(Hoek Loos, very pure) for at least 20 min. The sample starting concentrations were 0.3–1.0 mM of host. After each manual addition (Hamilton syringes with a total volume of 50 μL or 250 μL were used) of guest (0.25–5.0 equiv from 50–500 mM in 0.1 M solutions of $Et_4N^+ClO_4^-$ in CH_3CN), polarograms were recorded in triplicate in the DC-tast mode with scan speed of 5 mV/s. The number of additions was 5–8. The values of half-wave potential, limiting current and slope of the log plot, were calculated by a computerized curve-fitting method described by Zollinger et al.[29] Stability constants were obtained from the polarographic data (half-wave potential and limiting current) with POLAG[30] using least-squares fitting procedures. The error between experimental and calculated values for the half-wave potentials were <1 mV; to achieve this accuracy deviations in the slope must be <3 mV. Estimated accuracy of the association constants is 20%.

Cyclic voltammetry was carried out with a AUTOLAB-computerized system for electrochemistry (ECO CHEMIE, Utrecht, The Netherlands). The measurements were performed at a stationary hanging mercury drop electrode (Metrohm, 663 VA) with a scan rate of 4–6 V/s in the range −0.7/−1.3 V. The electrode types and fillings were the same as used in polarography. The solvent and the supporting electrolyte were also the same as used in polarography. Oxygen was expelled by bubbling CH_3CN-saturated nitrogen (Hoek Loos, very pure) through for at least 5 min.

Coulometry was carried out with a Metrohm coulostat E524 and a Metrohm integrator E525. The coulostat was operated with a constant potential (potentiostatic coulometry) of −1.3 V. The electrode types and fillings were the same as used in polarography. The solvent and the supporting electrolyte were also the same as used in polarography and cyclic voltammetry. A mercury pool was used as cathode and it was separated from the platinum counter electrode by a salt bridge. Oxygen was expelled by bubbling CH_3CN-saturated nitrogen (Hoek Loos, very pure) through for at least 10 min.

Acknowledgment. We gratefully acknowledge Prof. T. W. Bell for a generous gift of receptor 7. We are indebted to T. W. Stevens for recording the mass spectra, to A. M. Montanaro-Christenhusz for performing the elemental analyses and Karl Fischer titrations, and to W. Lengton for daily assistance with the polarographic experiments.

Supplementary Material Available: Tables of positional and thermal parameters of all non-hydrogen atoms, bond distances and angles, and dihedral angles of the compounds **1**(n=5)·MeOH, **6b**·urea, and **6d**·urea, and 2D COSY spectra of **5b** and **6b**·urea and a 2D NOESY spectrum of **5b** (23 pages). Ordering information is given on any current masthead page.

Synthesis of the Bicyclo[3.2.0] Ring Systems from 4-Allylcyclobutenones. Intramolecular Ketene/Alkene Cycloadditions

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Received January 11, 1991 (Revised Manuscript Received June 17, 1991)

A general synthesis of bicyclo[3.2.0]heptenones from 4-allylcyclobutenones is described. The rearrangement is envisaged to involve an electrocyclic ring opening of the cyclobutenone and subsequent intramolecular 2 + 2 cycloaddition of the resulting vinylketene to the nonconjugated allylic alkene moiety. This method is particularly suitable for the synthesis of highly substituted derivatives since the regiochemistry of the substitution pattern is conveniently controlled. The scope of the rearrangement and the mechanism are discussed.

Introduction

Intermolecular ketene/alkene cycloadditions have received detailed attention.[1,2] In view of this it is surprising that the intramolecular versions have received much less study. However, those reports that have appeared point to a potentially powerful method for the synthetic arsenal.[3] In this conjunction we now provide the details of a study focussing on the generation of vinylketenes from 4-allylcyclobutenones and their intramolecular cycloadditions to tethered alkenes, thus providing highly functionalized bicyclo[3.2.0]heptenone derivatives.

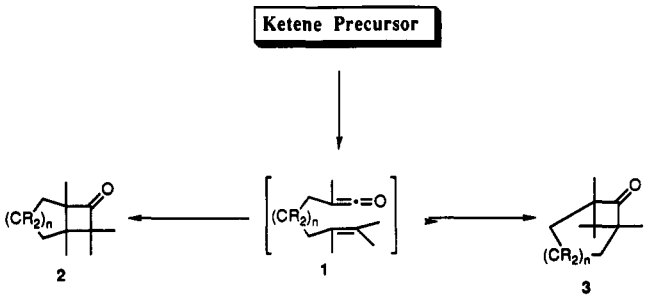
Most systematic studies of intramolecular ketene/alkene cycloadditions and their applications in the synthesis of complex natural products have appeared during the past decade.[4] In general, these report the ketene syntheses by standard methods including the elimination of HCl from the corresponding acid halide and/or the pyrolysis of esters, the photo-Wolff rearrangement of diazo ketones, and, to a less extent, the electrocyclic ring opening of a cyclobutenone.[5-7] In general, intramolecular ketene/al-

(1) For a review, see: Ulrich, H. *Cycloaddition Reactions of Heterocumulenes*; Academic Press: New York, London, 1967.
(2) Ghosez, L.; O'Donnell, M. J. *Pericyclic Reactions*; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. II, pp 79–140.
(3) For an excellent review on intramolecular ketene/alkene cycloadditions, see: Snider, B. B. *Chem. Rev.* **1989**, *88*, 793.

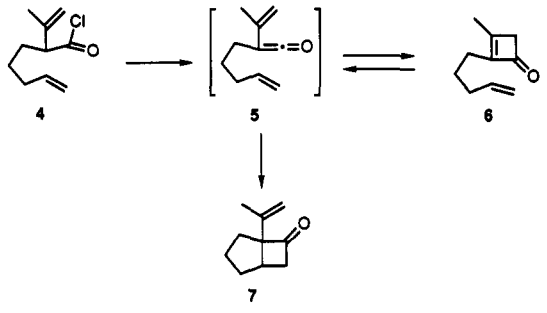
(4) For leading references, see: (a) Snider, B. B.; Ron, E.; Burbaum, B. W. *J. Org. Chem.* **1987**, *52*, 5413. (b) Snider, B. B.; Kulkarni, Y. S. *J. Org. Chem.* **1987**, *52*, 307. (c) Oppolzer, W.; Nakao, A. *Tetrahedron. Lett.* **1986**, *27*, 5471. (d) Corey, E. J.; Desai, M. C.; Engler, T. A. *J. Am. Chem. Soc.* **1985**, *107*, 4339. (e) Mori, K.; Miyake, M. *Tetrahedron* **1987**, *43*, 2229. (f) Becker, D.; Birnbaum, D. *J. Org. Chem.* **1980**, *45*, 570. (g) Ireland, R. E.; Dow, W. C.; Godfrey, J. D.; Thaisrivongs, S. *J. Org. Chem.* **1984**, *49*, 1001. (h) Leyendecker, F. *Tetrahedron* **1976**, *32*, 349. (i) Leyendecker, F.; Bloch, R.; Conia, J. M. *Tetrahedron. Lett.* **1972**, 3703. (j) Maujean, A.; Marcy, G.; Chuche, J. *J. Chem. Soc., Chem. Commun.* **1980**, 92. (k) Arya, F.; Bouquant, J.; Chuche, J. *Tetrahedron Lett.* **1986**, *27*, 1913. (l) Smit, A.; Kok, J. G. J.; Geluk, H. W. *J. Chem. Soc., Chem. Commum.* **1975**, 513. (m) Brady, W. T.; Marchand, A. P.; Giang, Y. F.; Wu, A.-H. *Synthesis* **1987**, 395.
(5) For a review concerning synthetic routes to ketenes, see: Patai, S., Ed. *Chemistry of the Quinones*, Vol. 1–2; Wiley and Sons: New York, 1974.

0022-3263/91/1956-6094$02.50/0

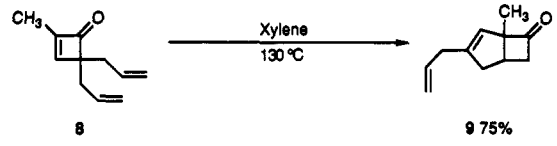
Scheme I



Scheme II



Scheme III



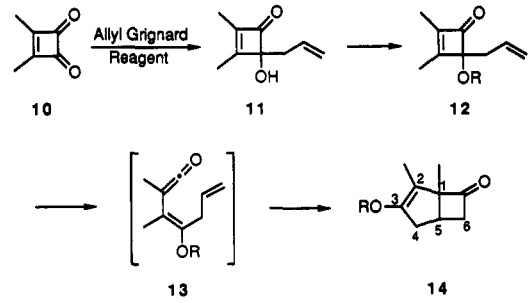
kene cycloadditions were found to be most useful for the synthesis of bicyclic cyclobutenones of the types formally outlined in Scheme I. Furthermore, the regiospecificity of the cycloadditions were observed to be controlled by the alkyl substituents on the alkene double bond. For example, alkenes in which the internal carbon is more highly substituted give the bicyclic systems **2** and those in which the terminal carbon is more highly substituted lead to **3**.

Two close analogies to the work described in this paper are outlined in Scheme II and Scheme III. Both involve cyclobutenone/vinylketene interconversions. The first shows the interconversion of unsaturated ketenes and cyclobutenones.[8] That is, thermolysis of acid chloride **4** in toluene (100 °C, 3 h) gave a 56% yield of cyclobutenone **6**. At higher temperature (125–130 °C, 4 days) this reversible transformation was driven to the more stable bicycloheptanone **7**. The second example concerns the thermal rearrangement of 4,4-diallyl-2-methylcyclobutenone (**8**) (refluxing *p*-xylene) to the bicyclo[3.2.0]-heptenone **9** (Scheme III).[6]

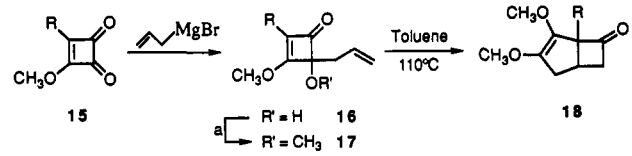
Results and Discussion

The generalized contribution presented in this paper is outlined in Scheme IV, i.e., methodology is presented allowing the facile synthesis of bicyclo[3.2.0]heptenones **14** from 4-allylcyclobutenones **12**, which are readily available from cyclobutenediones.[9] Treatment of **10** with allyl

Scheme IV



Scheme V



a = CH_3I, Ag_2O, K_2CO_3/CH_3CN, RT

Entry	R	% 16	% 17	% 18
a	—OCH_3	71	89	83
b	—n-C_4H_9	27	89	85
c	—$CH{=}CH_2$	53	87	90
d	—C_6H_5	58	95	86
e	—≡—n-C_4H_9	42	80	72
f	—≡—TMS	38	---	

Grignard reagents provides 4-allyl-4-hydroxycyclobutenones **11**. These are then protected as the alkyl ether **12**. Thermolysis of these results in stereoselective ring opening to form vinylketene **13** that then undergoes intramolecular 2 + 2 cycloaddition with the allylic double bond to provide bicycloheptenone **14**.

It is noteworthy that addition of Grignard reagents to cyclobutenediones was previously reported to provide 1,4-addition products.[10] In contrast, we have found allylmagnesium bromide to give 1,2-adducts as the major products.[11] However, attempts to generate 4-allylcyclobutenones by addition of allyllithium, generated from tetraallyltin, were unsuccessful.

The synthesis of 2,3-dimethoxybicyclo[3.2.0]hep-2-en-7-ones having a variety of substituents at the 1-position is shown in Scheme V. Starting from readily available substituted cyclobutenediones **15** and the corresponding allyl Grignard reagent, 4-allyl-4-hydroxycyclobutenones **16** were obtained in moderate yields. Methylation of **16** with methyl iodide provided **7** in excellent yields except for entry f.[12] Compounds **17a–e** were then subjected to thermolysis in refluxing toluene to give bicyclo[3.2.0]heptenones **18a–e** in excellent yields.

The structure assignments of the products are based upon their characteristic spectral properties. For example,

(6) Ernst, B.; de Mesmaeker, A.; Greuter, H.; Veenstra S. J. in *Strain and its Implication in Organic Chemistry*; de Meijere, A., Blechert, S., Eds.; Kluwer Academic Publishers: 1989; pp 221–222.

(7) For a preliminary account of this work, see Xu, S. L.; Moore, H. W. *J. Org. Chem.* **1989**, *54*, 6018.

(8) Lee, S. Y.; Kulkarni, Y. S.; Burbaum, B. W.,; Johnston, M. I.; Snider, B. B. *J. Org. Chem.* **1988**, *53*, 1848.

