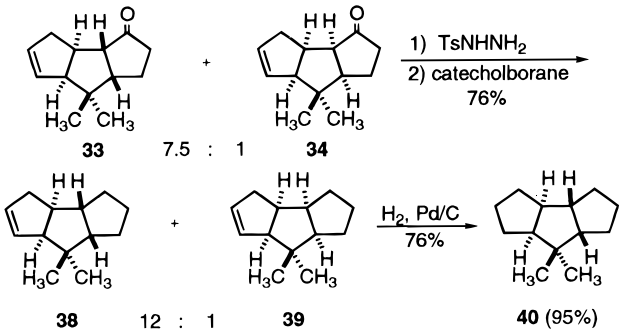


and **32** was deoxygenated by conversion to the tosylhydrazones and treatment with catecholborane to afford a mixture of the alkenes **36** and **37**. The alkene mixture was hydrogenated to give the known triquinanes **23** and **22** in a 2.2:1 ratio favoring the cis-anti-cis isomer **23**. The two isomers were distinguished by comparison with the reported ^{13}C NMR spectra.[12] The dimethyl-substituted adduct containing isomers **33** and **34** was similarly deoxygenated, giving the alkenes **38** and **39** in a 12:1 ratio. The structure of the third isomer was unassignable, as it was a minor component of the product mixture. The alkene mixture was hydrogenated, producing the nearly pure cis-anti-cis compound **40** (Scheme 7). While the dimethyl-substituted triquinane was not known in the literature, the two diastereomers could be distinguished from the ^{13}C NMR spectrum. The cis-anti-cis compound has a C_2 axis of symmetry, so both methyl groups are equivalent and seven peaks are expected. The cis-syn-cis isomer has a plane of symmetry cutting through the two methyl groups and thus these groups are not equivalent and eight peaks are expected. The ^{13}C NMR spectrum of **40** contained only seven peaks, confirming our assignment.

The photolysis of the ester-activated alkenylcyclopropanes produced mixed results. The substrates tethered to terminal alkenes **28** and **29** failed to cyclize after 2 weeks of photolysis. The compound bearing a trisubstituted alkene as the radical trap, **30**, cyclized within 60 h to give a mixture of three isomers (**41**−**43**). The stereochemical assignments were based on those determined for cyclization of the keto-substituted analog. The major isomer, the cis-anti-cis compound **41**, comprised 72% of the product. The cis-syn-cis isomer **42** was obtained as 17% of the product. The identification of the minor compound **43** (11%) is tentative.



Scheme 7

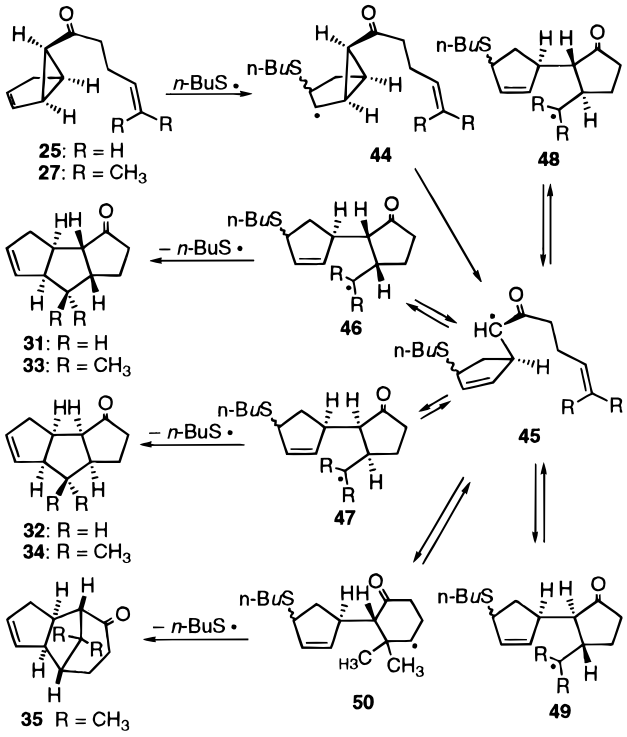


The appearance of a minor third product from intramolecular trapping with trisubstituted alkenes was unexpected. We assumed that the minor product was derived either from 6-endo cyclization or from trans ring fusion. Calculations of the relative energies of the possible products revealed that the 6-endo cyclization adduct is 1.5 kcal/mol more stable than the most stable trans-fused product.[16] Cyclization of an unsubstituted 5-hexenyl radical is kinetically controlled and gives a 98:2 ratio of methylcyclopentane and cyclohexane.[17] However, a literature survey revealed that the cyclization of keto- and ester-stabilized 5-hexenyl radicals frequently affords significant amounts of the 6-endo cyclization product.[18] Therefore, we tentatively assigned the structures **35** and **43**, derived from 6-endo cyclization, to the minor products.

While we observed minor amounts of the 6-endo cyclization product from the reaction of **27** and **30**, only 5-exo cyclization products were observed from the trapping of a keto-stabilized radical intermediate with a terminal alkene. A reasonable explanation is that the terminal methyl groups stabilize the intermediate radical obtained from the initial 5-exo cyclization, increasing its lifetime and, therefore, the reversibility of the cyclization. This reversibility leads to the formation of minor amounts of 6-endo cyclization product.

The preference for cis-anti-cis stereochemistry in our intramolecular tandem cyclizations is set by the first 5-exo cyclization. This stereocontrol could be due to either of two factors: stereochemical induction during alkene trapping by the stereocenter on the cyclopentene ring or the achievement of the most energetically favorable stereochemistry through a reversible cyclization of the keto-stabilized 5-hexenyl radical. Our results clearly show that no stereocontrol is achieved during intermolecular trapping of similar keto- and ester-stabilized bicyclo[3.1.0]hexenes. Therefore, stereoinduction cannot explain our results. Because cyclization of the keto- or ester-stabilized 5-hexenyl radical is reversible, the most energetically favorable stereoisomer is preferentially formed. The five potential radical intermediates **46**−**50** from the cyclization of the radical **45** generated by addition of the butylthio radical to the substrates **25** and **27** are shown (Scheme 8). Intermediates **46** and **47** lead to the two potential cis-fused products, while **48** and **49** lead to the less energetically favorable trans-fused isomers. The reversibility of the 5-exo cyclization permits

Scheme 8



intermediates **48** and **49** to revert to **45**. So while these two intermediates are probably formed, the trans-fused products are not observed. Instead, the lowest-energy intermediate, **46**, is preferentially formed. This intermediate undergoes a second cyclization in which the stereochemistry is controlled by the preference for cis ring fusion; therefore, **31** and **33** are the major products obtained. The cyclization of **47** is slower than that of **46**, because products **32** and **34** are higher in energy than **31** and **33**. Because **47** has a longer lifetime than **46**, it is more likely to revert to **45**. This is the source of the observed cis-anti-cis selectivity. In the cyclization of **27**, intermediate **50**, corresponding to the product of a 6-endo cyclization, usually reverts to **45** but occasionally cyclizes to give **35**.

Stereocontrol in radical reactions is an area of current interest.[19] While there are many examples of stereoselectivity in radical reactions caused by steric and conformational factors, very little has been reported concerning stereocontrol through reversible radical cyclization. Our results, therefore, represent a relatively unrecognized method for achieving stereoselective radical cyclizations.

Experimental Section

^{1}H and ^{13}C NMR were recorded on Bruker AM-360 and AMX-400 spectrometers. Infrared spectra were recorded on a Nicolet 510 infrared spectrophotometer as a liquid film (neat). High-resolution mass spectra (MS) were recorded on a VG Analytical Autospec double-focusing instrument. All mass spectra are electron impact unless otherwise noted. Gas chromatographic analyses were performed using a Hewlett-Packard 5790A Series chromatograph equipped with an SE-30 crosslinked methyl silicone gum column (12 m × 0.2 m × 0.33 mm film thickness).

