Intramolecular Cycloaddition Reactions of Dienyne Ethers. The Synthesis of Bridgehead Dienes and Their Thermal Rearrangements

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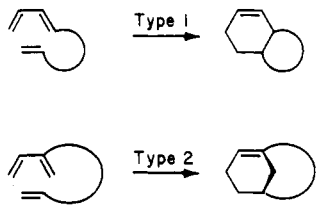
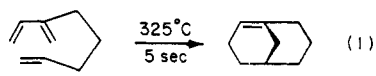
The type 2 intramolecular Diels–Alder cycloaddition of dienyne ethers **13–16**, **18**, **19**, and **22–25** have been surveyed in both gas and solution phase. The dienyne ethers undergo cycloaddition to yield a novel class of bridgehead dienes of general structure **4**. The stability and mode of thermal reactivity of the resulting bridgehead dienes varies as a function of the tether length. Bridgehead diene **37** has a half-life of 7 h at room temperature in dilute solution. The homologous bridgehead dienes **28** and **40**, although reactive molecules, are considerably more stable than **37**. At elevated temperatures, bridgehead diene **37** rearranges to propellanes **35** and **36**, while bridgehead diene **41** undergoes dehydrogenation to yield metacyclophane **42**. All intramolecular Diels–Alder reactions are found to give a single regioisomeric cycloadduct.

Introduction

Two basic structural variants of the intramolecular Diels–Alder cycloaddition can be achieved by altering the point of attachment of the dienophile to the diene. We refer to these two modes as type 1 and type 2 intramolecular Diels–Alder cycloaddition. The former gives rise



to a fused ring junction, while the latter results in a bridged skeleton. An interesting consequence of type 2 intramolecular Diels–Alder cycloadditions is the formation of molecules that contain bridgehead double bonds.[1] We have explored the scope of this reaction with particular emphasis upon the construction of novel, highly strained bridgehead alkenes.[2-6] Quite remarkably, representatives of the most highly strained, isolable bridgehead alkenes are available by this method, for example, bicyclo[3.3.1]-non-1-ene is produced from the gas-phase thermolysis of 3-methylene-1,7-octadiene (eq 1).[5]



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As part of our program of the synthesis of bridgehead dienes,[7-10] molecules that contain two torsionally distorted carbon–carbon double bonds held in close proximate relationship, we undertook a study of the intramolecular

Table I

reactn	$\Delta H°_{reactn}$, kcal/mol
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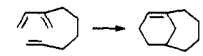
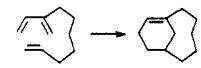
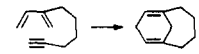
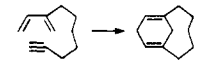
	-25
	-24
	-54
	-26
	-33

cycloaddition of dienynes of general structure **1** as a potential entry into bicyclo[*n*.3.1] bridgehead dienes **2** (eq 2). The bridgehead diene cycloadducts are structurally


(2)

1 **2**

related to novel *trans,trans*-1,4-cycloalkadienes with two torsionally distorted double bonds locked in a parallel array. The cycloaddition strategy permits simultaneous introduction of both bridgehead double bonds. Owing to the reactivity of bridgehead double bonds, this approach offers significant advantages over their sequential introduction.

The constraints of utilizing *pericyclic reactions* for the synthesis of strained molecules resides in the balance between product strain energy and reaction enthalpy. The thermodynamics of several pertinent Diels–Alder cycloadditions are summarized in Table I.[11,12]

Inspection of Table I reveals that replacement of an ethylenic dienophile with an acetylenic dienophile increases the exothermicity of the bimolecular Diels–Alder reactions by 14 kcal/mol. This additional thermodynamic driving force may be important for the successful preparation of the bridgehead dienes since it is also noted that bridgehead dienes have greater strain energies than the corresponding