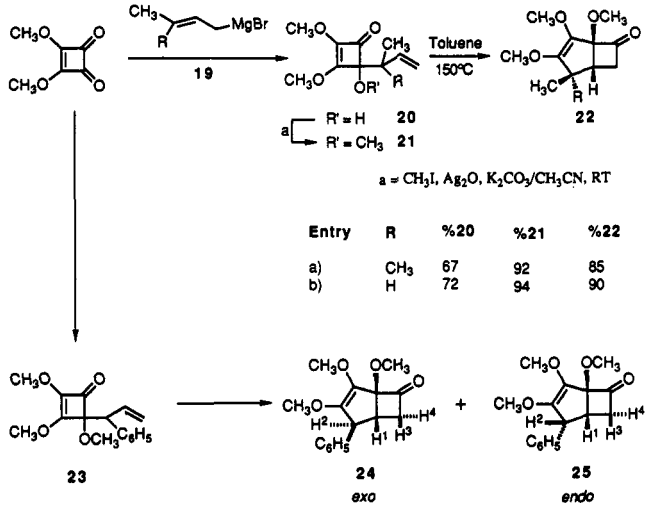
(9) For leading references, see: See: Schmidt, A. H.; Reid, W. *Synthesis* **1978**, 1. Knorr, H.; Ried, W. *Synthesis* **1978**, 649. Schmidt, A. H.; Ried, W. *Synthesis* **1978**, 869. Reed, M. W.; Pollart, D. J.; Perri, S. T.; Foland, L. D.; Moore, H. W. *J. Org. Chem.* **1988**, *53*, 2477. Liebeskind, L. S.; Fengl, R. W.; Wirtz, K. R.; Shawe, T. T. *J. Org. Chem.* **1988**, *53*, 2482. Liebeskind, L. S.; Fengl. R. W. *J. Org. Chem.* **1990**, *55*, 5359. Liebeskind, L. S.; Wirtz, K. R. *J. Org. Chem.* **1990**, *55*, 5350. Liebeskind, L. S.; Wang, J. *Tetrahedron Lett.* **1990**, 4293. Xu, S. L; Yerxa, B. R.; Sullivan, R. W.; Moore, H. W. *Tetrahedron Lett.* In press.

(10) Kraus, J. L. *Tetrahedron Lett.* **1985**, *26*, 1867.

(11) In the case of dimethyl squarate, a diadduct was obtained as the minor product with a yield of 15%.

(12) A similar method was used to convert 4-hydroxycyclobutenones to 4-(allyloxy)cyclobutenones, see: Foland, L. D.; Decker, O. H. W.; Moore, H. W. *J. Am. Chem. Soc.* **1989**, *111*, 989.

Scheme VI



their IR spectra show carbonyl absorptions around 1775 cm^{-1}. The ^{13}C NMR spectra also indicate the presence of carbonyl signals. The ^1H NMR spectra show two methylene groups with geminal coupling and further coupling to a bridgehead proton.

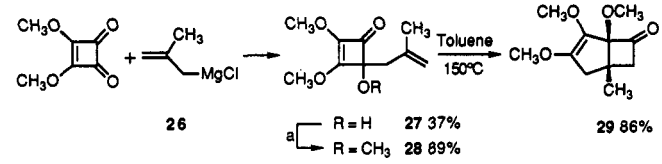
Bicyclo[3.2.0] ring systems with unsaturated substituents at the 1-position thus obtained are very interesting compounds. On the basis of close analogy, they are potentially versatile precursors to a number of other systems including five-, six-, seven-, and eight-membered rings.[13]

Modifying the starting cyclobutenedione or the allyl Grignard reagent provides a convenient method for synthesizing other bicyclo[3.2.0]heptenones. For example, substituents at the 4-position of bicyclo[3.2.0]heptenones are introduced by employing substituted allyl Grignard reagents (Scheme VI). Addition of Grignard reagents **19a,b** to dimethyl squarate occurred with allylic rearrangement to give **20a,b**.[14] In the case of entry a, the Barbier process was employed due to the coupling reaction during the generation of the Grignard reagent, i.e., the Grignard reagent was generated in the presence of the electrophile dimethyl squarate (see Experimental Section).[15] The resulting adduct **20** was converted to its methyl ether **21** and subjected to thermolysis in toluene in a sealed tube at 150°C to give the bicycloheptenone products **22**.

Table I. Chemical Shifts for 24 and 25

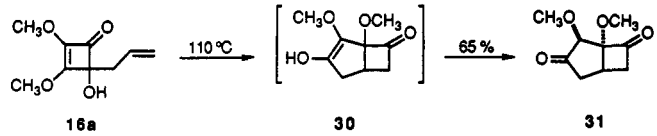
	H^1	H^2	H^3	H^4
exo	2.59	3.68	3.19	2.86
endo	2.97	4.49	2.48	2.64
$\Delta\delta$	−0.38	−0.81	0.71	0.22

Scheme VII[a]



[a] (a) = CH_3I, Ag_2O, K_2CO_3/CH_3CN, rt.

Scheme VIII



For entry b, a 6:1 mixture of isomers was obtained. The major isomer was assigned the structure shown with the methyl substituent on the convex face of the molecule (^{13}C NMR and ^1H NMR analysis). In the ^{13}C NMR spectrum, the methyl group and C_6 of the major isomer absorb at δ 19.41 and 47.61, respectively. The corresponding carbons of the minor isomer are assigned a cis relationship since the absorptions experience an upfield shift to δ 11.44 and 41.33 (γ effect). Furthermore, the coupling pattern in the ^1H NMR spectrum is very revealing. For the major isomer, the methine proton next to the double bond appears as a clean quartet with no coupling to the vicinal proton at the bridgehead position. This indicates that the dihedral angle between the two methine protons is very close to 90°; therefore, the methyl substituent is on the convex face. Such an observation is consistent with related systems previously reported.[16]

In a similar manner bicyclo[3.2.0]heptenones **24** and **25** were obtained from **23** as a mixture of exo and endo isomers in a respective ratio of 12:1. The assignment of their structures is based upon the following: (1) the ^1H NMR spectrum of **24** shows no coupling between the bridgehead proton H_1 and the benzylic proton H_2 (dihedral angel is about 90°); (2) the bridgehead proton in **24** is only coupled with the cyclobutanone methylene protons H_3 and H_4; (3) in the endo isomer, the bridgehead proton absorption appears as a doublet of doublet of doublets pattern, as expected if it is coupled to the benzylic H_2 as well as the cyclobutanone methylene protons H_3 and H_4. It is also interesting to note the changes in the chemical shift for these four protons in the two isomers. The chemical shifts for each proton in the two isomers are listed in Table I. Molecular models show that while the phenyl group can rotate freely in the exo isomer **24**, its rotation is blocked in endo isomer **25** by the methylene group at the 6-position and the methoxy methyl at the 3-position. Thus, H_1 and H_2 are more deshielded by the phenyl ring in the endo isomer than in the exo isomer. On the other hand, H_3 and H_4 in the endo isomer fall into the shielding region of the phenyl ring and are shifted upfield.

Still another modification is outlined in Scheme VII. This allows the introduction of substituents at the 5-

(13) For selected examples of the conversion of bicyclo[3.2.0]heptanes to other ring systems, see the following. Five-membered ring systems: (a) Corey, E. J.; Kang, M.; Desai, M. C.; Ghosh, A. K.; Houpis, I. N. *J. Am. Chem. Soc.* **1988**, *110*, 649. (b) De Mesmaeker, A.; Veenstra, S. J.; Ernst, B. *Tetrahedron Lett.* **1988**, 459. (c) Jackson, D. A.; Rey, M.; Dreiding, A. S. *Tetrahedron Lett.* **1983**, 4817. (d) Matz, J. R.; Cohen, T. *Tetrahedron Lett.* **1981**, 2549. (e) Wenkert, E.; Arrhenius, T. S. *J. Am. Chem. Soc.* **1983**, *105*, 2030. Six-membered ring systems: (f) Cohen, T.; Bhupathy, M.; Matz, J. R. *J. Am. Chem.. Soc.* **1983**, *105*, 520. (g) Bhupathy, M.; Cohen, T. *J. Am. Chem. Soc.* **1983**, *105*, 6978. (h) Danheiser, R. L.; Martinez-Davila, C.; Sard, H. *Tetrahedron* **1981**, *37*, 3943. (i) Snider, B. B.; Niwa, M. *Tetrahedron Lett.* **1988**, 3175. Seven-membered ring systems: (j) Huston, R.; Rey, M.; Dreiding, A. S. *Helv. Chim. Acta* **1982**, *65*, 451. (k) Huston R.; Rey, M.; Dreiding, A. S. *Helv. Chim. Acta* **1982**, *65*, 1563. (l) Hwang, C. S.; Reusch, W. *Synthesis* **1989**, 428. (m) Oppolzer, W.; Wylie, R. D. *Helv. Chim. Acta* **1980**, *63*, 1198. (n) Imafuku, K.; Arai, K. *Synthesis* **1989**, 501. Eight-membered ring systems: (o) Gadwood, R. C.; Lett, R. M. *J. Org. Chem.* **1982**, *47*, 2268. (p) Gadwood, R. C.; Lett. R. M.; Wissinger, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 6343. (q) Paquette, L. A.; Colapret, J. A.; Andrews, D. R. *J. Org. Chem.* **1985**, *50*, 201. (r) Birch, A. M.; Pattenden, G. *J. Chem. Soc., Chem. Commun.* **1980**, 1195. Norbornene ring system: (s) Wilson S. R.; Mao, D. T. *J. Chem. Soc., Chem. Commun.* **1978**, 479.

(14) Similar allylic rearrangement was observed, see: Idrissi, M. E.; Santelli, M. *J. Org. Chem.* **1988**, *53*, 1010.

(15) For a review on the Barbie reaction, see: Blomberg, C.; Hartog, F. A. *Synthesis* **1977**, 18.

(16) (a) Gadwood, R. C.; Lett, R. M.; Wissinger, E. *J. Am. Chem. Soc.* **1986**, *108*, 6343. (b) Snider, B. B.; Allentoff,, A. J.; Kulkarni, Y. S. *J. Org. Chem.* **1988**, *53*, 5320.

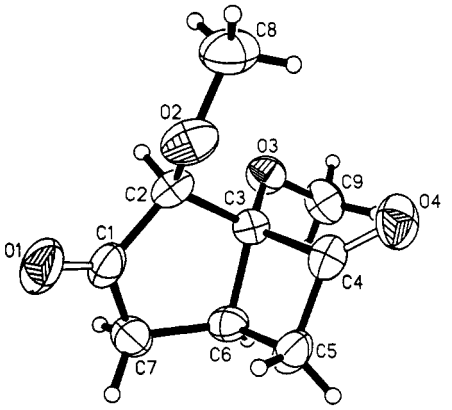


Figure 1. ORTEP plot of compound **31**.

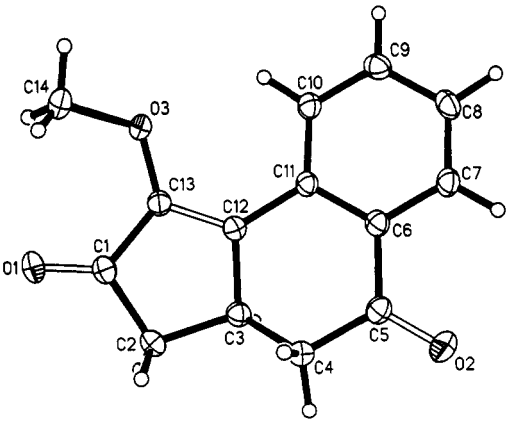
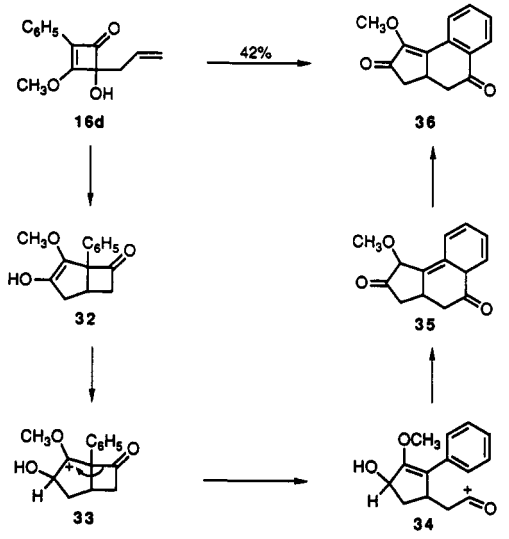
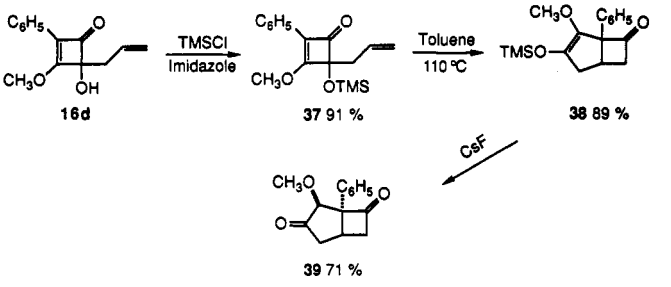


Figure 2. ORTEP plot of compound **36**.