(16) MM2 minimizations were performed using PC Model, version KS 2.95, on a VAX datastation (Houk Computational Installation Organet Cluster, UCLA).

(17) Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron* **1985**, *41*, 3925.

(18) (a) Julia, M.; Maumy, M. *Bull. Soc. Chim. Fr.* **1966**, 434. (b) Julia, M.; Maumy, M. *Bull. Soc. Chim. Fr.* **1969**, 2427. (c) Curran, D. P.; Chang, C.-T. *Tetrahedron Lett.* **1987**, *28*, 2477.

(19) For recent reviews, see: (a) Rajanbabu, T. V. *Acc. Chem. Res.* **1991**, *24*, 139. (b) Porter, N. A.; Giese, B.; Curran, D. P. *Acc. Chem. Res.* **1991**, *24*, 296. (c) Giese, B. *Angew. Chem., Intl. Ed. Engl.* **1989**, *28*, 969.

(20) LaRochelle, R. W.; Trost, B. M.; Krepski, L. *J. Org. Chem.* **1971**, *36*, 1126.

The following solvents and reagents were distilled from the indicated agent under dry nitrogen: tetrahydrofuran, diethyl ether, and benzene from sodium benzophenone ketyl; hexane, dichloromethane, and chloroform from calcium hydride. Dimethyl sulfoxide was distilled from calcium hydride under reduced pressure and dried over 4 Å molecular sieves.

All reactions were performed under an inert atmosphere of argon.

(±)-1,5α-Bicyclo[3.1.0]hex-2-ene-6β-carboxaldehyde (7).[10] *m*-CPBA (68.7%, 21.81 g, 86.82 mmol) was added in portions over 1 h to a 0 °C solution of 2,5-bicyclo[2.2.1]heptadiene (**5**) (norbornadiene, 8.00 g, 86.82 mmol) in 300 mL of dichloromethane. The resulting mixture was stirred for 2 h and filtered. The precipitated acid was washed thoroughly with dichloromethane, and the organic layer was evaporated. To the resulting oil were added 100 mL of methanol and 7 g of sodium methoxide. The mixture was refluxed for 24 h and cooled. Water (150 mL) was added, and the solution was extracted twice with ether. The organic layer was washed with water and sodium chloride solution, dried ($MgSO_4$), and evaporated to afford 6.8 g (72%) of the aldehyde **7** as a yellow oil. When desired, the oil was purified by Kugelrohr distillation: bp 163−165 °C; ^{1}H NMR ($CDCl_3$) δ 9.29 (d, J = 4.5 Hz, 1 H), 5.93 (dt, J = 2.0, 5.5 Hz, 1 H), 5.57 (dd, J = 2.6, 5.5 Hz, 1 H), 2.75 (bdd, J = 6.7, 19.0 Hz, 1 H), 2.57 (m, 1 H), 2.48 (dd, J = 2.2, 19.0 Hz, 1 H), 2.35 (m, 1 H), 1.23 (dd, J = 2.6, 2.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 201.3, 132.5, 131.7, 41.1, 36.9, 36.1, 27.7.

(±)-1,5α-Bicyclo[3.1.0]hex-2-ene-6β-carboxylic Acid (8).[10] The aldehyde **7** (4.00 g, 36.99 mmol) was dissolved in 23 mL of 95% ethanol. A solution of silver nitrate (21.30 g, 125.30 mmol) in 55 mL of distilled water was added. Sodium hydroxide solution (99 mL of 2 M solution, 190.00 mmol) was added dropwise to the colorless solution over 1 h. The resulting dark mixture was stirred at room temperature for 4 h and filtered. The dark solid was thoroughly washed with water. The aqueous layer was washed with ether, acidified to pH 1, and extracted twice with ether. The organic layer was washed with water and sodium chloride solution, dried ($MgSO_4$), and evaporated to give 3.4 g (74%) of the acid **8** as a pale yellow solid: mp 78−79 °C; ^{1}H NMR ($CDCl_3$) δ 11.36 (bs, 1 H), 5.91 (dt, J = 2.0, 5.5 Hz, 1 H), 5.54 (dd, J = 2.3, 5.5 Hz, 1 H), 2.70 (tdd, J = 2.0, 6.9, 18.6 Hz, 1H), 2.51−2.43 (m, 2 H), 2.28 (m, 1 H), 0.944 (dd, J = 2.2, 2.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 180.9, 132.6, 131.5, 36.9, 36.1, 30.9, 27.8.

(±)-Methyl 1,5α-bicyclo[3.1.0]hex-2-ene-6β-carboxylate (3).[7] The acid **8** (2.0 g, 16.11 mmol) was dissolved in 75 mL of dry methanol and 25 mL of 2,2-dimethoxypropane. *p*-Toluenesulfonic acid (0.65 g, 4.00 mmol) was added, and the resulting solution was stirred at room temperature for 24 h. Ether and water were added, and the extracted organic layer was washed with water and sodium chloride solution, dried ($MgSO_4$), and evaporated to provide 2.15 g (97%) of the ester **3** as a pale yellow oil: ^{1}H NMR ($CDCl_3$) δ 5.88 (m, 1H), 5.51 (m, 1 H), 3.62 (s, 3 H), 2.68−2.13 (m, 4 H), 0.949 (dd, J = 2.4, 2.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 174.6, 132.8, 131.2, 52.3, 36.9, 35.2, 30.8, 26.9.

(±)-6β-Ethenyl-1,5α-bicyclo[3.1.0]hexan-2-one (4).[8] *tert*-Butyllithium (15.54 mL of a 1.7 M solution in pentane, 26.42 mmol) was added to a pale gray mixture of allylphenylbenzenesulfonium tetrafluoroborate[20] (8.30 g, 26.42 mmol) in 100 mL of tetrahydrofuran at −78 °C. The resulting dark yellow solution was stirred for 0.5 h, and cyclopentenone (2.17 g, 26.42 mmol) was added dropwise. The reaction was warmed to 25 °C after 1 h. The reaction was stirred for another 2 h, quenched with water, and extracted with ether. The organic layer was washed with water and sodium chloride solution and then dried ($MgSO_4$). The solvent was removed under reduced pressure, and the resulting oil was chromatographed (10% ether in pentane) to afford **4** (0.97 g, 30%) as a colorless oil. The NMR spectra were consistent with those reported in the literature.[8]

Sulfur Radical-Mediated Cyclizations: General Procedure. The cyclopropane, trapping agent, and disulfide were combined in degassed solvent and photolyzed at room temperature using a Hanovia model 73A36 550W medium-pressure mercury lamp. Reactions were monitored by GC for completion and diastereomer ratios. When complete, excess trapping agent and solvent were removed under reduced pressure and the residue was chromatographed (5% ether in pentane) to afford the cyclization product.

Methyl 3-Ethoxy-1,2,3,3a,6,6a-hexahydropentalene-1-carboxylate (9). The cyclopropyl ester **3** (0.10 g, 0.72 mmol), ethyl vinyl ether (0.52 g, 7.24 mmol), and *n*-butyl disulfide (0.021 g, 0.12 mmol) were combined in 2 mL of degassed benzene. The solution was photolyzed for 12 h. Chromatography afforded **9** (0.14 g, 88%) as a colorless oil consisting of four partially separable diastereomers in a ratio of 3.3:2.2:2.0:1.0: ^{1}H NMR ($CDCl_3$) diastereomers 1−3 (inseparable mixture, 77%): δ 5.71−5.48 (m, 2 H), 3.98−3.37 (m, 2 H), 3.64 (s, 3 H), 3.15−1.18 (m, 11 H); diastereomer 4 (23%), δ 5.76 (m, 1 H), 5.57 (m, 1 H), 3.84 (m, 1 H), 3.68 (s, 3 H), 3.54 (q, J = 6.5 Hz, 2 H), 3.30−1.18 (m, 10 H); ^{13}C NMR ($CDCl_3$) diastereomer 1 (38%), δ 175.6, 132.4, 131.1, 84.2, 64.4, 58.7, 52.1, 47.4, 41.6, 36.8, 31.9, 16.2; diastereomer 2 (26%), δ 177.3, 131.6, 130.0, 81.6, 65.8, 54.8, 52.5, 49.7, 44.1, 41.3, 35.5, 16.2; diastereomer 3 (12%), δ 174.7, 133.0, 129.6, 82.2, 65.9, 52.6, 52.2, 45.3, 41.1, 38.2, 31.6, 16.2; diastereomer 4 (23%), δ 175.7, 132.7, 130.8, 85.3, 65.0, 58.3, 50.2, 43.4, 39.6, 36.8, 36.0, 16.2; IR (neat) 1734 (s), 1198 (s), 1123 (bs) cm^{-1}; CI HRMS m/z calcd for $C_{12}H_{18}O_3$ 210.1256, found 210.1251.