(1) (a) Shea, K. J. *Tetrahedron* **1982**, *36*, 1683. (b) Szeimies, G. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1983; p 299. (c) Wentrup, C., *Reactive Molecules*; Wiley: New York, 1984; Chapter 5.
(2) Shea, K. J.; Gilman, J. W. *Tetrahedron Lett.* **1983**, *24*, 657.
(3) Shea, K. J.; Wada, E. *J. Am. Chem. Soc.* **1982**, *104*, 5715.
(4) Shea, K. J.; Wise, S.; Burke, L. D.; Davis, P. D.; Gilman, J. W.; Greeley, A. C. *J. Am. Chem. Soc.* **1982**, *104*, 5708.
(5) Shea, K. J.; Wise, S. *Tetrahedron Lett.* **1979**, 1011.
(6) Shea, K. J.; Wise, S. *J. Am. Chem. Soc.* **1978**, *100*, 6519.
(7) Shea, K. J.; Greeley, A. C.; Nguyen, S.; Beauchamp, P. S.; Wise, S. *Tetrahedron Lett.* **1983**, *24*, 4173.
(8) Shea, K. J.; Greeley, A. C.; Nguyen, S.; Beauchamp, P. D.; Aue, D. H.; Witzeman, J. S. *J. Am. Chem. Soc.* **1986**, *108*, 5901.
(9) Shea, K. J.; Burke, L. D.; Doedens, R. J. *Tetrahedron Symp. Print* **1986**, *42*, 1841.
(10) (a) Shea, K. J.; Burke, L. D. *J. Org. Chem.* **1986**, *50*, 725. (b) Shea, K. J.; Burke, L. D. *Tetrahedron Lett.* **1987**, *28*, 735.

(11) Enthalpies of reaction were calculated by using Benson group equivalents and the Allinger MM2 force field.[12] Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976. Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *86*, 196.
(12) (a) Maier, W. H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 1891. (b) McEwen, A. B.; Schleyer, P. v. R., *J. Am. Chem. Soc.* **1986**, *108*, 3981. (c) Warner, P. M.; Peacock, S. *J. Comput. Chem.* **1982**, *3*, 417. (d) Warner, P. M.; Peacock, S. *Tetrahedron Lett.* **1983**, 4169.

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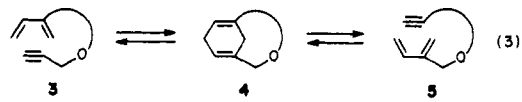
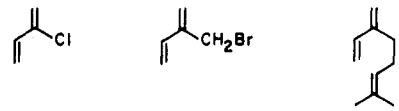
bridgehead alkenes.[12] Interestingly, despite the significant strain energies associated with the bridgehead diene products, the intramolecular cycloadditions summarized in Table I are all predicted to be exothermic. The conclusion derived from this analysis is that the intramolecular Diels–Alder reaction appears to be sufficiently exothermic to allow formation of even the most highly strained bicyclo[n.3.1] bridgehead dienes. In this paper we report our efforts directed toward the synthesis of these compounds.[13] The kinetic and mechanistic features of this reaction are taken up in the accompanying paper.[14]

Results and Discussion

The initial choice of dienynes used for this study was based upon the potential for incorporation of a diagnostic feature that would permit recognition of the onset of cycloaddition regardless of whether bridgehead diene accumulated during the reaction. To this end we synthesized the series of dienyne ethers of general structure **3** and **5**. Cycloaddition (eq 3) would result in an bridgehead diene **4**. As a result of the symmetry of the cycloadduct, retro-Diels–Alder reaction can result in formation of either dienyne **3** or the oxygen-scrambled isomer **5**. In the absence of direct observation of bridgehead diene **4**, the appearance of oxygen scrambling can be used as evidence for the formation of bridgehead diene as a reaction intermediate.



Synthesis of Dienyne Ethers. The requisite dienyne ethers **3** and **5** were prepared by the methods outlined in Schemes I and II. Three sources of 2-substituted 1,3-butadienes were used for their synthesis. They are derived from chloroprene, 2-(bromomethyl)-1,3-butadiene, and myrcene.



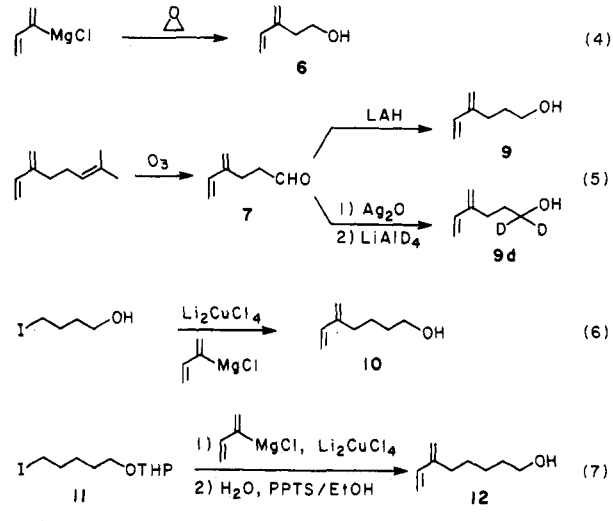
Diene alcohol **6** was prepared by condensation of chloroprene Grignard with ethylene oxide in a 57% yield (eq 7).[15]