Scheme IX



Scheme X



position of the bicycloheptenone. That is, compound **27** was obtained (37%) by addition of **26** to dimethyl squarate. Methylation of **27** gave **28** (89%) and this rearranged to **29** (86%) upon thermolysis in toluene in a sealed tube at 150 °C.

Thermolysis of the 4-hydroxy-4-allylcyclobutenone analogue **16a** was also studied (Scheme VIII). Here, the bicyclo[3.2.0]heptane-3,7-dione **31** was obtained in 65% yield, a product envisaged to arise from its initially formed tautomer **30**. Formation of these products is of note since one might have expected polymerization to arise from the reaction of the hydroxyl group, in the intermediate corresponding to **13**, with the ketene moiety.

Analysis of the ^{1}H NMR spectrum of the crude reaction mixture revealed the presence of the diastereomer of **31** as a minor product. However, this is labile and is easily converted to **31** upon treatment with silica gel.

The structure assignment of **31** is based on its spectroscopic data and was confirmed by a complete X-ray crystallographic study, which clearly shows the methoxy groups to be trans to one another (Figure 1).

In an attempt to expand the scope of the above bicyclo[3.2.0]heptanedione synthesis, the thermolysis of **16d** was investigated (Scheme IX). When it was subjected to the same reaction conditions used in the thermolysis of **16a**, compound **36** instead of a bicycloheptanedione was isolated in 42% yield.

The assigned structure of **36** was determined by its spectroscopic properties as well as an X-ray crystallographic analysis. Two intense carbonyl absorption at 1710 and 1700 cm^{-1} were present in its infrared spectrum. An AA'BB' pattern was evident in the aromatic region of the ^{1}H NMR spectrum, and DEPT experiments indicated the presence of two methylene groups with each proton appearing as doublet of doublets in the ^{1}H NMR spectrum (Figure 2).

The mechanism proposed in Scheme IX accounts for this unusual transformation. It is assumed that the initially formed bicycloheptenone **32** undergoes an acid-catalyzed 1,3-acyl group migration to give **35**, via the carbocation intermediates **33** and **34**.[17] Dehydrogenation of **35** and/or one of its possible tautomeric isomers under the reaction conditions would then provide the observed product **36**.

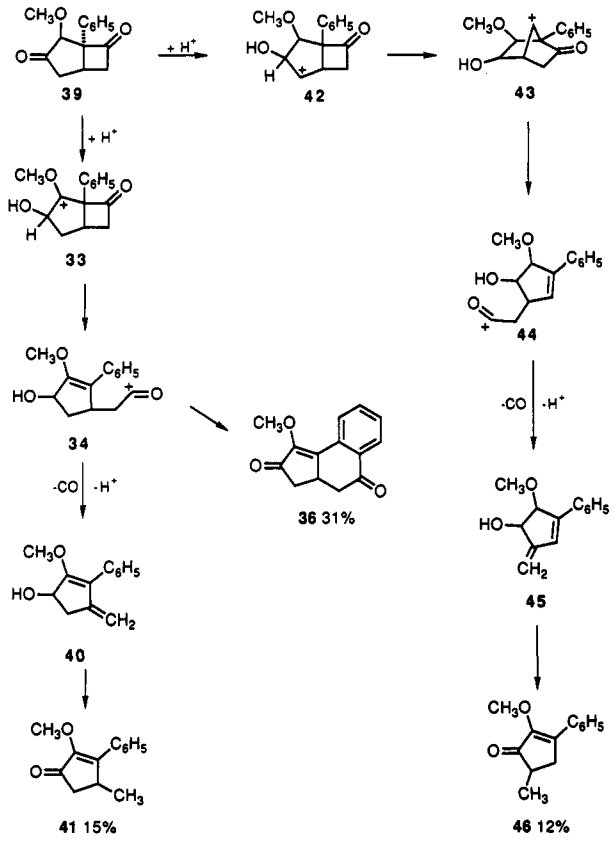
Evidence concerning this proposed mechanism, as well as an example extending the synthetic scope of the allylcyclobutenone rearrangement, was obtained from an investigation of the thermolysis of 4-allyl-3-methoxy-2-phenyl-4-[(trimethylsilyl)oxy]cyclobutenone (**37**) (Scheme X). This was prepared from its hydroxy precursor **16d** by treatment with TMSCl and imidazole. Thermolysis of **37** gave a high yield of bicycloheptenone **38**, a compound analogous to its 4-methoxy derivative **18d**. Treatment of **38** with CsF gave **39** (71%) as a 8:1 mixture of diastereomers.

Compound **39** was found to be stable when subjected to thermolysis in refluxing toluene (conditions used for the rearrangement of **16d** to **36**). However, it was converted to **36** (31%), along with the cyclopentenones **41** (15%) and **46** (12%), in refluxing toluene in the presence of a few drops of glacial acetic acid (Scheme XI).

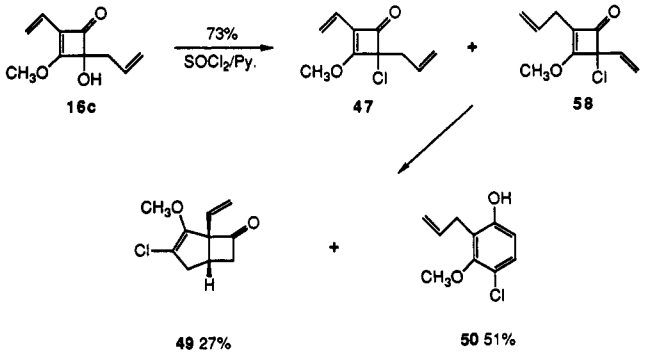
The structure assignments of **41** and **46** are based on their spectroscopic data. Mass spectra for both compounds indicate the loss of CO. Carbonyl absorptions around 1700

(17) Previously reported 1,3-acyl group migrations in the bicyclo[3.2.0]heptanone series require high temperature or photolysis. See, for example: (a) Bertrand, M.; Gil, G.; Junino, A.; Maurin, R. *Tetrahedron Lett.* **1977**, 1779. (b) Lyle, T. A.; Frei, B. *Helv. Chim. Acta* **1981**, *64*, 2598. (c) Lyle, T. A.; Mereyala, H. B.; Pascual, A.; Frei, B. *Helv. Chim. Acta* **1984**, *67*, 774.

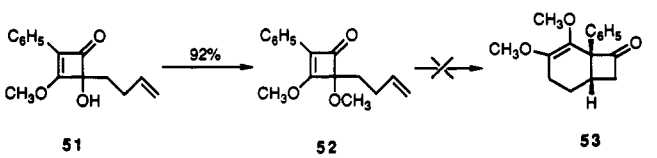
Scheme XI



Scheme XII



Scheme XIII



cm^{-1} are present in their infrared spectra. The methine proton at position-4 in **41** appears as a multiplet at δ 2.50 while the methine proton at position-5 in **46** appears as a multiplet at δ 3.40.

A proposed mechanism accounting for the formation of these cyclpentenones is outlined in Scheme XI. Cations **33** and **42** are formed from **39** in the presence of acetic acid and proceed to give **34** and **42**, respectively. Bond scission in **43** leads to **44** and subsequent loss of CO generates **45** and this gives **46** upon proton shift. Analogously, bond scission in **33** gives **34** and loss of CO provides **40**, the ultimate precursor to **41**.

It was of interest to probe the rearrangement of 4-allylcyclobutenones with substituents other than hydroxy, alkoxy, or silyloxy groups at position-4. Thus, **16c** was treated with thionyl chloride/pyridine to give a mixture of chlorides (Scheme XII).[18] This mixture was thermolyzed directly in toluene to give bicyclo[3.2.0]heptenone **49** and the *p*-chlorophenol **50** in 27% and 51% yield, respectively. It was previously shown that treatment of 4-hydroxycyclobutenones with thionyl chloride involves a carbocation intermediate and that chloride attack occurs at the position gaining the more cation stabilization. As a result, the formations of **49** and **50** are viewed as arising respectively from the 4-chlorocyclobutenones **47** and **48**.

One attempt to generate bicyclo[4.2.0]octadienones is give in Scheme XIII. Addition of 4-lithiobutene to 3-methoxy-4-phenyl-3-cyclobutene-1,2-dione resulted in the formation of adduct **51**, which was converted to its methyl ether **52** in excellent yield. However, this was found to be stable in refluxing *p*-xylene at 138 °C for a prolonged period of time. Presumably the ketene intermediate, if formed, does not undergo cycloaddition to the alkene due to the less favorable entropy of activation associated with six-membered ring formation.[19] This agrees with other reported observations. For example, intramolecular cummulene/alkene cycloaddition reactions having the alkene moiety separated by a tether longer than three atoms are rare and have been achieved only with keteniminium salts,[20] alkoxy ketenes,[21] and in cases with conformationally restricted tethers.

Conclusion

The stereospecific [2 + 2] cycloaddition of ketenes to alkenes is a valuable method for the synthesis of cyclobutanones and compounds that can derive from them. It is one of the few general methods for the carbofunctionalization of alkenes. The generation of ketenes from 4-allylcyclobutenones and subsequent intramolecular cycloaddition to bicyclo[3.2.0] ring systems are general and effective. This new methodology has the advantages that the bicyclic ring can be easily prepared with high regiocontrol of the substitution pattern.

Experimental Section

General Procedures. All reactions were performed in flame-dried glassware under a positive pressure of argon. Reaction mixtures were stirred magnetically. Air-sensitive solutions were transferred via cannula and were introduced into the reaction vessels through rubber septa. Butyllithium was introduced to the reaction mixture vessels via syringe. Reaction solutions were concentrated on a Buchi rotary evaporator at 15–20 mmHg. Column chromatography was performed by using E. Merck silica gel (230–400 mesh), with hexanes and ethyl acetate as the eluants.

Product Purity. The purity of those new compounds reported here for which no C, H analyses were obtained are based upon ^{1}H NMR and ^{13}C NMR analyses. These data as well as X-ray crystallographic data for compounds **31** and **36** are available as supplementary material.

4-Hydroxy-2,3-dimethoxy-4-(2-propenyl)-2-cyclobuten-1-one (16a). A solution of 0.50 g (3.5 mmol) of 3,4-dimethoxy-3-cyclobutene-1,2-dione in 120 mL of THF was cooled to −78 °C. To the solution was added via syringe 3.70 mL (3.70 mmol) of allylmagnesium bromide (Aldrich, 1.0 M solution in THF). The

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(19) For similar results, see: Snider, B. B.; Walner, M. *Tetrahedron* **1989**, *45*, 3171.

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(21) Snider, B. B.; Hui, R. A. H. F.; Kulkarni, Y. S. *J. Am. Chem. Soc.* **1985**, *107*, 2194.

resulting solution was stirred at −78 °C for 15 min and quenched by being poured into a separatory funnel containing 10 mL of H_2O and 20 mL of ether. The organic phase was washed with brine (2 × 10 mL) and dried ($MgSO_4$). Removal of the solvent gave a slightly yellow oil, which was purified by flash chromatography (3:1 hexanes–EtOAc) to provide 0.45 g (71%) of **16a** as a colorless wet solid: mp 34–37 °C; IR ($CHCl_3$) 3380, 3020, 2960, 1780, 1630, 1470, 1440, 1350, 1240, 1050, 1000, 930, 890, 870 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.44 (s, 1 H), 2.61 (d, J = 9.0 Hz, 1 H), 3.96 (s, 3 H), 4.14 (s, 3 H), 5.19 (d, J = 12.0 Hz, 1 H), 5.21 (d, J = 15.0 Hz, 1 H), 5.78–5.93 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 37.5, 58.3, 60.0, 85.5, 119.0, 131.9, 133.5, 167.9, 186.8; MS (CI), m/z (rel intensity) 185 (100), 167 (32), 153 (20); MS (EI), m/z (rel intensity) 156 (17), 141 (19), 124 (8), 115 (22), 99 (14), 81 (27), 69 (20), 53 (100); exact mass calcd for $C_9H_{12}O_4$ 184.0736, found 184.0736.

2-Butyl-4-hydroxy-3-methoxy-4-(3-propenyl)-2-cyclobuten-1-one (16b). In a manner similar to that used for the synthesis of **16a**, 0.44 g (2.60 mmol) of 3-butyl-4-methoxy-3-cyclobutene-1,2-dione in 150 mL of THF (−100 °C (N_2/isooctane) and 2.88 mL (2.88 mmol) of allylmagnesium bromide provided 49 mg (27%) of **16b** as a colorless oil: IR (film) 3460, 2970, 2940, 2880, 1760, 1750, 1620, 1610, 1465, 1360, 1090, 1000, 920 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, J = 7.5 Hz, 3 H), 1.26–1.38 (m, 2 H), 1.43–1.54 (m, 2 H), 2.04–2.15 (m, 2 H), 2.58 (dd, J = 14.1, 7.4 Hz, 1 H), 2.67 (dd, J = 14.1, 7.4 Hz, 1 H), 2.77 (s, 1 H), 4.12 (s, 3 H), 5.13–5.23 (m, 2 H), 5.73–5.87 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.5, 21.4, 22.3, 29.5, 37.6, 59.2, 90.3, 118.6, 127.1, 132.0, 183.4, 193.8; MS (EI), m/z (rel intensity) 210 (3), 181 (1), 169 (2), 153 (3), 140 (6), 139 (6), 125 (9), 111 (7), 97 (19), 81 (33), 71 (100); exact mass calcd for $C_{12}H_{18}O_3$ 210.1256, found 210.1242.