Methyl 3-(Acetyloxy)-1,2,3,3a,6,6a-hexahydro-3-methylpentalene-1-carboxylate (10). The cyclopropyl ester **3** (0.10 g, 0.72 mmol), isopropenyl acetate (1.09 g, 10.86 mmol), and *n*-butyl disulfide (0.019 g, 0.11 mmol) were combined in 2.5 mL of degassed benzene. After 2 days of photolysis, the reaction was worked up as described above to give 0.15 g (87%) of **10** as a colorless oil consisting of four inseparable diastereomers in a ratio of 1.9:1.6:1.1:1.0: ^{1}H NMR ($CDCl_3$) (diastereomeric mixture) δ 5.62−5.40 (m, 2 H), 3.61 (s, 3 H), 1.93 (s, 0.5 H), 1.91 (s, 1.1 H), 1.89 (s, 0.6 H), 1.87 (s, 0.8 H), 1.53 (s, 0.5 H), 1.45 (s, 1.7 H), 1.40 (s, 0.8 H), 3.00−1.57 (m, 7 H); ^{13}C NMR ($CDCl_3$) diastereomer 1 (35%), δ 174.9, 171.1, 133.0, 129.9, 91.7, 60.3, 52.1, 46.6, 42.1, 39.3, 36.9, 23.2, 21.0; diastereomer 2 (28%), δ 176.0, 171.1, 132.0, 130.6, 90.7, 61.4, 50.7, 43.4, 42.7, 40.6, 39.3, 22.9, 21.8; diastereomer 3 (19%), δ 177.1, 171.1, 131.6, 130.2, 89.4, 66.5, 50.0, 44.6, 42.7, 40.6, 36.9, 25.2, 23.0; diastereomer 4 (18%), δ 174.4, 170.9, 132.9, 130.5, 87.6, 63.2, 52.4, 45.2, 40.7, 37.8, 36.9, 25.5, 22.5; IR (neat) 1732 (s), 1175 (bs), 1090 (m) cm^{-1}; CI HRMS m/z calcd for $C_{13}H_{19}O_4$ 239.1263 (MH^+), found 239.1242 (MH^+).

Dimethyl 1,2,3,3a,6,6a-Hexahydropentalene-1,3-dicarboxylate (11). The cyclopropyl ester **3** (0.075 g, 0.62 mmol), methyl acrylate (0.53 g, 6.15 mmol), and *n*-butyl disulfide (0.033 g, 0.19 mmol) were combined in 3 mL of degassed benzene. After 2 days of photolysis, the product was purified as usual to provide 0.075 g (54%) of **11** as a colorless oil. The product was composed of three partially separable diastereomers in a ratio of 1.2:1.1:1.0: ^{1}H NMR ($CDCl_3$) (diastereomeric mixture) δ 5.73−5.40 (m, 2 H), 3.67 (s, 6 H), 3.00−1.62 (m, 8 H); ^{13}C NMR ($CDCl_3$) diastereomer 1 (33%), δ 176.9, 174.9, 132.7, 131.9, 54.1, 52.6, 51.8, 47.5, 45.2, 41.2, 34.9, 31.8; diastereomer 2 (31%), δ 176.7, 175.0, 133.9, 133.0, 55.0, 52.2, 52.1, 49.0, 48.5, 43.0, 36.7, 30.4; diastereomer 3 (36%), δ 174.5, 174.1, 133.8, 129.6, 52.8, 52.3, 52.2, 48.8, 48.4, 42.3, 37.6, 28.7; IR (neat) 1736 (s), 1167 (m), 1024 (m) cm^{-1}; HRMS m/z calcd for $C_{12}H_{16}O_4$ 224.1048, found 224.1048.

Dimethyl 1,3a,6,6a-Tetrahydropentalene-1,3-dicarboxylate (12). The cyclopropyl ester **3** (0.060 g, 0.43 mmol), methyl propiolate (0.36 g, 4.34 mmol), and *n*-butyl disulfide (0.019 g, 0.11 mmol) were combined in 2 mL of degassed benzene. After 2 weeks of photolysis, the product was chromatographed to afford 0.069 g (71%) of the diester **12** as a colorless oil which was a mixture of two diastereomers in a 1.2:1.0 ratio by GC analysis: ^{1}H NMR ($CDCl_3$) diastereomer 1 (55%), δ 6.60 (dd, J = 1.8, 2.2 Hz, 1 H), 5.85 (m, 1 H), 5.69 (m, 1 H), 4.05 (m, 1 H), 3.76 (s, 3 H), 3.72 (s, 3 H), 3.45−3.30 (m, 2 H), 2.80−2.24 (m, 2 H); diastereomer 2 (45%), δ 6.62 (dd, J = 2.0, 2.1 Hz, 1 H), 5.72 (m, 1 H), 5.42 (m, 1 H), 3.85−3.61 (m, 2 H), 3.76 (s, 3 H), 3.72 (s, 3 H), 2.66−2.47 (m, 3 H); ^{13}C NMR ($CDCl_3$) diastereomer 1, δ 173.3, 164.8, 139.8, 138.9, 130.9, 129.6, 58.6, 57.1, 52.1, 51.5, 43.2, 39.6; diastereomer 2, δ 172.1, 165.0, 140.5, 138.0, 131.5, 128.6, 53.6, 51.7, 51.4, 50.6,

46.6, 37.8; IR (neat) 1743−1719 (bs), 1260 (s), 1100 (s) cm^{-1}; HRMS *m/z* calcd for $C_{12}H_{14}O_4$ 222.0892, found 222.0889.

Methyl 2,3,3a,3b,6,6a,7,7a-Octahydro-3-oxo-1*H*-cyclopenta[*a*]pentalene-7-carboxylate (13). The cyclopropyl ester **3** (0.50 g, 3.62 mmol), cyclopentenone (1.19 g, 14.50 mmol), and *n*-butyl disulfide (0.52 g, 2.90 mmol) were combined in 5 mL of degassed benzene. After 4 days of photolysis, chromatography afforded 0.66 g (83%) of **13** as a colorless oil consisting of three partially separable diastereomers in a ratio of 1.2:1.1:1.0: ^{1}H NMR ($CDCl_3$) (diastereomeric mixture) δ 5.65−5.62 (m, 2 H), 3.72 (s, 1.1 H), 3.71 (s, 1.0 H), 3.69 (s, 0.9 H), 3.10−1.57 (m, 11 H); ^{13}C NMR ($CDCl_3$) diastereomer 1 (36%), δ 221.1, 174.5, 134.6, 129.4, 57.7, 55.3, 54.8, 52.4, 45.7, 43.3, 40.0, 38.5, 24.1; diastereomer 2 (34%), δ 221.8, 174.2, 135.3, 130.9, 60.2, 57.7, 53.7, 53.2, 45.6, 42.6, 38.1, 36.1, 23.2; diastereomer 3 (31%), δ 221.6, 173.9, 132.4, 131.3, 57.7, 57.6, 52.4, 52.2, 47.1, 43.4, 41.3, 39.5, 25.1; IR (neat) 1732 (bs), 1169 (bs) cm^{-1}; HRMS *m/z* calcd for $C_{13}H_{16}O_3$ 220.1100, found 220.1100.