Diene aldehyde **7** or diene alcohol **9** is prepared by ozonolysis of myrcene in a 46% yield.[16] For the preparation of diene alcohol **9d**, the silver oxide oxidation of dienal **7** to the diene carboxylic acid **8** proceeded efficiently in a yield of 94%. Diene carboxylic acid **8** could also be obtained in a 67% yield by oxidation of dienol **9** with PDC in DMF.[17] Reduction of diene carboxylic acid **8** with lithium aluminum tetradeutride gave the dideuterio diene alcohol **9d** in a 67% yield and an isotopic purity >98% as established by ^{1}H NMR.

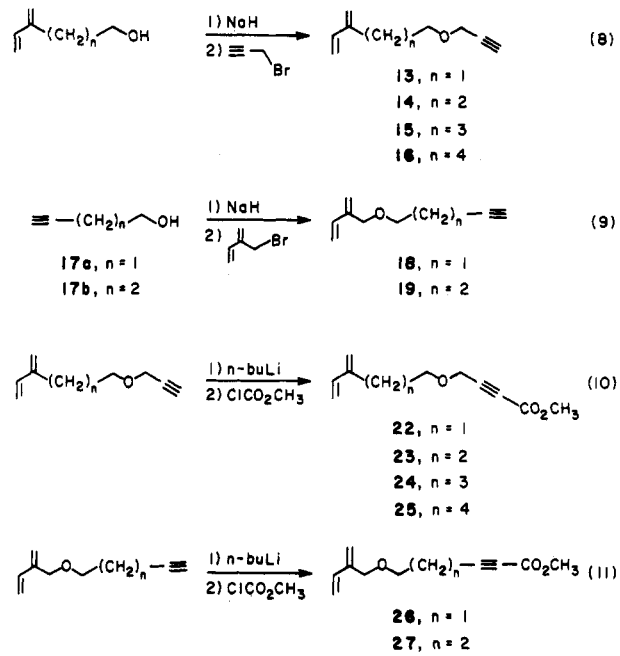
Diene alcohol **10** was readily prepared by refluxing THF with aqueous HI to give the labile 4-iodo-1-butanol. Copper-catalyzed cross-coupling of chloroprene Grignard to the iodo alcohol yields the diene alcohol **10** in a 79% yield.[18] Synthesis of diene alcohol **12** entails THP monoprotection of 1,5-pentanediol (65%) mesylation and then treatment with sodium iodide to give the iodo THP-protected alcohol **11**. Copper-catalyzed cross-coupling of **11** with chloroprene Grignard followed by deprotection (pyridinium p-toluenesulfonate)[19] gave diene alcohol **12** in an 85% yield from the iodo THP-protected alcohol.

(13) For a preliminary report, see ref 10.
(14) Shea, K. J.; Burke, L. D.; England, W. P. *J. Am. Chem. Soc.*, in press.

Scheme I



Scheme II



The short synthetic entries into the diene alcohols **6**, **9**, **9d**, **10**, and **12** provides the primary synthetic units for the dienyne ethers (eq 8). Thus, propargyl bromide was added to the sodium salt of the diene alcohols (NaH) to afford dienyne ethers **13–16** in yields of 70–80% (Scheme II).

2-(Bromomethyl)-1,3-butadiene[20] served as a common precursor to dienyne ethers **18** and **19**. Reaction of this bromo diene with the sodium salt of the acetylenic alcohols **17a,b** gave the corresponding dienyne ethers **18** and **19** in yields of 70–80% (eq 9). Both series of dienyne ethers **13–16** and **18**, **19** are converted to the carbomethoxy esters **22–25** and **26**, **27** by treatment with 1 equiv of n-butyllithium (−78 °C) followed by methyl chloroformate. Yields range between 80% and 90%.