2-Ethenyl-4-hydroxy-3-methoxy-4-(3-propenyl)-2-cyclobuten-1-one (16c). In a manner similar to that used for the synthesis of **16a**, 0.200 g (1.45 mmol) of 3-ethenyl-4-methoxy-3-cyclobutene-1,2-dione in 80 mL of THF (−78 °C (N_2/isooctane) and 1.59 mL (1.59 mmol) of allylmagnesium bromide provided 139 mg (53%) of **16c** as a colorless oil: IR (film) 3380, 2980, 1760, 1750, 1650, 1590, 1470, 1360, 1090, 1000, 930, 740 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.58–2.73 (m, 2 H), 4.19 (s, 3 H), 5.15–5.25 (m, 2 H), 5.39 (dd, J = 11.0, 2.0 Hz, 1 H), 5.76–5.90 (m, 1 H), 5.96 (dd, J = 17.6, 2.0 Hz, 1 H), 6.18 (dd, J = 18.0, 11.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 37.8, 60.0, 90.7, 119.2, 121.5, 121.7, 123.3, 131.7, 180.7, 191.0; MS (CI), m/z (rel intensity) 181 (100), 163 (9); MS (EI), m/z (rel intensity) 180 (1), 165 (4), 152 (14), 137 (11), 120 (7), 111 (22), 91 (39), 83 (82), 79 (100), 68 (68), 53 (78); exact mass calcd for $C_{10}H_{12}O_3$ 180.0786, found 180.0783.

4-Hydroxy-3-methoxy-2-phenyl-4-(2-propenyl)-2-cyclobuten-1-one (16d). In a manner similar to that used for the synthesis of **16a**, 0.500 g (2.66 mmol) of 3-methoxy-4-phenyl-3-cyclobutene-1,2-dione in 120 mL of THF (−100 °C (N_2/isooctane) and 2.95 mL (2.92 mmol) of allylmagnesium bromide provided 0.36 (58%) of **16d** as a white solid: mp 101–104 °C; IR ($CDCl_3$) 3330, 3000, 1760, 1635, 1600, 1500, 1470, 1450, 1370, 1340, 1320, 1010, 1000, 690 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.73 (ddt, J = 14.2, 7.2, 1.0 Hz, 1 H), 2.85 (s, 1 H), 2.87 (ddt, J = 14.2, 7.6, 1.0 Hz, 1 H), 4.27 (s, 3 H), 5.15–5.30 (m, 2 H), 5.78–5.92 (m, 1 H), 7.26–7.40 (m, 3 H), 7.70–7.73 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 38.5, 59.9, 92.1, 119.2, 124.0, 126.9, 128.0, 128.2, 128.3, 131.7, 181.9, 190.9; MS (CI), m/z (rel intensity) 231 (100), 213 (16); MS (EI), m/z (rel intensity) 230 (3), 202 (12), 189 (7), 161 (22), 145 (16), 141 (6), 133 (39), 129 (84), 118 (100), 89 (59), 63 (37); exact mass calcd for $C_{14}H_{14}O_3$ 230.0943, found 230.0935. Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 72.77; H, 6.13.

2-Hexynyl-4-hydroxy-3-methoxy-4-(3-propenyl)-2-cyclobuten-1-one (16e). In a manner similar to that used for the synthesis of **16a**, 0.500 g (2.60 mmol) of 3-hexynyl-4-methoxy-3-cyclobutene-1,2-dione in 150 mL of THF (−100 °C (N_2/isooctane) and 3.12 mL (3.12 mmol) of allylmagnesium bromide provided 0.256 g (42%) of **16e** as white crystals (hexane): mp 57–58 °C; IR ($CHCl_3$) 3370, 2960, 2940, 2880, 2240, 1770, 1615, 1460, 1360, 1240, 990, 930, 640 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, J = 7.2 Hz, 3 H), 1.40–1.60 (m, 4 H), 2.33 (t, J = 7.0 Hz, 2 H), 2.60 (d, J = 7.4 Hz, 2 H), 2.67 (s, 1 H), 4.33 (s, 3 H), 5.17–5.25 (m, 2 H), 5.76–5.90 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.4, 19.1, 21.9, 30.2, 37.3, 60.7, 66.9, 90.0, 95.4, 108.2, 119.3, 131.3, 184.6, 190.0; MS (EI), m/z (rel intensity) 234 (2), 206 (21), 193 (15), 191 (20), 163 (47), 149 (45), 131 (38), 121 (37), 103 (37), 91 (68), 79 (100); MS (Ci), m/z (rel intensity) 235 (MH^+, 100); exact mass calcd for $C_{14}H_{18}O_3$ 234.1256, found 234.1258. Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.45; H, 7.54.

4-Hydroxy-4-(3-propenyl)-3-methoxy-2-[(trimethylsilyl)ethynyl]-2-cyclobuten-1-one (16f). In a manner similar to that used for the synthesis of **16a**, 0.45 g (2.16 mmol) of 3-methoxy-4-[(trimethylsilyl)ethynyl]-3-cyclobutene-1,2-dione in 100 mL of THF (−100 °C (N_2/isooctane) and 2.2 mL (2.2 mmol) of allylmagnesium bromide provided 0.21 g (39%) of **16f** as a slightly yellow oil: IR (film) 3400, 2970, 2160, 1770, 1610, 1450, 1350, 990, 960, 880, 850 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.95 (s, 9 H), 2.60 (d, J = 6.0 Hz, 2 H), 4.37 (s, 3 H), 5.18–5.27 (m, 2 H), 5.77–5.90 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.4, 37.4, 61.0, 90.2, 90.4, 100.1, 107.6, 120.2, 131.0, 185.5, 188.8; MS (EI) m/z (rel intensity) 250 (0.3), 235 (3), 222 (2), 207 (5), 175 (6), 165 (2), 149 (5), 138 (3), 123 (8), 97 (4), 89 (23), 75 (32), 73 (100), 59 (16), 53 (12); exact mass calcd for $C_{13}H_{18}SiO_3$ 250.1025, found 250.1014.

2,3,4-Trimethoxy-4-(3-propenyl)-2-cyclobuten-1-one (17a). A solution of 0.270 g (1.47 mmol) of **16a**, 0.91 mL (14.7 mmol) of methyl iodide, 0.68 g (2.93 mmol) of silver(I) oxide, and 2.03 g (14.7 mmol) of potassium carbonate in 6 mL of acetonitrile was stirred at ambient temperature for 11 h. The suspension obtained was filtered through a pad of Celite and rinsed with ether. Concentration gave a slightly yellow oil, which was chromatographed (4:1 hexanes–EtOAc) to give 0.256 g (88%) of **17a** as a colorless oil: IR (film) 2990, 2960, 2840, 1780, 1650, 1470, 1440, 1350, 1225, 1140, 1120, 1055, 1020, 1000, 950, 930, 890, 850 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.54 (dd, J = 14.4, 7.5 Hz, 1 H), 2.63 (dd, J = 14.4, 7.2 Hz, 1 H), 3.33 (s, 3 H), 3.97 (s, 3 H), 4.12 (s, 3 H), 5.10–5.15 (m, 1 H), 5.70–5.84 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 36.5, 51.8, 58.2, 59.6, 91.4, 118.2, 132.0, 134.5, 167.0, 185.8; MS (CI), m/z (rel intensity) 199 (MH^+, 100), 167 (54); MS (EI), m/z (rel intensity) 183 (2), 170 (6), 155 (31), 139 (13), 127 (25), 113 (19), 95 (24), 81 (39), 69 (39), 53 (100); exact mass calcd for $C_{10}H_{14}O_4$ 198.0892, found 198.0884.

2-Butyl-3,4-dimethoxy-4-(3-propenyl)-2-cyclobuten-1-one (17b). In a similar manner, 82 mg (0.39 mmol) of **16b**, 0.24 mL (3.9 mmol) of methyl iodide, 0.18 g (0.78 mmol) of Ag_2O, and 0.54 g (3.9 mmol) of potassium carbonate in 5 mL of acetonitrile gave 78 mg (89%) of **17b** as a colorless oil: IR (film) 2970, 2950, 2880, 1770, 1635, 1625, 1470, 1460, 1360, 1290, 1120, 1000, 930 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, J = 7.2 Hz, 3 H), 1.30–1.40 (m, 2 H), 1.45–1.55 (m, 2 H), 2.10–2.16 (m, 2 H), 2.51 (ddt, J = 14.4, 7.6, 1.0 Hz, 1 H), 2.69 (ddt, J = 14.4, 7.0, 1.2 Hz, 1 H), 3.34 (s, 3 H), 4.10 (s, 3 H), 5.06–5.17 (m, 2 H), 5.65–5.79 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.5, 21.4, 22.3, 29.7, 36.9, 52.3, 58.9, 96.7, 118.2, 129.1, 132.1, 182.4, 191.7; MS (EI), m/z (rel intensity) 224 (7), 209 (20), 196 (2), 181 (8), 167 (19), 153 (15), 139 (22), 121 (17), 109 (17), 97 (17), 91 (30), 79 (60), 69 (50), 55 (100), 53 (66); exact mass calcd for $C_{13}H_{20}O_3$ 224.1412, found 224.1401.

2-Ethenyl-3,4-dimethoxy-4-(3-propenyl)-2-cyclobuten-1-one (17c). In a similar manner, 150 mg (0.83 mmol) of **16c**, 0.52 mL (8.3 mmol) of methyl iodide, 0.39 g (1.67 mmol) of silver(I) oxide, and 0.58 g (4.2 mmol) of potassium carbonate in 5 mL of acetonitrile gave 0.140 g (87%) of **17c** as a colorless oil: IR (film) 3000, 2960, 2840, 1760, 1650, 1590, 1470, 1460, 1410, 1360, 1300, 1140, 1120, 1000, 930 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.55 (ddt, J = 14.4, 7.6, 1.0 Hz, 1 H), 2.71 (ddt, J = 14.4, 7.0, 1.2 Hz, 1 H), 3.36 (s, 3 H), 4.16 (s, 3 H), 5.07–5.18 (m, 2 H), 5.40 (dd, J = 11.0, 2.1 Hz, 1 H), 5.69–5.83 (m, 1 H), 5.97 (dd, J = 17.6, 2.1 Hz, 1 H), 6.17 (dd, J = 17.6, 11.0 Hz, 1 H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 37.1, 52.8, 59.7, 96.9, 118.6, 121.4, 121.6, 124.8, 131.8, 180.2, 189.8; MS (EI), m/z (rel intensity) 194 (3), 179 (13), 166 (6), 151 (31), 135 (12), 125 (23), 123 (19), 119 (13), 108 (20), 95 (23), 91 (81), 77 (42), 65 (38), 58 (43), 53 (100); exact mass calcd for $C_{11}H_{14}O_3$ 194.0943, found 194.0956.

3,4-Dimethoxy-2-phenyl-4-(3-propenyl)-2-cyclobuten-1-one (17d). In a similar manner, 80 mg (0.35 mmol) of **16d**, 0.41 g (1.8 mmol) of Ag_2O, 0.22 mL (3.5 mmol) of methyl iodide, and 0.48 g (3.5 mmol) of potassium carbonate in 5 mL of acetonitrile gave 80 mg (95%) of **17d** as a colorless oil: IR (film) 3000, 2960, 2840, 1760, 1630, 1600, 1500, 1365, 1340, 1320, 1140, 1120, 1100, 1000, 790, 700, 620 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.65 (ddt, J = 14.5, 7.7, 1.0 Hz, 1 H), 2.90 (ddt, J = 14.5, 7.0, 1.3 Hz, 1 H), 3.43

(s, 3 H), 4.23 (s, 3 H), 5.08–5.23 (m, 2 H), 5.71–5.85 (m, 1 H), 7.26–7.36 (m, 3 H), 7.75–7.80 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 37.8, 52.9, 59.7, 98.3, 118.8, 125.5, 126.9, 128.0, 128.1, 128.4, 131.8, 181.1, 188.9; MS (EI), *m/z* (rel intensity) 244 (13), 229 (13), 215 (12), 203 (16), 201 (16), 185 (16), 175 (15), 159 (12), 141 (56), 129 (24), 128 (20), 115 (42), 89 (100), 77 (28), 69 (40), 63 (51); exact mass calcd for $C_{15}H_{16}O_3$ 244.1099, found 244.1093.