Methyl 2,3,3a,4,4a,5,7a,7b-Octahydropentaleno[1,2-*b*]furan-4-carboxylate (14). The cyclopropyl ester **3** (0.075 g, 0.54 mmol), 2,3-dihydrofuran (0.31 g, 4.34 mmol), and *n*-butyl disulfide (0.064 g, 0.36 mmol) were combined in 1.5 mL of degassed benzene and photolyzed for 7 days. Purification afforded 0.094 g (83%) of **14** as four partially separable diastereomers in a ratio of 2.0:1.7:1.0:1.0: ^{1}H NMR ($CDCl_3$) diastereomers 1−3 (inseparable mixture, 70%), δ 5.74−5.56 (m, 2 H), 3.98−3.76 (m, 2 H), 3.68 (s, 3 H), 3.60−1.58 (m, 9 H); diastereomer 4 (30%), δ 5.72 (m, 1 H), 5.65 (m, 1 H), 4.54 (t, J = 8.0 Hz, 1 H), 3.94 (dt, J = 2.0, 8.3 Hz, 1 H), 3.70 (s, 3 H), 3.68 (m, 2 H), 3.26−1.65 (m, 7 H); ^{13}C NMR ($CDCl_3$) diastereomer 1 (35%), δ 174.2, 131.1, 130.6, 89.1, 67.3, 56.3, 52.7, 51.4, 44.8, 44.7, 35.5, 29.8; diastereomer 2 (18%), δ 174.2, 129.5, 129.0, 86.8, 68.0, 55.0, 54.8, 51.7, 49.8, 44.8, 37.9, 30.5; diastereomer 3 (17%), δ 173.6, 131.0, 130.5, 85.3, 70.6, 54.2, 51.3, 47.3, 46.6, 43.3, 38.0, 29.5; diastereomer 4 (30%), δ 175.6, 132.2, 129.6, 85.7, 68.4, 58.5, 52.7, 47.8, 46.2, 41.8, 37.6, 29.3; IR (neat) 1736 (s), 1175 (bs), 1063 (m) cm^{-1}; HRMS *m/z* calcd for $C_{12}H_{16}O_3$ 208.1100, found 208.1101.

Methyl 3b-(Acetyloxy)-3a,3b,4,5,6,6a,7,7a-octahydro-1*H*-cyclopenta[*a*]pentalene-7-carboxylate (15). The cyclopropyl ester **3** (0.080 g, 0.58 mmol), 1-(acetyloxy)cyclopentene[21] (0.73 g, 5.79 mmol), and *n*-butyl disulfide (0.023 g, 0.13 mmol) were combined in 2 mL of degassed benzene. After 2 weeks of photolysis, the reaction was worked up as above to yield 0.024 g of recovered starting material and 0.075 g of **15** (70% based on recovered starting material) as a colorless oil consisting of three inseparable diastereomers in a ratio of 1.9:1.6:1.0: ^{1}H NMR ($CDCl_3$) (diastereomeric mixture) δ 5.69 (m, 1 H), 5.63 (m, 1 H), 3.69 (s, 3 H), 2.03 (s, 0.7 H), 2.01 (s, 1.2 H), 2.00 (s, 1.1 H), 3.10−1.20 (m, 12 H); ^{13}C NMR ($CDCl_3$) diastereomer 1 (43%), δ 174.6, 171.4, 131.9, 131.2, 100.4, 60.6, 55.9, 52.0, 51.0, 44.8, 38.7, 34.3, 28.1, 25.6, 23.4; diastereomer 2 (35%), δ 174.4, 171.6, 132.8, 132.2, 99.5, 60.3, 57.4, 54.0, 52.1, 48.0, 43.9, 37.3, 28.8, 26.0, 22.8; diastereomer 3 (22%), δ 176.0, 175.0, 132.0, 131.1, 99.3, 61.8, 56.7, 52.6, 46.8, 40.9, 38.3, 34.9, 28.5, 25.8, 22.5; IR (neat) 1736 (s), 1190 (bs) cm^{-1}; HRMS *m/z* calcd for $C_{15}H_{20}O_4$ 264.1362, found 264.1355.

Methyl 3a,3b,4,5,6,6a,7,7a-Octahydro-1*H*-cyclopenta[*a*]pentalene-7-carboxylate (16). The cyclopropyl ester **3** (0.40 g, 2.89 mmol), cyclopentene (4.94 g, 72.40 mmol), and *n*-butyl disulfide (0.33 g, 1.81 mmol) were combined in 10 mL of degassed benzene. After 2 weeks of photolysis, the reaction was 50% complete; further photolysis had no effect. Chromatographic purification afforded recovered starting material and 0.18 g (33%; 66% based on unreacted starting material) of **16**. The product was a colorless oil consisting of four partially separable diastereomers in a ratio of 1.8:1.6:1.1:1.0: ^{1}H NMR ($CDCl_3$) (diastereomeric mixture) δ 5.68−5.53 (m, 2 H), 3.68 (s, 1.16 H), 3.67 (s, 1.84 H), 2.75−1.25 (m, 13 H); ^{13}C NMR ($CDCl_3$) diastereomer 1 (33%), δ 174.9, 134.3, 128.7, 56.5, 53.8, 50.9, 46.3, 45.7, 37.8, 35.2, 33.0, 30.3, 25.2; diastereomer 2 (29%), δ 174.4, 132.4, 130.4, 52.9, 51.2, 49.8, 49.1, 46.8, 44.9, 37.8, 29.0, 27.3, 27.0; diastereomer 3 (20%), δ 175.0, 135.4, 127.4, 58.8, 54.5, 51.0, 48.4, 47.7, 43.0, 37.8, 34.9, 28.6, 26.6; diastereomer 4 (18%), δ 176.6, 132.2, 128.6, 56.6, 53.4, 51.5, 50.3, 48.6, 46.8, 37.3, 30.4, 28.6, 26.5; IR (neat) 1736 (s), 1196 (s), 1169 (s) cm^{-1}; HRMS *m/z* calcd for $C_{13}H_{18}O_2$ 206.1307, found 206.1307.

4-Ethenyl-5-ethoxy-1,2,3,3a,4,5,6,6a-Octahydropentalen-1-one (17). The cyclopropyl ketone **4** (0.060 g, 0.49 mmol), ethyl vinyl ether (0.53 g, 7.37 mmol), and *n*-butyl disulfide (0.013 g, 0.074 mmol) were combined in 1 mL of degassed benzene. After 4 days of photolysis, purification afforded 0.063 g (66%) of **17** as a colorless oil consisting of four diastereomers in a ratio of 1.4:1.2:1.0:1.0: ^{1}H NMR ($CDCl_3$) diastereomer 1 (30%), δ 5.74 (ddd, J = 7.2, 10.2, 17.2 Hz, 1 H), 5.14 (d, J = 17.2 Hz, 1 H), 5.06 (d, J = 10.2 Hz, 1 H), 3.45 (q, J = 6.5 Hz, 2 H), 3.00−1.10 (m, 13 H); diastereomer 2 (22%), δ 5.87 (ddd, J = 3.0, 10.2, 17.2 Hz, 1 H), 5.14 (d, J = 17.2 Hz, 1 H), 5.06 (d, J = 10.2 Hz, 1 H), 3.38 (q, J = 6.8 Hz, 2 H), 3.00−1.10 (m, 13 H); diastereomer 3 (26%), δ 5.94 (ddd, J = 7.2, 11.1, 18.4 Hz, 1 H), 5.11 (d, J = 18.4 Hz, 1 H), 5.03 (d, J = 11.1 Hz, 1 H), 3.36 (q, J = 6.8 Hz, 2 H), 3.00−1.10 (m, 13 H); diastereomer 4 (22%), δ 5.75 (ddd, J = 7.2, 11.1, 18.4 Hz, 1 H), 5.11 (d, J = 18.4 Hz, 1 H), 5.03 (d, J = 11.1 Hz, 1 H), 3.45 (q, J = 6.8 Hz, 2 H), 3.00−1.10 (m, 13 H); ^{13}C NMR ($CDCl_3$) diastereomer 1, δ 213.8, 139.6, 116.1, 90.9, 66.0, 59.5, 54.9, 51.9, 43.0, 28.8, 25.7, 16.1; diastereomer 2, δ 222.8, 136.9, 118.0, 83.1, 66.0, 53.7, 48.9, 43.1, 39.7, 34.8, 23.6, 16.2; diastereomer 3, δ 224.2, 140.0, 116.3, 85.8, 65.3, 55.3, 49.7, 44.6, 36.6, 34.8, 24.9, 16.1; diastereomer 4, δ 223.3, 137.7, 117.0, 85.0, 65.6, 56.6, 51.0, 45.4, 36.8, 35.3, 23.2, 14.5; IR (neat) 1740 (s), 1119 (bs) cm^{-1}; HRMS *m/z* calcd for $C_{12}H_{18}O_2$ 194.1307, found 194.1310.