(15) Kondo, K.; Dobashi, S.; Matsumoto, M. *Chem. Lett.* **1976**, 1007.
(16) Bertele, E.; Schudel, P. S. *Helv. Chem. Acta* **1967**, *50*, 2445.
(17) Corey, E. J.; Schmidt, G. *Tetrahedron Lett.* **1979**, 399.
(18) (a) Shea, K. J.; Pham, P. Q. *Tetrahedron Lett.* **1983**, 1003. (b) Nunomoto, S.; Kawakami, Y.; Yamashita, Y. *J. Org. Chem.* **1983**, *48*, 1912.
(19) Miyashita, M.; Yoshikashi, A.; Grieco, P. A. *J. Org. Chem.* **1977**, *42*, 4772.
(20) Krug, R. C.; Yen, F. T. *J. Org. Chem.* **1956**, *21*, 1082.

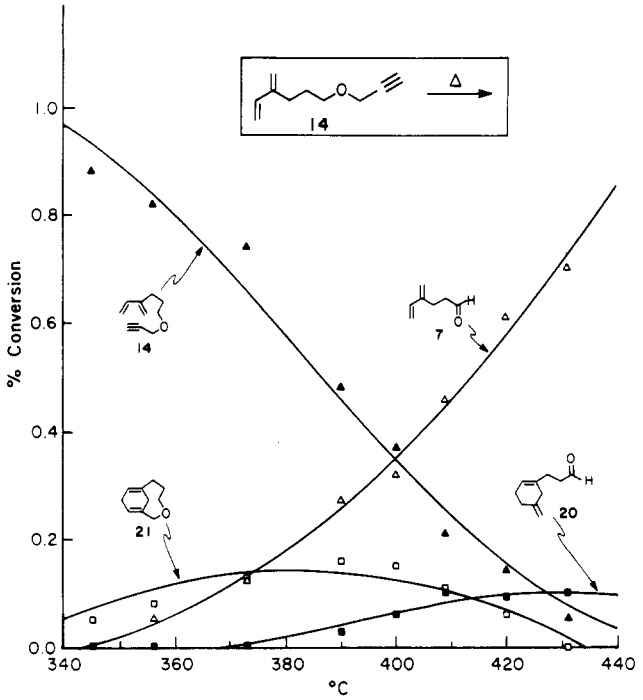
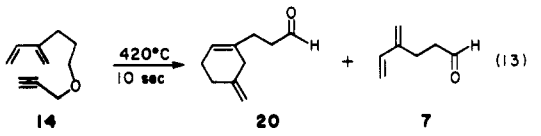


Figure 1. Product–temperature profile for the gas-phase thermolysis of dienyne ether **14** (atmospheric pressure).

Thermolysis of Dienyne Ethers. [5.3.1] Bridgehead Dienes. The choice of gas-phase thermolysis conditions for dienyne ether **14** was influenced by our earlier experience with 3-methylene-1,9-decadiene, which required temperatures in excess of 400 °C (contact time 10 s) to affect cycloaddition (eq 12).[6] We have explored the thermolysis of dienyne ether **14** over a range of temperatures (340–440 °C) in the gas phase at atmospheric pressure (contact time 10–15 s).

(12)

At the higher end of this temperature range (440 °C) two aldehydes dominate the product distribution. Dienal **7** arises from a precedented retro-hetero-ene reaction (eq 13) of propargylic ethers.[21a] Dienal **20**, however, was an unexpected product. Its presence provided evidence for

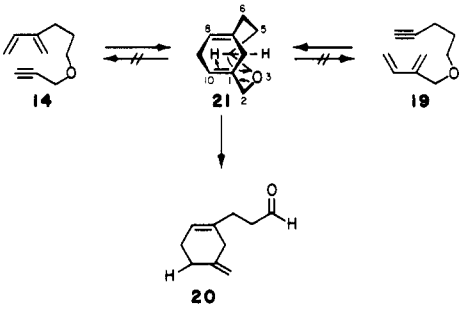


(13)

the formation of bridgehead diene **21** since intramolecular retro hetero-ene of **21** could account for dienal **20**.[21b] Evidence for the generation of **21** at these high temperatures was secured from thermolysis of dienyne ether **19**. Although this ether was found to require temperatures in excess of 450 °C for reaction, the product isolated from the thermolysis was shown by ^{1}H NMR spectroscopy and analytical GC to be identical to **20**, the product obtained from the thermolysis of dienyne ether **14**. The common product from both dienyne ethers argues for a common reaction intermediate in the thermolysis. In subsequent studies at lower temperatures (350 °C), bridgehead diene **21** was found to accumulate under the reaction conditions

(21) (a) Viola, A.; Collins, J. J.; Filipp, N. *Tetrahedron* **1981**, *37*, 3765. (b) Tobe, Y.; Ueda, Y.; Matsumoto, M.; Sakai, Y.; Odaira, Y. *Tetrahedron Lett.* **1982**, *23*, 537.