2-Hexynyl-3,4-dimethoxy-4-(3-propenyl)-2-cyclobuten-1-one (17e). In a similar manner, 120 mg (0.51 mmol) of **16e**, 0.31 mL (5.1 mmol) of methyl iodide, 0.12 g (0.51 mmol) of silver(I) oxide, and 0.70 g (5.1 mmol) of potassium carbonate in 4 mL of acetonitrile gave 0.100 g (80%) of **17e** as a colorless oil: IR (film) 2970, 2940, 2240, 1775, 1650, 1640, 1470, 1460, 1360, 1130, 990, 930, 720 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, *J* = 7.2 Hz, 3 H), 1.38–1.60 (m, 4 H), 2.35 (t, *J* = 6.9 Hz, 2 H), 3.4 (s, 3 H), 4.33 (s, 3 H), 5.10–5.18 (m, 2 H), 5.69–5.83 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.5, 19.1, 21.9, 30.2, 36.4, 53.0, 60.5, 66.7, 95.6, 96.5, 109.7, 118.8, 131.5, 184.7, 189.5; MS (EI), *m/z* (rel intensity) 248 (9), 233 (19), 220 (19), 205 (57), 191 (18), 163 (67), 147 (23), 135 (32), 119 (33), 105 (55), 103 (42), 91 (100), 79 (56), 77 (90), 65 (35); exact mass calcd for $C_{15}H_{20}O_3$ 248.1412, found 248.1416.

3,4,5-Trimethoxybicyclo[3.2.0]hept-3-en-6-one (18a). A solution of 120 mg of **17a** in 50 mL of freshly distilled *p*-xylene was heated at reflux for 50 h. The colorless solution obtained was cooled to ambient temperature and the solvent was removed under reduced pressure. The residue was chromatographed (10:1 hexanes–EtOAc) to provide 99.2 mg (83%) of **18a** as a colorless oil: IR (film) 2990, 2960, 2860, 1785, 1770, 1680, 1470, 1460, 1330, 1340, 1300, 1260, 1235, 1150, 1100, 1075, 1020, 1000, 800 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.30 (d, *J* = 16.2 Hz, 1 H), 2.55–2.70 (m, 2 H), 2.90 (dd, *J* = 16.2, 7.0 Hz, 1 H), 3.10 (dd, *J* = 17.4, 9.1 Hz, 1 H), 3.32 (s, 3 H), 3.68 (s, 3 H), 3.81 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.2, 32.7, 47.8, 52.2, 57.1, 58.3, 103.3, 127.5, 142.1, 203.8; MS (EI), *m/z* (rel intensity) 170 (19), 155 (51), 141 (19), 127 (44), 113 (24), 95 (26), 83 (35), 67 (45), 55 (100), 53 (85); MS (CI), *m/z* (rel intensity) 199 (100), 167 (98), 105 (6); exact mass calcd for $C_{10}H_{14}O_4$ 198.0892, found 198.0875.

1-Butyl-2,3-dimethoxybicyclo[3.2.0]hept-2-en-7-one (18b). A solution of 60 mg of **17b** in 25 mL of freshly distilled *p*-xylene was heated at reflux for 5 h. The colorless solution obtained was cooled to ambient temperature and the solvent was removed under reduced pressure. The residue was chromatographed (30:1 hexanes–EtOAc) to provide 51.2 mg (85%) of **18b** as a colorless oil: IR (film) 2960, 2940, 2860, 1780, 1675, 1465, 1390, 1335, 1290, 1255, 1230, 1220, 1160, 1090, 1080, 1025, 1000 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, *J* = 7.2 Hz, 3 H), 1.20–1.35 (m, 4 H), 1.65–1.75 (m, 2 H), 2.30 (d, *J* = 15.4 Hz, 1 H), 2.30–2.38 (m, 1 H), 2.80 (dd, *J* = 15.7, 8.1 Hz, 1 H), 2.89 (dd, *J* = 18.1, 5.6 Hz, 1 H), 3.18 (dd, *J* = 17.9, 8.6 Hz, 1 H), 3.65 (s, 3 H), 3.71 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.8, 22.8, 25.0, 26.34, 28.1, 33.1, 51.0, 57.2, 58.7, 77.4, 131.6, 138.1, 209.9; MS (CI), *m/z* (rel intensity) 225 (100); MS (EI), *m/z* (rel intensity) 224 (3), 196 (49), 181 (39), 167 (59), 154 (69), 153 (74), 139 (100), 125 (22), 109 (21), 95 (19), 91 (18), 79 (37), 77 (22); exact mass calcd for $C_{13}H_{20}O_3$ 224.1412, found 224.1401.

1-Ethenyl-2,3-dimethoxybicyclo[3.2.0]hept-2-en-7-one (18c). A solution of 108 mg of **17c** in 40 mL of freshly distilled toluene was heated at reflux for 6 h. The colorless solution obtained was cooled to ambient temperature and the solvent was removed under reduced pressure. The residue was chromatographed (3:1 hexanes–EtOAc) to provide 97.4 mg (90%) of **18c** as a colorless oil: IR (film) 2980, 2940, 2850, 1780, 1770, 1680, 1465, 1455, 1340, 1300, 1260, 1240, 1100, 1000, 930 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.33 (d, *J* = 15.7 Hz, 1 H), 2.45–2.53 (m, 1 H), 2.85–2.96 (m, 2 H), 3.27 (dd, *J* = 18.1, 9.1 Hz, 1 H), 3.64 (s, 3 H), 3.74 (s, 3 H), 5.25 (d, *J* = 10.7 Hz, 1 H), 5.38 (d, *J* = 16.2 Hz, 1 H), 5.97 (dd, *J* = 17.5, 10.7 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.4, 32.7, 50.9, 57.2, 58.8, 78.7, 116.6, 131.6, 133.1, 138.5, 206.6; MS (EI), *m/z* (rel intensity) 194 (20), 166 (34), 151 (85), 137 (48), 123 (49), 108 (47), 94 (28), 91 (100), 79 (71), 77 (74), 66 (69), 65 (77), 57 (44), 55 (63), 53 (68), 51 (77); exact mass calcd for $C_{11}H_{14}O_3$ 194.0943, found 194.0932.

2,3-Dimethoxy-1-phenylbicyclo[3.2.0]hept-2-en-7-one (18d). A solution of 50 mg of **17d** in 25 mL of THF was heated at reflux for 14 h. The solvent was removed under reduced pressure to give a colorless residue, which upon chromatography (20:1 hexanes–EtOAc) provided 43.2 mg (86%) of **18d** as a colorless oil: IR (film) 2960, 2860, 1775, 1680, 1500, 1465, 1450, 1395, 1340, 1310, 1260, 1240, 1080, 760, 700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.42 (d, *J* = 15.9 Hz, 1 H), 2.62–2.66 (m, 1 H), 3.00–3.07 (m, 2 H), 3.35 (dd, *J* = 18.1, 9.2 Hz, 1 H), 3.53 (s, 3 H), 3.78 (s, 3 H), 7.26–7.39 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.9, 33.0, 51.4, 57.4, 59.0, 79.7, 126.2, 127.2, 128.5, 132.6, 137.8, 139.2, 206.6; MS (EI), *m/z* (rel intensity) 244 (2), 235 (7), 217 (15), 216 (100); exact mass calcd for $C_{15}H_{16}O_3$ 244.1099, found 244.1098.

1-Hexynyl-2,3-dimethoxybicyclo[3.2.0]hept-2-en-7-one (18e). A solution of 80 mg of **17e** in 40 mL of freshly distilled *p*-xylene was heated at reflux for 7 h. The colorless solution obtained was cooled to ambient temperature and the solvent was removed under reduced pressure. The residue was chromatographed (10:1 hexanes–EtOAc) to provide 57.3 mg (72%) of **18e** as a colorless oil: IR (film) 2970, 2950, 2870, 1790, 1680, 1470, 1400, 1340, 1300, 1260, 1230, 1180, 1100, 1075, 1030, 1000 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.5 Hz, 3 H), 1.33–1.51 (m, 4 H), 2.20–2.30 (m, 3 H), 2.55–2.61 (m, 1 H), 2.91 (dd, *J* = 15.7, 8.1 Hz, 1 H), 2.98 (dd, *J* = 18.3, 5.9 Hz, 1 H), 3.35 (dd, *J* = 18.3, 9.2 Hz, 1 H), 3.70 (s, 3 H), 3.73 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.5, 18.7, 21.8, 29.2, 30.6, 33.0, 52.1, 57.3, 59.0, 68.8, 74.0, 89.3, 129.9, 138.4, 201.8; MS (EI), *m/z* (rel intensity) 248 (0.4), 220 (29), 205 (44), 191 (14), 177 (23), 163 (43), 147 (15), 135 (18), 119 (23), 105 (48), 91 (100), 77 (87), 65 (59); MS (CI), *m/z* (rel intensity) 249 (100); exact mass calcd for $C_{15}H_{20}O_3$ 248.1412, found 248.1410.

4-Hydroxy-2,3-dimethoxy-4-(1,1-dimethyl-2-propenyl)-2-cyclobuten-1-one (20a). To a flask charged with 3 mL of ether and 0.17 g (7.1 mmol) of magnesium ribbon (freshly sandpapered) was added 0.15 g of 1-bromo-3-methyl-2-butene. A small iodine crystal was then added and the mixture was vigorously stirred. After gas evolution was observed, the rest of the bromide (0.27 g in 4 mL of ether) and 0.20 g (1.4 mmol) of dimethyl squarate were added simultaneously to the reaction mixture from two addition funnels. The brown suspension obtained was stirred at ambient temperature for 5 min and quenched being poured into a separatory funnel containing 10 mL of ether and 5 mL of 5% NH_4Cl. Concentration gave a yellow oil, which was chromatographed (2:1 hexanes–EtOAc) to give, along with 0.08 g of starting material (dimethyl squarate), 0.12 g of **20a** (67% based on recovered starting material) as a colorless oil: IR (film) 3540, 3440, 2980, 2960, 1770, 1630, 1465, 1340, 1330, 1230, 1130, 1070, 1010, 990, 930, 870 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.16 (s, 3 H), 1.17 (s, 3 H), 2.35 (s, 1 H), 3.97 (s, 3 H), 4.14 (s, 3 H), 5.15–5.20 (m, 2 H), 6.04 (dd, *J* = 17.0, 10.5 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.2, 22.8, 42.0, 58.5, 60.4, 89.6, 114.5, 134.3, 143.3, 166.5, 185.9; MS (CI), *m/z* (rel intensity) 213 (100), 195 (21), 181 (34); MS (EI), *m/z* (rel intensity) 197 (7), 169 (21), 143 (100), 115 (46), 109 (11), 83 (26), 69 (43), 58 (60), 55 (31); exact mass calcd for $C_{11}H_{17}O_4^+$ (HRCI) 213.1127, found 213.1124.

4-(1-Methyl-2-propenyl)-4-hydroxy-2,3-dimethoxy-2-cyclobuten-1-one (20b). In a similar manner, 274 mg of magnesium ribbon (11.3 mmol, freshly sandpapered), 1 mL of 1-bromo-2-butene (0.76 g in 6 mL of ether), and 0.20 g (1.4 mmol) of dimethyl squarate in 15 mL of THF at 0 °C gave 0.20 g (72%) of **20b** (a mixture of diastereomers) as a colorless oil: IR (film) 3400, 2980, 2960, 1770, 1640, 1630, 1620, 1470, 1340, 1050, 1020, 990, 970, 890, 850 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.09 (s, 3 H), 1.11 (s, 3 H), 2.42 (s, 1 H), 2.53 (s, 1 H), 2.63–2.76 (m, 2 H), 3.96 (s, 3 H), 3.97 (s, 3 H), 4.13 (s, 6 H), 5.17–5.24 (m, 4 H), 5.80–5.99 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.3, 15.3, 41.4, 41.8, 58.2, 58.2, 60.0, 60.1, 87.7, 87.8, 116.4, 116.7, 133.9, 133.9, 138.4, 138.5, 167.5, 167.5, 186.2; MS (CI), *m/z* (rel intensity) 199 (100), 181 (18), 167 (27); MS (EI), *m/z* (rel intensity) 170 (5), 155 (18), 143 (19), 115 (35), 95 (29), 87 (19), 67 (71), 55 (100); exact mass calcd for $C_{10}H_{15}O_4^+$ (HRCI) 199.0970, found 199.0962.