7-Ethenyl-2,3,3a,3b,4,5,6,6a,7,7a-decahydro-3(1*H*)-cyclopenta[*a*]pentalenone (18). The cyclopropyl ketone **4** (0.20 g, 1.64 mmol) and cyclopentene (2.24 g, 32.78 mmol) were combined with *n*-butyl disulfide (0.18 g, 0.98 mmol) in 6 mL of benzene. After 2 weeks of photolysis, the reaction was 40% complete. Concentration and chromatography gave the adduct **18** (0.085 g, 68% based on unreacted starting material) as a colorless oil consisting of four partially separable diastereomers in a ratio of 2.0:1.9:1.2:1.0: ^{1}H NMR ($CDCl_3$) diastereomers 1−2 (47%), δ 5.80 (ddd, J = 7.8, 10.4, 17.0 Hz, 1 H), 5.07 (ddd, J = 0.9, 1.9, 10.4 Hz, 1 H), 5.03 (ddd, J = 1.0, 1.9, 17.0 Hz, 1 H), 2.68−1.24 (m, 15 H); diastereomer 3−4 (53%), δ 5.77 (ddd, J = 7.6, 10.3, 17.1 Hz, 1 H), 5.05 (ddd, J = 1.0, 1.8, 17.1 Hz, 1 H), 4.98 (ddd, J = 0.8, 1.8, 10.3 Hz, 1 H), 2.75−1.23 (m, 15 H); ^{13}C NMR ($CDCl_3$) diastereomer 1 (31%), δ 222.8, 138.5, 115.5, 61.4, 51.2, 50.0, 45.2, 44.4, 35.2, 34.9, 27.3, 25.0, 21.3; diastereomer 2 (16%), δ 219.6, 136.1, 126.7, 57.2, 51.2, 44.3, 39.6, 38.4, 33.6, 31.4, 29.5, 25.0, 21.9; diastereomer 3 (33%), δ 213.1, 140.4, 114.2, 66.5, 53.5, 53.4, 42.8, 31.8, 30.8, 25.1, 25.0, 24.3, 21.9; diastereomer 4 (20%), δ 219.7, 136.1, 126.7, 57.2, 56.5, 44.3, 39.6, 37.2, 33.6, 30.3, 29.6, 28.0, 24.6; IR (neat) 1734 (s), 1154 (w) cm^{-1}; HRMS *m/z* calcd for $C_{13}H_{18}O$ 190.1358, found 190.1357.

3a,3b,4,5,6,6a,7,7a-Octahydro-1*H*-cyclopenta[*a*]pentalene-7-carboxaldehyde (19). A solution of the ester **16** (0.60 g, 2.91 mmol) in 10 mL of ether was added to DIBAL (9.47 mL of a 1 M solution in hexane, 9.47 mmol) in 20 mL of ether. The resulting solution was stirred for 2 h and quenched with 1 M NaOH solution. The organic layer was decanted, washed with water, and evaporated. The residual oil (0.48 g, 2.69 mmol) was dissolved in 40 mL of dichloromethane. PCC (0.70 g, 3.26 mmol) and Celite (0.75 g) were added, and the mixture was stirred at room temperature for 3 h. Ether was added, and the reaction mixture was filtered through a pad of Florisil. The resulting solution was concentrated to afford the aldehyde **19** (0.37 g, 72%) as a colorless oil. The product was a mixture of four diastereomers in a ratio of 1.9:1.5:1.3:1.0: ^{1}H NMR ($CDCl_3$) (diastereomeric mixture) δ 9.81 (d, J = 2.0 Hz, 0.34 H), 9.80 (d, J = 2.9 Hz, 0.18 H), 9.64 (d, J = 2.8 Hz, 0.25 H), 9.60 (d, J = 3.8 Hz, 0.23 H), 5.73−5.50 (m, 2 H), 3.15−1.26 (m, 13 H); ^{13}C NMR ($CDCl_3$) diastereomer 1 (33%), δ 205.3, 136.0, 129.7, 62.3, 50.9, 46.4, 38.4, 34.9, 34.9, 34.6, 31.8, 26.5; diastereomers 2−4 (67%, indistinguishable), δ 206.6(2 C), 205.3, 136.1, 133.8, 133.0, 131.0, 129.6, 128.4, 65.9, 63.5, 60.1, 58.9, 58.3, 54.6, 54.5, 49.9, 49.8, 48.4, 48.1, 47.9, 47.1, 46.5, 45.5, 41.7, 37.8, 36.8, 34.9, 31.0, 29.4, 29.0, 28.7, 28.6,

(21) Jones, R. A.; Stokes, M. J. *Tetrahedron* **1984**, *40*, 1051.
(22) Ohta, S.; Shimabayashi, A.; Aono, M.; Okamoto, M. *Synthesis* **1982**, 833.

28.5, 27.9, 27.4; IR (neat) 2710 (m), 1717 (s) cm^{-1}; HRMS *m/z* calcd for $C_{12}H_{16}O$ 176.1201, found 176.1195.

(±)-3aα,3bα,4,5,6,6aα,7,7aα-Octahydro-1*H*-cyclopenta[*a*]pentalene (20) and 3aα,3bβ,4,5,6,6aβ,7,7aα-Octahydro-1*H*-cyclopenta[*a*]pentalene (21). The aldehyde **19** (0.15 g, 0.85 mmol) and tris(triphenylphosphine)rhodium(I) chloride (0.79 g, 0.86 mmol) were combined in 10 mL of benzonitrile. The resulting dark red solution was heated to 160 °C for 3 h. A precipitate appeared during the course of the reaction. The reaction was cooled and poured directly onto a chromatography column which was eluted with hexanes. The alkene (0.084 g, 67%) was obtained as a colorless oil which was a 52:48 mixture of the two distereomers **20** and **21** favoring the cis-syn-cis isomer **20**: ^{1}H NMR ($CDCl_3$) (diastereomeric mixture) δ 5.71−5.47 (m, 2 H), 2.88−1.12 (m, 14 H); ^{13}C NMR ($CDCl_3$) compd **20** (52%), δ 135.2, 132.2, 57.0, 45.5, 44.9, 43.4, 39.2, 34.1, 31.8, 27.8, 18.0; compd **21** (48%), δ 134.6, 131.6, 57.3, 45.4, 44.5, 41.5, 38.4, 32.2, 31.7, 28.3, 19.2; CI HRMS *m/z* calcd for $C_{11}H_{17}$ 149.1330 (MH^+), found 149.1333 (MH^+).