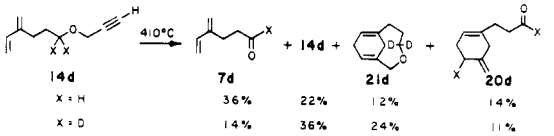
Scheme III



(Figure 1). This reactive diolefin could be isolated by preparative GC or by chromatography on silica gel. Details of its characterization are included in the Experimental Section. When the bridgehead diene **21** is subjected to the reaction conditions (410 °C) **21** is partially transformed to dienal **20** (49%).

Since the product distribution from the thermolysis of **14** varies with temperature, it is informative to display a product distribution vs temperature profile (Figure 1). The accumulation of dienal **20** at higher temperatures is commensurate with the decline in bridgehead diene yield, typical of a secondary reaction product.

To verify the proposed retro-hetero-ene reaction manifolds, dideuterio dienyne **14d** was thermolyzed. Isolation of products **7d** and **20d** permitted unambiguous assignment of the location of deuteriums, in each case the position and distribution is entirely consistent with the proposed mechanism.



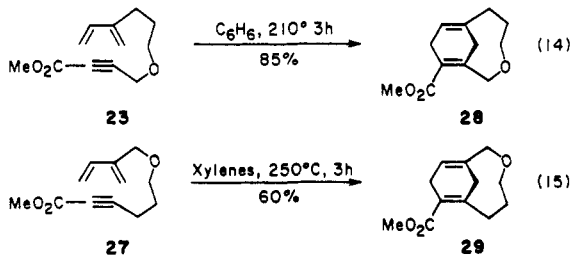
Deuterium isotope effects were also observed in the product distribution. These data are summarized above. Deuterium substitution results in a diminution in **7** and an increase in the amount of bridgehead diene **21**. Both observations are consistent with a *primary* deuterium isotope effect. The primary isotope effect in the conversion of **21** to **20** would render unlikely a mechanism that involves rate determining homolytic cleavage of the C_2–O_1 bond followed by intramolecular hydrogen transfer from the resulting diyl. Additional information that is pertinent to the analysis of this reaction is the finding that no conditions were observed in which **19** was formed from thermolysis of **14** or vice versa.

The available data provide compelling evidence that the gas-phase thermolysis of either dienyne ether **14** or **19** results in an *irreversible* cycloaddition to yield the bridgehead diene **21** (Scheme III). Inspection of a molecular model of **21** reveals a CX_2O-methylene hydrogen is positioned beneath the bridgehead double bonds facilitating the retro-hetero-ene reaction. Despite the opportunity to transfer H(D) to either double bond, the reaction is completely regiospecific, H(D) is transferred exclusively to the C1(10) double bond resulting in carbonyl formation.

Competing retro-hetero-ene reactions detract from the preparative value of this reaction. From a consideration of the entropy and enthalpy of activation of typical cycloadditions and retro-hetero-ene reactions[14,21] and from the product-temperature profile (Figure 1), temperatures in the range of 250–275 °C should greatly favor the cycloaddition reaction. Indeed, solution-phase thermolysis of **14** (260 °C, 2 h) returns only starting material and

cycloadduct **21**; aldehydes **7** and **20** were not detected. Nevertheless, higher molecular weight materials, resulting from bimolecular reactions, detracted from the synthetic utility of this approach.

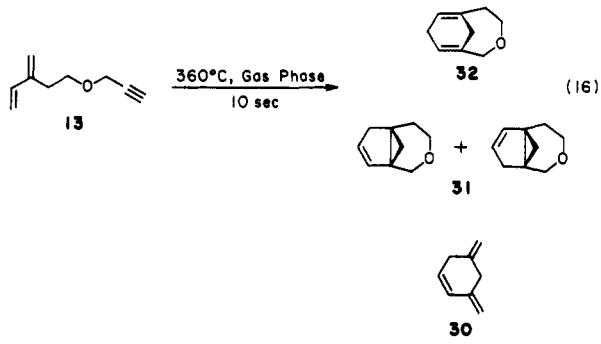
The most direct approach for inducing the cycloadditions under milder conditions is dienophile activation by carboxymethylation of the acetylenic group. This one-step procedure affords dienyne ester **23**, which undergoes cycloaddition in solution (0.1 M, benzene, 210 °C, 2.8 h) to give, after filtration through silica gel, bridgehead diene ester **28**, in 85% isolated yield. The reaction makes available multigram quantities of bridgehead diene for further studies. In a similar manner, dienyne **27** affords