4-(1,1-Dimethyl-2-propenyl)-2,3,4-trimethoxy-2-cyclobuten-1-one (21a). A solution of 0.12 g (0.57 mmol) of **20a**, 0.35 mL (5.7 mmol) of methyl iodide, 0.31 g (2.3 mmol) of potassium carbonate, and 0.26 g (1.1 mmol) of silver(I) oxide in 3 mL of acetonitrile was stirred at ambient temperature for 12 h. The suspension obtained was filtered through a pad of Celite and rinsed with ether. Concentration provided a yellow oil, which was chromatographed to give 119 mg (92%) of **21a** as a slightly pale

yellow oil: IR (film) 2960, 1770, 1640, 1630, 1465, 1430, 1345, 1335, 1220, 1100, 1040, 980, 870 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.11 (s, 3 H), 1.12 (s, 3 H), 3.28 (s, 3 H), 3.95 (s, 3 H), 4.12 (s, 3 H), 4.99–5.04 (m, 2 H), 5.99 (dd, J = 17.5, 10.8 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.9, 23.0, 41.6, 52.1, 58.5, 60.1, 95.9, 112.1, 135.3, 144.1, 167.3, 187.1; MS (CI), m/z (rel intensity) 227 (100), 195 (5), 157 (10), 117 (49); MS (EI), m/z (rel intensity) 211 (2), 198 (2), 183 (9), 157 (100), 129 (39), 86 (14), 69 (13), 53 (21); exact mass calcd for $C_{12}H_{19}O_4^+$ (HRCI) 227.1283, found 227.1267.

4-(1-Methyl-2-propenyl)-2,3,4-trimethoxy-2-cyclobuten-1-one (21b). In a similar manner, 195 mg (0.98 mmol) of **20b**, 0.54 g (3.9 mmol) of potassium carbonate, 0.60 mL (9.8 mmol) of methyl iodide, and 0.23 g (0.98 mmol) of silver(I) oxide in 3 mL of acetonitrile gave 196 mg (94%) of **21b** as a colorless oil: IR (film) 2980, 2960, 2950, 1775, 1640, 1630, 1470, 1430, 1350, 1340, 1220, 1120, 1100, 1060, 1020, 990, 970, 880, 860 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.11 (d, J = 6.6 Hz, 3 h), 1.13 (d, J = 6.6 Hz, 3 H), 2.64–2.75 (m, 2 H), 3.33 (s, 6 H), 3.97 (s, 6 H), 4.11 (s, 3 H), 4.13 (s, 3 H), 5.04–5.12 (m, 4 H), 5.78–5.95 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.2, 40.8, 51.7, 51.7, 58.2, 59.7, 59.7, 93.7, 93.8, 115.0, 115.1, 134.8, 134.8, 138.6, 138.8, 166.7, 166.9, 186.0, 186.1; MS (CI), m/z (rel intensity) 213 (100), 181 (45); MS (EI), m/z (rel intensity) 197 (1), 184 (6), 169 (19), 157 (48), 129 (26), 109 (12), 95 (13), 86 (14), 79 (17), 67 (28), 55 (100); exact mass calcd for $C_{11}H_{17}O_4^+$ (HRCI) 213.1127, found 213.1110.

4,4-Dimethyl-1,2,3-trimethoxybicyclo[3.2.0]hept-2-en-7-one (22a). A solution of 90 mg of **21a** in 20 mL of distilled toluene was heated in a sealed tube with the bath temperature around 150 °C for 48 h. The tube was allowed to cool to ambient temperature and the solvent removed in vacuo. The slightly yellow oil obtained was chromatographed (8:1 hexanes–EtOAc) to provide 76.3 mg (85%) of **22a** (a mixture of diastereomers) as a colorless oil: IR (film) 2980, 2950, 2840, 1780, 1670, 1470, 1400, 1330, 1290, 1220, 1150, 1105, 1100, 1040, 1000, 845, 660 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.02 (s, 3 H), 1.18 (s, 3 H), 2.40 (dd, J = 9.2, 6.9 Hz, 1 H), 2.72 (dd, J = 18.0, 9.3 Hz, 1 H), 2.85 (dd, J = 18.0, 6.9 Hz, 1 H), 3.37 (s, 3 H), 3.55 (s, 3 H), 3.88 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 19.5, 28.7, 38.3, 40.5, 43.0, 53.2, 58.5, 58.8, 101.7, 126.7, 148.9, 204.5; MS (CI), m/z (rel intensity) 227 (100), 195 (90); MS (EI), m/z (rel intensity) 198 (28), 183 (100), 152 (29), 123 (19), 109 (16), 91 (27), 67 (37), 55 (79); exact mass calcd for $C_{12}H_{18}O_4$ 226.1205, found 226.1211.

4-Methyl-1,2,3-trimethoxybicyclo[3.2.0]hept-2-en-7-one (22b and 22b). A sealed tube containing 90 mg of **21b** in 8 mL of distilled toluene was heated with the bath temperature around 150 °C for 36 h. The tube was allowed to cool to ambient temperature and the solvent removed in vacuo. The slightly yellow oil obtained was chromatographed (8:1 hexanes–EtOAc) to provide 44.8 mg (90%) of a inseparable mixture of **22b** and **22b'** (6:1 mixture of stereoisomers) as a slightly yellow oil: IR (film) 2970, 2950, 2840, 1780, 1670, 1460, 1340, 1310, 1270, 1265, 1250, 1210, 1110, 1090, 1050, 990, 870 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, **22b**) δ 1.21 (d, J = 6.9 Hz, 3 H), 2.19 (dd, J = 9.6, 6.0 Hz, 1 H), 2.43 (q, J = 6.9 Hz, 1 H), 2.65 (dd, J = 18.0, 6.0 Hz, 1 H), 3.08 (dd, J = 18.0, 9.6 Hz, 1 H), 3.33 (s, 3 H), 3.64 (s, 3 H), 3.86 (s, 3 H); ^1H NMR (300 MHz, $CDCl_3$, **22b'**) δ 1.06 (d, J = 6.9 Hz, 3 H), 2.67–2.77 (m, 2 H), 2.88–3.07 (m, 2 H), 3.33 (s, 3 H), 3.60 (s, 3 H), 3.89 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$, **22b**) δ 19.4, 33.8, 41.0, 47.6, 52.6, 57.8, 58.4, 103.2, 126.9, 146.5, 204.1; ^{13}C NMR (125 MHz, $CDCl_3$, **22b'**) δ 11.44, 32.04, 35.28, 41.33, 52.46, 58.11, 101.82, 127.80, 145.12, 203.65; MS (CI), m/z (rel intensity) 213 9100), 181 (85); MS (EI), m/z (rel intensity) 184 (36), 169 (100), 153 (15), 141 (27), 138 (24), 127 (17), 109 (22), 95 (13), 79 (25), 67 (31), 55 (59), 53 (43); exact mass calcd for $C_{11}H_{16}O_4$ 213.1127, found 213.1114.

2,3-Dimethoxy-4-hydroxy-4-(1-phenyl-2-propenyl)-2-cyclobuten-1-one. To a solution of the Grignard reagent prepared from cinnamyl bromide (0.5 g, 2.5 mmol) and magnesium (100 mg, 3.5 mmol, freshly sandpapered) in THF (50 mL) at –78 °C was added a solution of 3,4-dimethoxy-3-cyclobutene-1,2-dione (106 mg, 0.7 mmol) in THF (20 mL). The reaction was quenched at –78 °C with aqueous ammonium chloride solution (5%, 50 mL). The organic layer was collected and the aqueous layer extracted with ether (3 × 20 mL). The combined extracts were dried over magnesium sulfate and the product (94 mg, 52%) was isolated as a white solid by flash chromatography using hexanes–ethyl acetate (55:45) as eluent: mp 73–75 °C; IR ($CDCl_3$) 3692, 3546, 1776, 1639, 1468, 1333, 1044, 992, 928 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 7.39 (5 H, m), 6.25 (1 H, m) 5.25 (2 H, m), 4.13 (3 H, s), 4.06 (3 H, s), 3.91 (1 H, m), 3.78 (3 H, s), 2.93 (1 H, s), 2.87 (1 H, s); ^{13}C NMR (75 MHz) ($CDCl_3$) δ 185.0, 184.7, 165.6, 165.3, 138.7, 138.5, 136.2, 136.0, 135.1, 135.1, 128.8, 128.6, 128.5, 128.4, 127.3, 119.3, 118.7, 88.1, 88.1, 60.3, 60.2, 58.5, 54.8, 54.4; MS (EI), m/z (rel intensity) 260 (0.1), 232 (12), 169 (10), 143 (100); MS (CI), m/z (rel intensity) 261 (100, 243 (25), 229 (28) 143 (10); HRMS calcd for $C_{15}H_{16}O_4$ 260.1049, found 260.1054.

4-(1-Phenyl-2-propenyl)-2,3,4-trimethoxy-2-cyclobuten-1-one (23). In a manner similar to that used for the synthesis of **20a**, 2,3-dimethoxy-4-hydroxy-4-(1-phenyl-2-propenyl)-2-cyclobuten-1-one (64 mg, 0.26 mmol), methyl iodide (0.3 mL, 5 mmol), potassium carbonate (50 mg, 0.37 mmol), and silver(I) oxide (85 mg, 0.37 mmol) in acetonitrile (2 mL) gave 54 mg (80%) of **23** (oil): IR ($CDCl_3$) 3026, 2990, 2830, 1775, 1638, 1466, 1339, 1218, 1115, 980, 921, 878, 703 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 7.33 (5 H, m), 6.25 (1 H, m), 5.20 (2 H, m), 4.12 (3 H, s), 4.03 (3 H, s), 3.95 (1 H, m), 3.80 (3 H, s), 3.76 (3 H, s), 3.36 (3 H, s); ^{13}C NMR (75 MHz) ($CDCl_3$) δ 185.6, 185.4, 166.3, 166.1, 140.0, 139.7, 136.8, 136.7, 136.0, 136.0, 129.0, 128.6, 128.2, 126.8, 126.7, 117.5, 117.3, 94.4, 94.3, 60.1, 59.9, 58.5, 53.7, 53.4, 52.4; MS (EI), m/z (rel intensity) 259 (4.1, M – CH_3), 157 (100), 129 (19), 117 (24); MS (CI), m/z (rel intensity) 275 (100), 243 (44), 157 (14) 113 (87); HRMS calcd for $C_{15}H_{18}O_3$ (M – CO) 246.1256, found 246.1242.

2-Phenyl-3,4,5-trimethoxybicyclo[3.2.0]hept-3-en-6-one (24 and 25). A solution of 4-(1-phenyl-2-propenyl)-2,3,4-trimethoxy-2-cyclobuten-1-one (*23*) (50 mg, 0.18 mmol) in *p*-xylene (10 mL) in a sealed tube was heated to 150 °C in an oil bath for 15 h. The solvent was then removed in vacuo and the product (38 mg, 76%) was first isolated by flash chromatography using hexanes–ethyl acetate (8.2) as eluent. Further separation by HPLC (hexanes:ethyl acetate = 9:1) resulted in 30.6 mg of the exo isomer **24** as a white solid (mp 79–80 °C) and 2.6 mg of the endo isomer **25**. **Exo isomer 24**: IR ($CDCl_3$) 2943, 1774, 1672, 1602, 1455, 1313, 1282, 1212, 1104, 1043, 924 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 7.34 (5 H, m), 3.81 (3 H, s), 3.75 (3 H, s), 3.68 (1 H, s), 3.37 (3 H, s), 3.19 (1 H, dd, J = 18.0, 9.7 Hz), 2.86 (1 H, dd J = 18.0, 6.0 Hz), 2.59 (1 H, dd, J = 9.7, 6.0 Hz); ^{13}C NMR (75 MHz) ($CDCl_3$) δ 204.0, 143.5, 141.9, 130.7, 128.8, 127.4, 127.1, 103.3, 58.7, 57.9, 53.5, 52.2, 48.1, 35.1; MS (EI), m/z (rel intensity) 246 (100, M – CO), 231 (32), 215 (45), 203 (16), 189 (17), 171 (20), 169 (24); MS (CI), m/z (rel intensity) 275 (88), 243 (100); HRMS calcd for $C_{16}H_{18}O_4$ 274.1205, found 274.1166. **Endo isomer 25**: oil; IR ($CDCl_3$) 2938, 1777, 1673, 1456, 1280, 1224, 1103, 1046 cm^{-1}; ^1H NMR (300 MHz) ($CDCl_3$) δ 7.39 (3 H, m), 7.21 (2 H, m), 4.49 (1 H, d, J = 7.8 Hz), 3.83 (3 H, s), 3.78 (3 H, s), 3.47 (3 H, s), 2.97 (1 H, ddd J = 9.8, 7.8, 6.6 Hz), 2.64 (1 H, dd, J = 18.6, 6.6 Hz) 2.48 (1 H, dd, J = 18.6, 9.8 Hz); ^{13}C NMR (75 MHz) ($CDCl_3$) δ 203.3, 142.2, 136.7, 131.1, 128.5, 128.3, 127.0, 107.9, 58.7, 57.7, 52.7, 46.6, 43.3, 32.8; MS (EI), m/z (relative intensity) 274 (2), 246 (100), 231 (38), 215 (56); MS (CI), m/z (rel intensity) 275 (100), 243 (73); HRMS calcd for $C_{16}H_{19}O_4$ 375.1283, found 275.1283.