(±)-2,3,3aα,3bα,4,5,6,6aα,7,7aα-Decahydro-1*H*-cyclopenta[*a*]pentalene (22) and 2,3,3aα,3bβ,4,5,6,6aβ,7,7aα-Decahydro-1*H*-cyclopenta[*a*]pentalene (23).[12] A solution of the two alkenes **20** and **21** (0.080 g, 0.54 mmol) in 4 mL of hexane was hydrogenated over 10% palladium on carbon (0.020 g) under an atmosphere of hydrogen for 24 h. The mixture was filtered, and the resulting solution was concentrated to afford the triquinanes **22** and **23** (0.066 g, 82%) in a 52:48 ratio. The ^{13}C NMR spectra obtained were consistent with those reported in the literature.[12]

General Procedure for Preparation of Ketones 25 and 27. Magnesium turnings in THF were activated by treatment with 1,2-dibromoethane. After ethylene evolution ceased, a solution of the bromoalkene in THF was added. Once the magnesium disappeared, a solution of the aldehyde **7** in THF was added dropwise. When the reaction was complete, the reaction mixture was cooled, quenched with water, and extracted with ether. The organic layer was dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed, affording the desired alcohol. A dichloromethane solution of the alcohol was treated with PCC and Celite. The mixture was stirred at room temperature until the reaction was complete. Ether was added, and the reaction mixture was filtered through a bed of Florisil. The solvent was evaporated, and the residual oil chromatographed, yielding the ketone.

(±)-6β-(1-Hydroxy-4-pentenyl)-1,5α-bicyclo[3.1.0]hex-2-ene (24). Following the general procedure, the Grignard reagent was formed from magnesium (0.88 g, 36.08 mmol) and 4-bromo-1-butene (3.87 g, 28.67 mmol) in 35 mL of THF. After treatment with the aldehyde **7** (1.50 g, 13.88 mmol), the reaction mixture was stirred at room temperature for 1 h and at 60 °C for 4 h. Workup as described above afforded the crude product, which was chromatographed (15% ether in pentane) to yield 1.95 g (85%) of the alcohol **24** as a pale yellow oil consisting of a partially separable mixture of two diastereomers: ^{1}H NMR ($CDCl_3$) diastereomer 1, δ 5.88 (m, 1 H), 5.85 (tdd, *J* = 6.6, 10.3, 17.0 Hz, 1 H), 5.40 (m, 1 H), 5.04 (dd, *J* = 1.6, 17.0 Hz, 1 H), 4.96 (dd, *J* = 1.6, 10.3 Hz, 1 H), 2.98 (m, 1 H), 2.58−1.46 (m, 9 H), 0.369 (m, 1 H); diastereomer 2, δ 5.87 (m, 1 H), 5.83 (tdd, *J* = 6.7, 10.1, 17.2 Hz, 1 H), 5.41 (m, 1 H), 5.04 (dd, *J* = 0.7, 17.2 Hz, 1 H), 4.96 (dd, *J* = 0.7, 10.1 Hz, 1 H), 2.99 (m, 1 H), 2.63−1.60 (m, 9 H), 0.365 (m, 1 H); ^{13}C NMR ($CDCl_3$) diastereomer 1, δ 139.3, 134.2, 129.4, 115.5, 75.0, 36.7, 36.5, 36.3, 30.8, 30.0, 21.4; diastereomer 2, δ 139.3, 133.8, 129.8, 115.5, 74.5, 37.3, 36.9, 36.7, 30.8, 29.6, 21.0; IR (neat) 3359 (bs), 1262 (m), 1075 (s) cm^{-1}; HRMS *m/z* calcd for $C_{11}H_{16}O$ 164.1201, found 164.1200.

(±)-6β-(1-Oxo-4-pentenyl)-1,5α-bicyclo[3.1.0]hex-2-ene (25). Following the general procedure, PCC (3.23 g, 15.00 mmol), and Celite (3.2 g) were added to a solution of the alcohol **24** (2.23 g, 13.61 mmol) in 50 mL of dichloromethane. The reaction was stirred at room temperature for 3 h. After workup, the crude product was chromatographed (10% ether in pentane) to afford the ketone **25** (1.90 g, 86%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 5.93 (m, 1 H), 5.80 (tdd, *J* = 6.5, 10.2, 17.1 Hz, 1 H), 5.57 (m, 1 H), 5.02 (dd, *J* = 1.7, 17.1 Hz, 1 H), 4.97 (dd, *J* = 1.7, 10.2 Hz, 1 H), 2.66 (m, 1 H), 2.60 (t, *J* = 7.2 Hz, 2 H), 2.45−2.39 (m, 2 H), 2.34 (q, *J* = 7.0 Hz, 2 H), 2.24 (m, 1 H), 1.28 (dd, *J* = 2.4, 2.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 209.7, 138.0, 133.2, 131.5, 115.9, 43.4, 39.5, 38.0, 37.3, 29.6, 28.7; IR (neat) 1692 (s), 1175 (w) cm^{-1}; HRMS *m/z* calcd for $C_{11}H_{14}O$ 162.1045, found 162.1046.

(±)-6β-(1-Hydroxy-5-methyl-4-hexenyl)-1,5α-bicyclo[3.1.0]hex-2-ene (26). The aldehyde **7** (1.50 g, 13.88 mmol) was added to the Grignard reagent formed from magnesium turnings (0.77 g, 31.43 mmol) and 5-bromo-2-methyl-2-pentene (3.92 g, 24.04 mmol) in THF. The reaction mixture was stirred at room temperature for 1 h and at 60 °C for 4 h. After workup as described above, the residue was chromatographed (10% ether in pentane) to yield 1.85 g (70%) of the alcohol **26** as a pale yellow oil consisting of a partially separable mixture of two diastereomers: ^{1}H NMR ($CDCl_3$) (diastereomeric mixture) δ 5.89 (m, 1 H), 5.41 (m, 1 H), 5.13 (t, *J* = 7.1 Hz, 1 H), 2.99 (m, 1 H), 2.63−1.55 (m, 9 H), 1.69 (s, 3 H), 1.62 (s, 3 H), 0.357 (m, 1 H); ^{13}C NMR ($CDCl_3$) diastereomer 1, δ 133.0, 131.8, 128.8, 124.1, 73.8, 37.0, 35.8, 35.7, 29.1, 25.6, 24.2, 20.1, 17.6; diastereomer 2, δ 133.5, 131.8, 128.4, 124.1, 74.3, 36.8, 36.5, 35.5, 28.8, 25.6, 24.2, 20.6, 17.6; IR (neat) 3360 (bs), 1075 (m), 1059 (m) cm^{-1}; HRMS *m/z* calcd for $C_{13}H_{20}O$ 192.1514, found 192.1506.

(±)-6β-(1-Oxo-5-methyl-4-hexenyl)-1,5α-bicyclo[3.1.0]-hex-2-ene (27). A dichloromethane solution of alcohol **26** (0.90 g, 4.68 mmol) was treated with PCC (1.11 g, 5.15 mmol) and Celite (1.2 g). The mixture was stirred for 3 h. After workup as described above, the crude product was chromatographed (5% ether in pentane) to afford the ketone **27** (0.72 g, 81%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 5.92 (m, 1 H), 5.55 (m, 1 H), 5.06 (t, *J* = 7.2 Hz, 1 H), 2.71−2.20 (m, 8 H), 1.66 (s, 3 H), 1.60 (s, 3 H), 1.26 (dd, *J* = 2.5, 2.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ: 209.4, 132.4 (2C), 130.6, 122.8, 43.5, 38.6, 37.1, 36.4, 28.6, 25.6, 22.6, 17.6; IR (neat) 1694 (s), 1175 (m) cm^{-1}; HRMS *m/z* calcd for $C_{13}H_{18}O$ 190.1358, found 190.1352.

General Procedure for Preparation of Esters 28−30. The acid **8**, 1,1-carbonyldiimidazole, and DMF were combined and heated for 1 h. The allylic alcohol and DBU were added, and the resulting mixture was stirred until the esterification was complete. The reaction mixture was chromatographed (10% ether in pentane) to give the desired ester.