bridgehead diene ester **29**. The interesting feature regarding this reaction is its sluggishness when compared with the oxygen-scrambled isomer **23**. The origin of the differences in reactivity between these two Diels–Alder precursors is discussed in an analysis of the kinetics of these reactions.[14]

[4.3.1] Bridgehead Dienes. The findings of the preceding section establish the type 2 intramolecular Diels–Alder cycloaddition as an efficient entry into bridgehead dienes of general structure **2**. The ability to prepare and isolate derivatives of (*Z*,*Z*)-bicyclo[5.3.1]undeca-1(10),7-(8)-diene prompted efforts to generate the (*Z*,*Z*)-bicyclo-[4.3.1]deca-1(9),6(7)-diene ring system as a probe of the limits of this strategy.

Heating **13** at 360 °C (10 s) in an atmospheric pressure flow pyrolysis apparatus followed by silica gel column chromatography and/or preparative GC allowed the isolation of triene **30** and propellanes **31** (an inseparable 1:1 mixture) (eq 16). Bridgehead diene **32**, an exceedingly



reactive compound proved difficult to isolate for characterization. Optimum conditions for its isolation involved rapid flash column chromatography followed by repeated preparative GC (it was important to exclude air from these operations). The origin of the reaction products can be established from a product distribution–temperature profile (Figure 2) and by resubmitting individual products to the reaction conditions.

Thermolysis of dienyne **13** (and ether **18**) results in an *irreversible* cycloaddition to yield bridgehead diene **32**. Diene **32** is a derivative of *trans,trans*-1,4-cyclononadiene containing two highly distorted bridgehead double bonds. An apparent consequence of this is the increased chemical reactivity of **32**, which differs markedly from that of homologue **21**. Presumably, the close proximity and spatial orientation of the p orbitals, in addition to the inherent strain of the bridgehead diene, facilitates a homodienyl 1,5-hydrogen shift resulting in formation of propellanes **31**. The usual thermodynamic driving force for this reaction, relief of the cyclopropane strain energy,[22,23] is *reversed* in the current example owing to the bridgehead olefin strain.

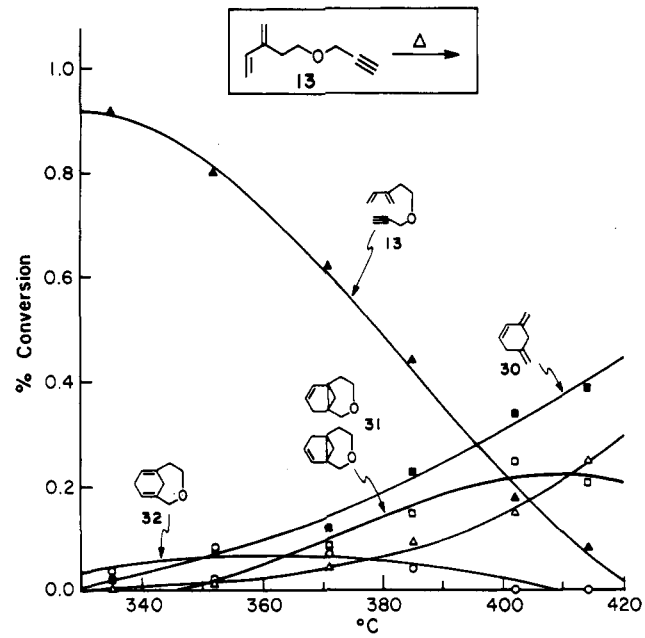
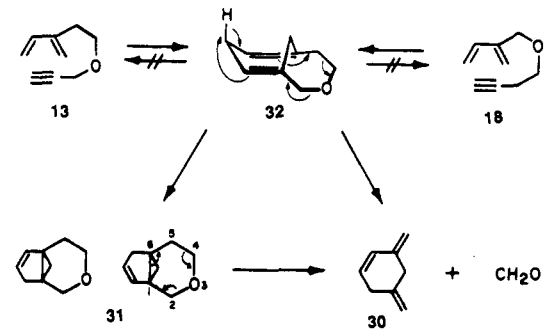


Figure 2. Product–temperature profile for the gas-phase thermolysis of dieneyne ether **13** (atmospheric pressure).