4-Hydroxy-2,3-dimethoxy-4-(2-methyl-2-propenyl)-2-cyclobuten-1-one (27). To a flask charged with 0.41 g of magnesium ribbon (freshly sandpapered) was added 2 mL of the 3-chloro-2-methylpropene solution (1.0 mL of the chloride in 10 mL of ether), and the reaction mixture was vigorously stirred. Gas evolution was observed after 2 min. The rest of the chloride solution was then added dropwise. A white suspension was obtained. The suspension was transferred via syringe to another flask containing 0.30 g (2.1 mmol) of dimethyl squarate in 15 mL of THF at 0 °C. The orange solution was quenched with 5% NH_4Cl solution, washed with brine, and dried ($MgSO_4$). Concentration gave an orange oil, which was chromatographed (3:1 hexanes–EtOAc) to yield 155 mg (37%) of **27** as a colorless oil: IR (film) 3392, 2979, 2952, 2928, 2917, 1770, 1630, 1470, 1434, 1376, 1338, 1218, 1076, 1043, 1031, 988, 949, 895, 822 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.83 (s, 3 H), 2.54 (dd, J = 15.0, 0.5 Hz, 1 H), 2.60 (dd, J = 15.0, 0.5 Hz, 1 H), 2.57 (s, 1 H), 3.96 (s, 3 H), 4.14, (s, 3 H), 4.88–4.99 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.0, 41.3, 58.3, 60.1, 84.9, 115.7, 133.6, 140.4, 167.3, 186.5; MS (CI), m/z (rel intensity) 199 (7), 181 (6), 167 (18), 143 (29), 141 (100); MS (EI), m/z (rel intensity) 170 (5), 155 (24), 143 (13), 123 (19), 115 (23), 99 (20), 95 (27), 83 (18), 69 (40), 67 (58), 55 (100); exact mass calcd for $C_{10}H_{14}O_4$ 199.0970, found 199.0951.

2,3,4-Trimethoxy-4-(2-methyl-2-propenyl)-2-cyclobuten-1-one (28). In a manner similar to that used for the synthesis of **20a**, 130 mg (0.66 mmol) of **27**, 0.41 mL (6.6 mmol) of methyl iodide, 0.15 g (0.66 mmol) of silver(I) oxide, and 0.36 g (2.6 mmol) of potassium carbonate in 4 mL of acetonitrile gave 124 mg (89%) of **28** as a colorless oil: IR (film) 2960, 1780, 1640, 1470, 1435, 1350, 1225, 1110, 1060, 1050, 1010, 990, 900, 890 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.75 (s, 3 H), 2.50 (d, J = 14.1 Hz, 1 H), 2.60 (d, J = 14.1 Hz, 1 H), 3.31 (s, 3 H), 3.96 (s, 3 H), 4.12 (s, 3 H), 4.79–4.82 (m, 1 H), 4.87–4.90 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.4, 40.2, 51.9, 58.5, 59.8, 91.7, 115.1, 134.8, 140.4, 166.8, 186.1; MS (CI), m/z (rel intensity) 23 (12), 181 (84), 167 (20), 157 (45), 73 (100); MS (EI), m/z (rel intensity) 169 (5), 59 (100); exact mass calcd for $C_{11}H_{17}O_4^+$ (HRCI) 213.1094, found 213.1119.

5-Methyl-1,2,3-trimethoxybicyclo[3.2.0]hept-2-en-7-one (29). A sealed tube containing 80 mg of **28** in 8 mL of distilled toluene was heated with the bath temperature around 150 °C for 26 h. The tube was allowed to cooled to ambient temperature and the solvent removed in vacuo. The slightly yellow oil obtained was chromatographed (6:1 hexanes–EtOAc) to provide 69 mg (86%) of **29** as a colorless oil: IR (film) 2960, 2850, 1770, 1675, 1465, 1450, 1330, 1290, 1245, 1200, 1120, 1100, 1080, 1050, 1010, 810 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.25 (s, 3 H), 2.55 (d, J = 15.9 Hz, 1 H), 2.62 (d, J = 16.0 Hz, 1 H), 2.62 (d, J = 18.2 Hz, 1 H), 2.91 (d, J = 17.3 Hz, 1 H), 3.33 (s, 3 H), 3.66 (s, 3 H), 3.79 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.8, 34.0, 40.2, 52.6, 55.0, 57.2, 58.1, 101.1, 128.2, 142.2, 204.2; MS (CI), m/z (rel intensity) 213 (100), 181 (62); MS (EI), m/z (rel intensity) 184 (29), 169 (93), 155 (31), 141 (35), 127 (30), 109 (29), 91 (82), 83 (41), 69 (67), 55 (100); exact mass calcd for $C_{11}H_{17}O_4$ 213.1094, found 213.1106.

1,2-Dimethoxybicyclo[3.2.0]heptane-3,7-dione (31). A solution of 105 mg of **16a** in 25 mL of freshly distilled toluene was heated at reflux for 10 h. The solution was allowed to cool to ambient temperature. Removal of solvent gave a slightly yellow oil, which upon chromatography (20:1 hexanes–EtOAc) provided 68 mg (65%) of **31** as a white solid: mp 79–82 °C; IR ($CHCl_3$) 3040, 3020, 2970, 2940, 2840, 1790, 1765, 1465, 1400, 1300, 1240, 1160, 1130, 1100, 1025, 650 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.45 (dd, J = 18.4, 6.7 Hz, 1 H), 2.53 (d, J = 17.4 Hz, 1 H), 2.92–3.14 (m, 2 H), 3.18–3.27 (m, 1 H), 3.49 (s, 3 H), 3.56 (s, 3 H), 4.12 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.5 (CH), 41.5 (CH_2), 46.7 (CH_2), 52.6 (CH_3), 59.3 (CH_3), 88.0 (CH), 101.7 (C), 201.7 (C), 209.3 (C); MS (CI), m/z (rel intensity) 185 (100), 157 (47), 153 (46); MS (EI), m/z (rel intensity) 156 (5), 142 (7), 125 (41), 114 (100), 87 (20), 71 (52), 69 (50), 59 (35), 55 (84), 53 (66); exact mass calcd for $C_9H_{12}O_4$ 184.0735, found 184.0736. Anal. Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.80; H, 6.62.

Compound 36. A solution of 83 mg of **16d** in 25 mL of freshly distilled toluene was heated and refluxed for 90 min. The solution was allowed to cool to ambient temperature. Removal of solvent gave a slightly yellow oil, which upon chromatography (20:1 hexanes–EtOAc) provided 35 mg (42%) of **36** as white needles: mp 139–141 °C; IR ($CHCl_3$) 3040, 3020, 2960, 1710, 1700, 1625, 1600, 1450, 1370, 1330, 1290, 1260, 1135, 1085, 985, 800 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.27 (dd, J = 18.7, 3.0 Hz, 1 H), 2.53 (dd, J = 15.8, 14.1 Hz, 1 H), 2.79 (dd, J = 18.7, 6.5 Hz, 1 H), 3.08 (dd, J = 15.8, 3.0 Hz, 1 H), 3.33–3.43 (m, 1 H), 4.17 (s, 3 H), 7.50 (td, J = 9.3, 1.2 Hz, 1 H), 7.65 (td, J = 8.1, 1.2 Hz, 1 H), 8.13 (d, J = 6.3 Hz, 1 H), 8.58 (d, J = 7.8 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 33.3 (CH), 40.3 (CH_2), 45.2 (CH_2), 58.3 (CH_3), 127.5 (CH), 128.2 (CH), 130.0 (CH), 131.7 (C), 134.0 (CH), 134.9 (C), 143.8 (C), 151.4 (C), 195.6 (C), 200.9 (C); MS (EI), m/z (rel intensity) 228 (89), 200 (13), 185 (26), 172 (27), 157 (53), 141 (54), 129 (80), 128 (86), 115 (100), 102 (21), 88 (38), 77 (37), 63 (64), 57 (51); exact mass calcd for $C_{14}H_{12}O_3$ 228.0786, found 228.0783. Anal. Calcd for $C_{14}H_{12}O_3$: C, 73.66; H, 5.30. Found: C, 73.56; H, 5.50.

3-Methoxy-2-phenyl-4-(3-propenyl)-4-[(trimethylsilyl)-oxy]-2-cyclobuten-1-one (37). To a flask containing 195 mg (0.85 mmol) of **16d** and 0.17 g (2.5 mmol) of imidazole in 5 mL of acetonitrile at ambient temperature was added 0.27 mL (2.1 mmol) of trimethylsilyl chloride (Fluka). The solution turned cloudy in 5 min. The suspension was sitrred for 3 h and then poured into a separatory funnel containing 20 mL of ether and 5 mL of water. The organic phase was washed with brine (2 × 5 mL) and dried ($MgSO_4$). Concentration gave a slightly yellow oil, which was chromatographed (6:1 hexanes–EtOAc) to provide 228 mg (89%) of **37** as a colorless oil: IR (film) 2960, 1760, 1630, 1600, 1500, 1450, 1370, 1260, 1120, 1000, 930, 890, 850, 770, 760, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.18 (s, 9 H), 2.62 (dd, J = 14.4, 7.8 Hz, 1 H), 2.85 (dd, J = 14.4, 6.9 Hz, 1 H), 4.24 (s, 3 H), 5.07 (d, J = 10.0 Hz, 1 H), 5.15 (dd, J = 17.0, 1.4 Hz, 1 H), 5.68–5.76 (m, 1 H), 7.25–7.37 (m, 3 H), 7.72–7.74 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.0, 59.6, 93.9, 118.6, 124.0, 126.8, 127.9, 128.4, 128.5, 132.2, 181.8, 189.0; MS (EI), m/z (rel intensity) 302 (8), 243 (2), 212 (5), 185 (11), 89 (8), 73 (100); exact mass calcd for $C_{17}H_{22}SiO_3$ 302.1338, found 302.1319.

2-Methoxy-1-phenyl-3-[(trimethylsilyl)oxy]bicyclo-[3.2.0]hept-2-en-7-one (38). A solution of 60 mg of **37** in 30 mL of freshly distilled toluene was heated and refluxed for 5 h. The colorless solution obtained was cooled to ambient temperature and the solvent was removed under reduced pressure. The residue was chromatographed (3:1 hexanes–EtOAc, Florisil) to provide 53.6 (89%) of **38** as a colorless oil: IR (film) 2970, 2920, 2860, 1770, 1680, 1450, 1390, 1340, 1300, 1250, 1100, 1075, 930, 870, 850, 760, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.26 (s, 9 H), 2.29 (d, J = 16.0, 7.5 Hz, 1 H), 2.57–2.62 (m, 1 H), 2.93 (dd, J = 15.5, 7.5 Hz, 1 H), 3.02 (dd, J = 18.0, 5.5 Hz, 1 H), 3.35 (dd, J = 18.0, 9.0 Hz, 1 H), 3.51 (s, 1 H), 7.24–7.27 (m, 2 H), 7.32–7.38 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.5, 30.4, 36.3, 51.5, 58.3, 79.1, 126.1, 127.1, 128.5, 134.4, 134.9, 138.0, 206.8; MS (EI), m/z (rel intensity) 302 (0.2), 274 (7), 259 (4), 170 (2), 144 (1), 141 (2), 129 (2), 128 (2), 116 (3), 115 (8), 89 (10), 73 (100), 59 (12), 58 (4); exact mass calcd for $C_{17}H_{22}SiO_3$ 302.1338, found 302.1318.

2-Methoxy-1-phenylbicyclo[3.2.0]heptane-3,7-dione (39). To a solution of 0.20 g (0.66 mmol) of **38** in 5 mL of acetonitrile was added 0.15 g (0.99 mmol) of CsF. The colorless solution turned orange. The reaction mixture was transferred to a short silica gel column saturated with 4:1 hexanes–EtOAc. The column was flushed with the same solvent (40 mL). Concentration gave a slightly yellow oil, which was chromatographed (10:1 hexanes–EtOAc) to provide 108 mg (71%) of **39** (an inseparable 8:1 mixture of stereoisomers) as a colorless oil: IR (film) 2980, 2920, 2840, 1780, 1760, 1600, 1490, 1450, 1410, 1390, 1210, 1140, 1130, 1080, 1050, 1040, 760, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ major isomer, 2.63 (d, J = 17.9 Hz, 1 H), 2.89 (dd, J = 17.9, 5.1 Hz, 1 H), 3.06 (dd, J = 17.6, 7.7 Hz, 1 H), 3.27–3.50 (m, 2 H), 3.54 (s, 3 H), 4.01 (s, 1 H), 7.31–7.48 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ major isomer, 29.6, 41.5, 51.5, 59.9, 75.9, 90.2, 125.4, 127.5, 129.0, 138.7, 202.6, 211.9; MS (EI) 230 (7), 198 (4), 188 (9), 171 (75), 160 (57), 142 (26), 128 (80), 17 (85), 115 (100), 102 (51), 91 (55), 89 (46), 77 (39), 63 (41); exact mass calcd for $C_{14}H_{14}O_3$ 230.0940, found 230.0937.