(±)-2-Propenyl 1,5α-Bicyclo[3.1.0]hex-2-ene-6β-carboxylate (28). Following the general procedure,[22] the acid **8** (0.75 g, 6.04 mmol) and 1,1-carbonyldiimidazole (0.98 g, 6.04 mmol) were combined in 8 mL of DMF and heated to 50 °C. Allyl alcohol (0.70 g, 12.08 mmol) and DBU (0.92 g, 6.04 mmol) were added, and the reaction was stirred at 50 °C for 20 h. The ester **28** (0.80 g, 80%) was isolated as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 5.92 (m, 1 H), 5.91 (tdd, *J* = 5.7, 10.4, 17.2 Hz, 1 H), 5.54 (m, 1 H), 5.31 (dd, *J* = 1.4, 17.2 Hz, 1 H), 5.24 (dd, *J* = 1.4, 10.4 Hz, 1 H), 4.56 (d, *J* = 5.7 Hz, 2 H), 2.71−2.20 (m, 4 H), 1.01 (dd, *J* = 2.6, 2.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 173.0, 132.2, 131.9, 130.4, 118.0, 65.0, 36.1, 34.5, 30.1, 26.2; IR (neat): 1725 (s), 1180 (s), 1157 (s) cm^{-1}; HRMS *m/z* calcd for $C_{10}H_{12}O_2$ 164.0837, found 164.0832.

(±)-1,1-Dimethyl-2-propenyl 1,5α-Bicyclo[3.1.0]hex-2-ene-6β-carboxylate (29). The acid **8** (0.80 g, 6.44 mmol) and 1,1-carbonyldiimidazole (1.04 g, 6.44 mmol) were combined in 7 mL of DMF and warmed to 65 °C for 1 h. 2-Methyl-3-buten-2-ol (2.22 g, 25.76 mmol) and DBU (0.98 g, 6.44 mmol) were added, and the reaction was stirred at 65 °C for 20 h. The ester **29** (0.77 g, 62%) was obtained as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 6.06 (dd, *J* = 10.9, 17.5 Hz, 1 H), 5.91−5.52 (m, 2 H), 5.15 (d, *J* = 17.5 Hz, 1 H), 5.05 (d, *J* = 10.9 Hz, 1 H), 2.70−2.12 (m, 4 H), 1.50 (s, 6 H), 0.915 (dd, *J* = 2.6, 2.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 172.2, 142.6, 132.0, 130.2, 112.3, 80.4, 36.0, 34.1, 31.1, 26.4 (2C), 25.7; IR (neat) 1725 (s), 1175 (bs), 1125 (bs) cm^{-1}; HRMS *m/z* calcd for $C_{12}H_{16}O_2$ 192.1150, found 192.1153.

(±)-3-Methyl-2-butenyl 1,5α-Bicyclo[3.1.0]hex-2-ene-6β-carboxylate (30). The acid **8** (0.25 g, 2.01 mmol) and 1,1-carbonyldiimidazole (0.33 g, 2.01 mmol) were combined in 5 mL of DMF and warmed to 50 °C for 1 h. 3-Methyl-2-buten-1-ol (0.35 g, 4.02 mmol) and DBU (0.31 g, 2.01 mmol) were added, and the reaction was stirred at 50 °C for 20 h. The ester **30** (0.31 g, 80%) was obtained as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 5.91 (m, 1 H), 5.53 (m, 1 H), 5.34 (t, *J* = 7.2 Hz, 1

H), 4.55 (d, $J = 7.2$ Hz, 2 H), 2.71−2.18 (m, 4 H), 1.75 (s, 3 H), 1.70 (s, 3 H), 0.979 (dd, $J = 2.7$, 2.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ: 173.4, 138.9, 132.0, 130.3, 118.6, 61.2, 36.1, 34.4, 30.3, 26.1, 25.7, 17.9; IR (neat) 1723 (s), 1157 (bs) cm^{-1}; HRMS *m*/*z* calcd for $C_{12}H_{16}O_2$ 192.1150, found 192.1153.

(±)-2,3,3aβ,3bα,4,6aα,7,7aβ-Octahydro-3(1*H*)-cyclopenta[*a*]pentalenone (31) and 2,3,3aα,3bα,4,6aα,7,7aα-Octahydro-3(1*H*)-cyclopenta[*a*]pentalenone (32). The cyclopropyl ketone **25** (0.125 g, 0.77 mmol) and *n*-butyl disulfide (0.068 g, 0.38 mmol) were combined in 4 mL of degassed benzene. The solution was photolyzed for 2 weeks and chromatographed to provide 0.091 g (73%) of the inseparable triquinanes **31** (65%) and **32** (35%) as a colorless oil: ^{1}H NMR ($CDCl_3$) compd **31** (65%), δ 5.71 (m, 2 H), 3.20−1.20 (m, 12 H); compd **32** (35%), δ 5.58 (m, 2 H), 3.20−1.20 (m, 12 H); ^{13}C NMR ($CDCl_3$) compd **31**, δ 213.8, 132.7, 131.3, 59.4, 55.1, 42.7, 40.8, 38.8, 35.0, 33.1, 30.7; compd **32**, δ 214.4, 132.2, 131.2, 55.4, 53.7, 43.2, 38.5, 36.4, 35.9, 33.1, 26.3; IR (neat) 1710 (s), 1235 (m) cm^{-1}; HRMS *m*/*z* calcd for $C_{11}H_{14}O$ 162.1045, found 162.1048.

(±)-7,7-Dimethyl-2,3,3aβ,3bα,4,6aα,7,7aβ-octahydro-3(1*H*)-cyclopenta[*a*]pentalenone (33), 7,7-Dimethyl-2,3,3aα,3bα,4,6aα,7,7aα-octahydro-3(1*H*)-cyclopenta[*a*]-pentalenone (34), and 11,11-Dimethyl-1β,2α,6α,7β-tricyclo[5.3.1.0^{2,6}]undec-3-en-8-one (35). The cyclopropyl ketone **27** (0.20 g, 1.05 mmol) and *n*-butyl disulfide (0.11 g, 0.63 mmol) were combined in 4 mL of degassed benzene and photolyzed for 10 days. Chromatography afforded the adduct (0.16 g, 81%) as a colorless oil. The product consisted of three inseparable isomers; the two major products were proven to be the cis-anti-cis (82%, **33**) and cis-syn-cis (11%, **34**) isomers. The third isomer (7%) was tentatively assigned structure **35**, corresponding to a 6-endo-trig cyclization product: ^{1}H NMR ($CDCl_3$) (diastereomeric mixture) δ 5.75−5.44 (m, 2 H), 3.09−1.54 (m, 10 H), 1.11 (s, 0.33 H), 1.08 (s, 0.21 H), 0.994 (s, 0.33 H), 0.944 (s, 2.46 H), 0.761 (s, 2.46 H), 0.712 (s, 0.21 H); ^{13}C NMR ($CDCl_3$) compd **33** (82%), δ 222.9, 130.7, 130.5, 63.8, 62.0, 51.9, 43.8, 42.3, 41.3, 37.6, 25.5, 24.5, 20.3; compd **34** (11%), δ 214.4, 129.9, 129.5, 64.2, 59.4, 54.5, 42.1, 40.5, 37.2, 35.5, 29.1, 20.1, 18.6; compd **35** (7%), δ 222.6, 133.2, 129.3, 68.9, 63.7, 54.7, 43.7, 42.7, 37.6, 34.9, 32.4, 24.1, 20.9; IR (neat) 1736 (s), 1171 (m) cm^{-1}; HRMS *m*/*z* calcd for $C_{13}H_{18}O$ 190.1358, found 190.1357.