Scheme IV



At higher temperatures the propellanes further rearrange by cleavage of the cyclopropyl bond and extrusion of formaldehyde, which leads to formation of a triene **30**. Interestingly, the *major* source of **30** arises via a 10-electron pericyclic reaction from bridgehead diene **32** since reexposure of propellanes **31** to the thermolysis conditions (400 °C, 17 s) gives rise to only 5% of triene **30** and unreacted propellanes, while bridgehead diene **32** yields triene **30** (32%) and propellanes **31** (56%). (*Retro*-Diels–Alder products **13** or **18** were not observed). The competing reactions are summarized in Scheme IV. With the exception of a significantly diminished reactivity,[14] dienyne ether **18** produces product distributions consistent with its entry into the product manifold via **32**. Gas-phase thermolysis of dienyne ethers **13** or **18** does not result in useful quantities of bridgehead diene **32**.

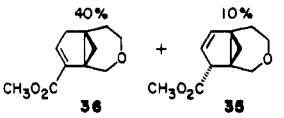
(22) Gajewski, J. J. *Hydrocarbon Thermal Isomerization*; Academic: New York, 1981.

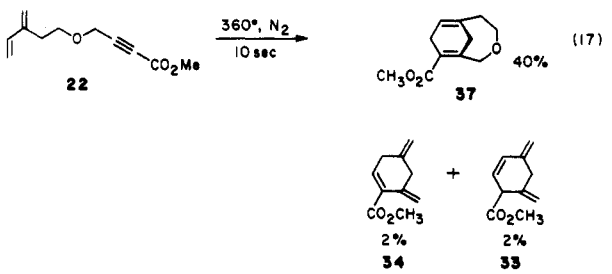
(23) For related reversals of the homo 1,5-hydrogen shifts, see: (a) Kirsch, R.; Priebe, H. *Tetrahedron Lett.* **1984**, *25*, 53. (b) Klarmer, F.; Rungeler, W.; Malfeld, W. *Angew. Chem., Int. Ed. Eng.* **1981**, *20*, 595.

This situation was not remedied at lower temperatures in the condensed phase. Although bridgehead diene **32** is the only low molecular weight product formed at 260 °C (2.7 h, benzene), low conversion and poor mass balances owing to bimolecular reactions, render this approach impractical.

Activation of the dienophile, dienyne ester **22**, lowers the temperature necessary for cycloaddition. For example, after 40 min at 210 °C in benzene, **22** is converted to bridgehead diene ester **37** (30%). In general, the mass balance and conversion are low for these solution-phase cycloadditions. The poor mass balance is not surprising in light of our estimate for the half-life of bridgehead diene **37** in dilute solution at room temperature of 7 h.

At the somewhat higher temperature and shorter reaction times available by the vertical drop solution phase thermolysis, a spectrum of products that parallels the reaction of **13** is observed. An overall mass balances of 50% is achieved. Characteristically, product distributions vary as a function of temperature and reaction time. A typical distribution is summarized in eq 17. The mechanism of formation of these products is analogous to that proposed for the gas-phase thermolysis of unactivated dienyne ether **13**.

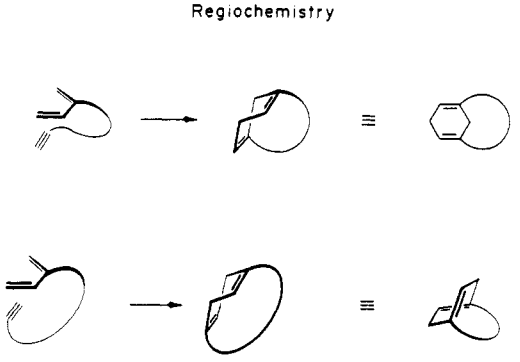




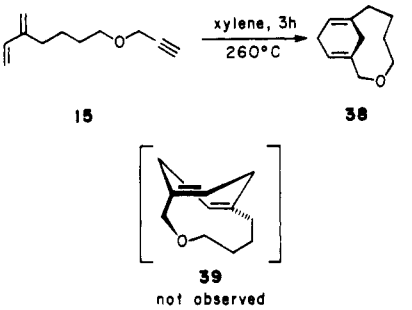
(17)

The successful isolation of bridgehead dienes **32** and **37** attest to the remarkable scope of the intramolecular Diels–Alder reaction. These dienes represent the current limits of isolatable bridgehead dienes.