2-Methoxy-4-methyl-3-phenylcyclopent-2-en-1-one (41). To a solution of 85 mg of **39** in 25 mL of toluene was added 10 drops of glacial acetic acid, and the solution was heated at reflux for 40 h. The yellow solution was cooled to ambient temperature and the solvent was removed under reduced pressure. The orange oil was purified by chromatography (20:1 hexanes–EtOAc) to afford, along with **36** and **46**, 11 mg (15%) of **41** as a colorless oil: IR (film) 2988, 2933, 2850, 1704, 1695, 1613, 1446, 1358, 1134, 1071, 1004, 884, 864, 781, 692 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.27 (d, J = 7.0 Hz, 3 H), 2.45 (dd, J = 17.0, 2.3 Hz, 1 H), 2.46–2.52 (m, 1 H), 3.13 (dd, J = 16.9, 6.7 Hz, 1 H), 4.06 (s, 3 H), 7.40–7.43 (m, 3 H), 7.88–7.90 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.7, 32.9, 37.7, 58.0, 127.4, 128.4, 129.7, 133.9, 145.9, 151.2, 206.4; MS (EI), m/z (rel intensity) 202 (100), 201 (70), 187 (17), 159 (14), 145 (26), 131 (35), 115 (38), 103 (70), 91 (45), 89 (50), 77 (53), 63 (45), 51 (55); exact mass calcd for $C_{13}H_{14}O_2$ 202.0993, found 202.1008.

2-Methoxy-5-methyl-3-phenylcyclopent-2-en-1-one (46). To a solution of 85 mg of **39** in 25 mL of toluene was added 10 drops of glacial acetic acid and the solution was heated at reflux for 40 h. The yellow solution was cooled to ambient temperature and the solvent was removed under reduced pressure. The orange oil was purified by chromatography (20:1 hexanes–EtOAc) to afford, along with **36** and **41**, 8.8 mg (12%) of **46** as a colorless oil: IR (film) 2960, 1700, 1690, 1610, 1440, 1350, 1200, 1140, 1100, 1080, 1000, 960, 780, 700, 690 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.16 (d, J = 6.0 Hz, 3 H), 2.12 (dd J = 18.4, 1.9 Hz, 1 H), 2.76 (dd, J = 18.7, 6.5 Hz, 1 H), 3.33–3.34 (m, 1 H), 3.96 (s, 3 H), 7.37–7.46 (m, 3 H), 7.69–7.72 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.0, 30.0, 41.8, 58.2, 128.0, 128.4, 129.2, 132.8, 151.3,

153.6, 203.0; MS (EI), m/z (rel intensity) 202 (100), 201 (42), 187 (28), 174 (44), 161 (38), 159 (43), 144 (44), 129 (46), 115 (86), 91 (62), 77 (33), 63 (20), 51 (36); exact mass calcd for $C_{13}H_{14}O_2$ 202.0994, found 202.0988.

1-Ethenyl-3-chloro-2-methoxybicyclo[3.2.0]hept-2-en-7-one (49). A solution of 95 mg (0.52 mmol) of **16c** and 0.43 mL (5.3 mmol) of pyridine in 3 mL of CH_2Cl_2 was cooled to 0 °C. To the solution was added dropwise 0.10 mL (1.4 mmol) of thionyl chloride. The orange solution obtained was transferred to a short silica gel column saturated with 10:1 hexanes–EtOAc. The column was then flushed with the same solvent (60 mL). Concentration gave 77 mg (73%) of a mixture of chlorides as a slightly yellow oil. A solution of 75 mg of the chlorides in 30 mL of toluene was heated at reflux for 4 h. The colorless solution obtained was cooled to ambient temperature. Concentration gave a slightly yellow oil, which was chromatographed (4:1 hexanes–EtOAc) to provide, along with **50**, 20 mg (27%) of **49** as a colorless oil: IR ($CHCl_3$) 2980, 2950, 2920, 2860, 1780, 1660, 1630, 1460, 1450, 1390, 1290, 1235, 1080, 1020, 1000, 935, 830, 780, 660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.45 (d, J = 18.0 Hz, 1 H), 2.61–2.69 (m, 1 H), 2.96–3.06 (m, 2 H), 3.32 (dd, J = 18.2, 9.1 Hz, 1 Hz, 1 H), 3.77 (s, 3 H), 5.28 (d, J = 12.0 Hz, 1 H), 5.36 (d, J = 18.0 Hz, 1 H), 5.97 (dd, J = 18.0, 12.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.6 (CH), 39.3 (CH_2), 51.3 (CH_2), 58.5 (CH_3), 80.5 (c), 108.2 (C), 117.6 (CH_2), 132.0 (CH), 147.6 (C), 204.3 (C); MS (EI), m/z (rel intensity) 200 (M + 2, 24), 198 (75), 183 (19), 169 (24), 155 (29), 148 (43), 141 (38), 131 (25), 119 (18), 115 (16), 103 (39), 91 (95), 77 (100); exact mass calcd for $C_{10}H_{11}ClO_2$ 198.0448, found 198.0439.

4-Chloro-3-methoxy-2-(3-propenyl)phenol (50). A solution of 95 mg (0.52 mmol) of **16c** and 0.43 mL (5.3 mmol) of pyridine in 3 mL of CH_2Cl_2 was cooled to 0 °C. To the solution was added dropwise 0.10 mL (1.4 mmol) of thionyl chloride. The orange solution obtained was transferred to a short silica gel column saturated with 10:1 hexanes–EtOAc. The column was then flushed with the same solvent (60 mL). Concentration gave 77 mg (73%) of chlorides as a slightly yellow oil. A solution of 75 mg of the chlorides in 30 mL of toluene was heated at reflux for 4 h. The colorless solution obtained was cooled to ambient temperature. Concentration gave a slightly yellow oil, which was chromatographed (4:1 hexanes–EtOAc) to provide, along with **49**, 38 mg (51%) of **50** as a colorless oil: IR (film) 3420, 2950, 1590, 1470, 1420, 1300, 1230, 1120, 1050, 920, 810, 680 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.50 (dt, J = 5.9, 1.7 Hz, 2 H), 3.82 (s, 3 H), 5.11 (s, 1 H), 5.12–5.18 (m, 2 H), 5.97–6.05 (m, 1 H), 6.59 (d, J = 9.0 Hz, 1 H), 7.14 (d, J = 9.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.6, 61.2, 112.6, 116.4, 119.5, 120.7, 128.4, 135.6, 154.1, 154.6; MS (EI), m/z (rel intensity) 200 (M + 2, 2), 198 (7), 156 (73), 141 (25), 121 (100), 91 (42), 77 (58); exact mass calcd for $C_{10}H_{11}ClO_2$ 198.0448, found 198.0449.

4-(3-Butenyl)-4-hydroxy-3-methoxy-2-phenyl-2-cyclobuten-1-one (51). To a flask containing 10 mL of ether and 0.50 g of sea sand were added a few pieces of freshly cut lithium wire. The flask was cooled to −40 °C and 0.12 mL of 4-bromo-1-butene was added. The muxture was stirred vigorously for 1 h and cooled to −78 °C. To this solution was added slowly a solution of 0.15 g (0.80 mmol) of 3-methoxy-4-phenyl-3-cyclobutene-1,2-dione in 30 mL of THF. The resulting mixture was stirred for 90 min and quenched with 5% NH_4Cl. The organic phase was washed with brine and dried ($MgSO_4$). Concentration gave a yellow oil, which was chromatographed (3:1 hexanes–EtOAc) to provide 105 mg (54%) of **51** as a colorless oil: IR (film) 3430, 2840, 2860, 1740, 1630, 1600, 1500, 1460, 1450, 1370, 1340, 1100, 1090, 990, 980, 790, 760, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.98–2.04 (m, 1 H), 2.08–2.23 (m, 2 H), 2.25–2.31 (m, 1 H), 4.26 (s, 3 H), 4.79 (s 1 H), 4.95–5.02 (m, 2 H), 5.75–5.83 (m, 1 H), 7.25–7.33 (m, 3 H), 7.66–7.68 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.4, 32.9, 59.7, 92.4, 115.5, 124.2, 126.8, 127.9, 128.3, 128.3, 137.0, 182.0, 191.1; MS (EI), m/z (rel intensity) 244 (2), 203 (89), 202 (39), 156 (9), 129 (42), 118 (39), 115 (100), 104 (46), 89 (56), 77 (36); exact mass calcd for $C_{15}H_{16}O_3$ 244.1099, found 244.1087.

3,4-Dimethoxy-4-(3-butenyl)-2-phenyl-2-cyclobuten-1-one (52). A solution of 98 mg (0.40 mmol) of **51**, 0.57 g (4.0 mmol) of methyl iodide, 0.23 g (1.0 mmol) of silver(I) oxide, and 0.55 g (4.0 mmol) of potassium carbonate in 3 mL of acetonitrile was stirred at ambient temperature for 12 h. The suspension was filtered through a pad of Celite and washed with ether. Concentration gave a yellow oil, which was chromatographed (4:1 hexanes–EtOAc) to afford 95 mg (92%) of **52** as a slightly yellow oil: IR (film) 3080, 3010, 2960, 1760, 1645, 1635, 1600, 1500, 1455, 1370, 1360, 1340, 1320, 1145, 1125, 1100, 990, 920, 790, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.90–2.30 (m, 4 H), 3.43 (s, 3 H), 4.23 (s, 3 H), 4.97–5.04 (m, 2 H), 5.75–5.84 (m, 1 H), 7.28–7.41 (m, 3 H), 7.70–7.80 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.2, 32.6, 52.7, 59.4, 98.4, 115.3, 125.5, 126.9, 128.1, 128.4, 137.1, 181.2, 189.4; MS (EI), m/z (rel intensity) 258 (15), 217 (100), 189 (11), 115 (51), 103 (35), 89 (66), 77 (40); exact mass calcd for $C_{16}H_{18}O_3$ 258.1256, found 258.1236.

Acknowledgment. We thank the National Institutes of Health (GM-36312) for financial support. We also thank Catherine A. Moore for technical support in obtaining high resolution mass spectral data and Dr. J. Ziller for the X-ray structure determinations. Funds for the purchases of the Nicolet R3m/V diffractometer system were made available for the National Science Foundation under Grant CHE 85-14495.

Registry No. **16a**, 124022-04-4; **16b**, 124022-06-6; **16c**, 124022-07-7; **16d**, 124022-08-8; **16e**, 124022-09-9; **16f**, 135396-56-4; **17a**, 124022-10-2; **17b**, 124022-11-3; **17c**, 124022-12-4; **17d**, 124022-13-5; **17e**, 124022-14-6; **18a**, 124042-14-4; **18b**, 124022-15-7; **18c**, 124022-16-8; **18d**, 124022-17-9; **18e**, 124022-18-0; **20a**, 135396-42-8; **20b**, 135396-57-5; **21a**, 135396-43-9; **21b**, 135396-58-6; **22a**, 135396-44-0; **22b**, 135396-59-7; **22b'**, 135501-71-2; **23**, 135396-45-1; **24**, 135396-46-2; **25**, 135501-69-8; **27**, 135396-47-3; **28**, 135396-48-4; **29**, 135396-49-5; **31**, 135501-70-1; **36**, 124022-20-4; **37**, 124022-21-5; **38**, 124022-22-6; **39**, 124022-23-7; **41**, 135396-50-8; **46**, 135396-51-9; **49**, 135396-52-0; **50**, 135396-53-1; **51**, 135396-54-2; **52**, 135396-55-3; 3,4-dimethoxy-3-cyclobutene-1,2-dione, 5222-73-1; 3-butyl-4-methoxy-3-cyclobutene-1,2-dione, 102683-52-3; 3-ethenyl-4-methoxy-3-cyclobutene-1,2-dione, 124022-02-2; 3-methoxy-4-phenyl-3-cyclobutene-1,2-dione, 711-78-4; 3-hexynyl-4-methoxy-3-cyclobutene-1,2-dione, 124022-03-3; 3-methoxy-4-[(trimethylsilyl)ethynyl]-3-cyclobutene-1,2-dione, 113976-89-9; 1-bromo-3-methyl-2-butene, 870-63-3; 1-bromo-2-butene, 4784-77-4; 2,3-dimethoxy-4-hydroxy-4-(1-phenyl-2-propenyl)-2-cyclobuten-1-one, 135396-60-0; cinnamyl bromide, 4392-24-9; 3-chloro-2-methylpropene, 563-47-3.

Supplementary Material Available: X-ray data for compounds **31** and **36** as well as the ^{13}C NMR spectra of the new compounds reported here for which no C, H analyses were obtained (66 pages). Ordering information is given on any current masthead page.