(±)-3aα,3bβ,4,5,6,6aβ,7,7aα-Octahydro-3*H*-cyclopenta[*a*]pentalene (36) and 3aα,3bα,4,5,6,6aα,7,7aα-Octahydro-3*H*-cyclopenta[*a*]pentalene (37). The ketones **31** and **32** (0.30 g, 1.85 mmol) and *p*-toluenesulfonohydrazide (0.38 g, 2.04 mmol) were combined in 8 mL of THF. The resulting solution was refluxed for 3 h and cooled. The solvent was evaporated, and 8 mL of chloroform was added. The solution was cooled to 0 °C, and catecholborane (0.22 g, 1.85 mmol) was added. After 1 h of stirring, sodium acetate trihydrate (0.78 g) was added, and the reaction was refluxed for 1 h. The mixture was filtered, the resulting solution was dried ($MgSO_4$) and concentrated. The residual oil was chromatographed with pentane as eluent to provide the triquinanes **36** (68%) and **37** (32%) as a colorless oil (0.24 g, 87%): ^{1}H NMR ($CDCl_3$) (diastereomeric mixture) δ 5.71−5.46 (m, 2 H), 2.87−1.12 (m, 14 H); ^{13}C NMR ($CDCl_3$) compd **36** (68%), δ 134.3, 131.3, 56.0, 44.5, 44.3, 42.3, 40.4, 34.9, 33.0, 32.5, 20.0; compd **37** (32%), δ 133.6, 130.7, 56.3, 43.8, 43.5, 38.1, 37.3, 32.6, 29.1, 28.6, 18.9; CI HRMS *m*/*z* calcd for $C_{11}H_{17}$ 149.1330 (MH^+), found 149.1326 (MH^+).

(±)-2,3,3aα,3bβ,4,5,6,6aβ,7,7aα-Decahydro-1*H*-cyclopenta[*a*]pentalene (23) and 2,3,3aα,3bα,4,5,6,6aα,7,7aα-Decahydro-1*H*-cyclopenta[*a*]pentalene (22).[9] Procedure B. A solution of alkenes **36** and **37** (0.040 g, 0.27 mmol) in 3 mL of hexane was hydrogenated over 10% palladium on carbon (0.010 g) under an atmosphere of hydrogen for 24 h. The mixture was filtered, and the resulting solution was concentrated to afford the triquinanes (0.031 g, 77%) as a colorless oil. The compounds were obtained in a 70:30 ratio favoring the cis-anti-cis isomer **23**. The ^{13}C NMR spectrum obtained matched those reported in the literature.[12]

7,7-Dimethyl-3aα,3bβ,4,5,6,6aβ,7,7aα-octahydro-3*H*-cyclopenta[*a*]pentalene (38) and 7,7-Dimethyl-3aα,3bα,4,5,6,6aα,7,7aα-octahydro-3*H*-cyclopenta[*a*]pentalene (39). The ketones **33**−**35** (0.060 g, 0.32 mmol) and *p*-toluenesulfonohydrazide (0.070 g, 0.38 mmol) were combined in 3 mL of THF. The resulting solution was refluxed for 3 h and cooled. The solvent was evaporated, and 3 mL of chloroform was added. The solution was cooled to 0 °C, and catecholborane (0.038 g, 0.032 mmol) was added. After 1 h of stirring, sodium acetate trihydrate (0.13 g) was added, and the reaction was refluxed for 1 h. The mixture was filtered, and the resulting solution was dried ($MgSO_4$) and concentrated. The residual oil was chromatographed with pentane as eluent to provide the alkenes (0.042 g, 76%) as a colorless oil; the cis-anti-cis isomer **38** comprised 88% of the mixture, while the cis-syn-cis isomer **39** was 8%. The alkene derived from deoxygenation of the minor tricyclic product **35** was present as only 4% of the mixture, and its NMR spectrum could not be assigned: ^{1}H NMR ($CDCl_3$) (diastereomeric mixture) δ 5.62 (bs, 2 H), 2.92 (bd, $J = 8.9$ Hz, 1 H), 2.52 (ddd, $J = 1.8$, 8.9, 16.5 Hz, 1 H), 2.36 (m, 1 H), 2.18−1.38 (m, 10 H), 1.16 (s, 0.12 H), 1.07 (s, 0.12 H), 1.00 (s, 2.64 H), 0.943 (s, 0.24 H), 0.918 (s, 0.24 H), 0.853 (s, 2.64 H); ^{13}C NMR ($CDCl_3$) compd **38** (88%), δ 131.4, 129.7, 63.2, 59.5, 52.4, 49.3, 43.0, 40.5 (2C), 32.7, 27.6, 27.0, 26.4; compd **39** (8%), δ 131.4, 129.6, 53.5, 52.7, 51.2, 48.1, 46.1, 42.1, 40.1, 34.0, 29.6, 27.4, 25.0; HRMS *m*/*z* calcd for $C_{13}H_{20}$ 176.1566, found 176.1571.

(±)-7,7-Dimethyl-2,3,3aα,3bβ,4,5,6,6aβ,7,7aα-decahydro-1*H*-cyclopenta-[*a*]pentalene (40). The alkenes **38** and **39** (0.018 g, 0.098 mmol) and cobalt chloride hexahydrate (0.0027 g, 0.11 mmol) were combined in 2 mL of a 3:1 ethanol−THF solution. Sodium borohydride (0.087 g, 0.23 mmol) was added in two portions. The resulting dark solution was stirred for 24 h. The reaction was poured into 1 M hydrochloric acid and extracted with ether. The ether layer was washed with water, dried ($MgSO_4$), and concentrated to afford the alkane **40** (0.013 g, 76%) as a colorless oil. The other isomers comprised only 5% of the mixture: ^{1}H NMR ($CDCl_3$) δ 2.14−1.43 (m, 16 H), 0.92 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 57.5, 51.8, 42.4, 33.0, 27.0 (2C), 26.9; HRMS *m*/*z* calcd for $C_{13}H_{22}$ 178.1722, found 178.1721.

(±)-7,7-Dimethyl-1,3,3aα,3bβ,4,6aβ,7,7aα-octahydropentaleno[1,2-*c*]furan-3-one (41), 7,7-Dimethyl-1,3,3aα,3bα,4,6aα,7,7aα-octahydropentaleno[1,2-*c*]furan-3-one (42), and 11,11-Dimethyl-1β,2α,6α,7β-tetrahydro-9-oxatricyclo-[5.3.1.0^{2,6}]undec-3-en-8-one (43). The cyclopropyl ester **30** (0.25 g, 1.30 mmol) and *n*-butyl disulfide (0.048 g, 0.26 mmol) were combined in 4 mL of degassed benzene and photolyzed for 2 days. After chromatography, the adduct (0.18 g, 70%) was isolated as a colorless oil which was an inseparable mixture of three isomers. The cis-anti-cis triquinane **41** was present as 72% of the mixture, and the cis-syn-cis isomer **42** comprised 17%. The third product was tentatively identified as **43**, the product of 6-endo cyclization (11%): ^{1}H NMR ($CDCl_3$) (diastereomeric mixture) δ 5.77−5.60 (m, 2 H), 4.13 (m, 2 H), 3.16−2.36 (m, 6 H), 1.11 (s, 0.35 H), 1.08 (s, 0.35 H), 1.06 (s, 4.3 H), 1.01 (s, 0.5 H), 0.90 (s, 0.5 H); ^{13}C NMR ($CDCl_3$) compd **41** (72%), δ 173.8, 130.9, 130.2, 68.0, 63.7, 53.2, 50.6, 42.2, 41.6, 35.2, 34.1, 24.3; compd **42** (17%), δ 178.8, 132.0, 131.0, 69.4, 67.1, 53.3, 47.7, 43.4, 42.1, 31.9, 23.1, 20.4; compd **43** (11%), δ 181.0, 131.5, 130.1, 69.6, 65.0, 52.3, 49.5, 43.4, 39.7, 35.2, 25.0, 23.9; IR (neat) 1767 (s), 1177 (m), 1157 (bm), 1109 (w) cm^{-1}; HRMS *m*/*z* calcd for $C_{12}H_{16}O_2$ 192.1151, found 192.1148.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of **9**−**21** and **24**−**43** (50 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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