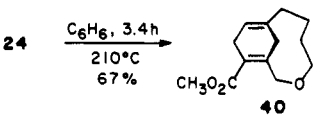
[6.3.1] and [7.3.1] Bridgehead Dienes. Lengthening the tether between diene and dienophile to six or seven atoms is expected to alter Diels–Alder reactivity. A quantitative analysis of these trends is presented in a related article.[14] In addition to changes in reactivity, a longer tether size also introduces the potential for the formation of regioisomeric products.



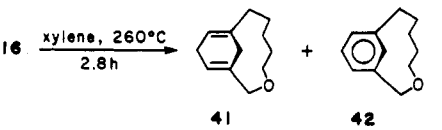
Briefly, our findings for the cycloaddition of Diels–Alder precursors **15** and **16** reveal a diminished rate of reaction compared with precursors containing shorter tethers (i.e., **14**) and, quite interestingly, no tendency to form the para regioisomer. Thermolysis of dienyne ether **15** in the *gas phase* did not produce cycloaddition products. Under these conditions retro-hetero-ene reaction competed favorably with the cycloaddition. Sealed tube solution-phase thermolysis (260 °C, 3 h) returns starting material, bridgehead diene **38** and unidentified higher molecular weight compounds. Cycloadduct **38** could be isolated by silica gel chromatography in only 7% yield. Analytical GC gave no indication of the formation of a regioisomeric cycloadduct (i.e., **39**).



As expected, activation of the dienophile facilitates cycloaddition, thus a benzene solution of **24** at 210 °C for 3.4 h gives cycloadduct **40** in a chromatographed yield of 67%.

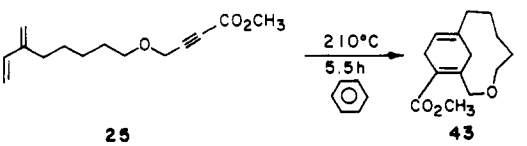


Homologation results in a noticeable cycloaddition rate retardation and the onset of yet another, and most interesting, side reaction. Dienyne ether **16** in *m*-xylene at 260 °C after 2.8 h gave, in addition to unreacted starting material, bridgehead diene **41** and metacyclophane **42**.



Once again the regioadduct was not detected. A most surprising observation is the formation of the [7]metacyclophane **42**. This product has been identified as a secondary reaction product derived from hydrogen extrusion of bridgehead diene **41**. Details of this reaction which has been developed into a useful synthesis of metacyclophanes have been described elsewhere.[24]

Despite dienophile activation, a seven-atom tether size diminishes reactivity in comparison with shorter tethers. Thus, after 5.5 h at 210 °C, a benzene solution of **25** yields starting material (21%) and Diels–Alder cycloadduct **43** in 33% yield.

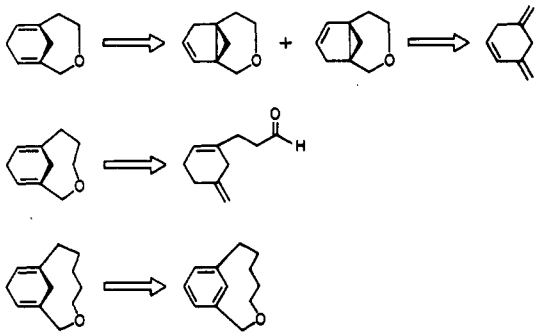


Conclusion

The preceding survey of type 2 intramolecular Diels–Alder cycloadditions of dienyne ethers affords a general entry into a novel class of bridgehead dienes of general structure **2**. The synthetic approach makes available a homologous series of bridgehead dienes containing progressively distorted carbon–carbon double bonds. The

(24) Shea, K. J.; Burke, L. D. *J. Am. Chem. Soc.* **1985**, *107*, 5305.

energetic and structural differences within this homologous series manifest themselves in the thermal reactions of each bridgehead alkene. This behavior is summarized in the equations below.



In addition, it is found that within a span of three methylene groups, the bridgehead dienes range from stable olefinic materials to highly reactive species ($t_{1/2}$ = 7 h, room temperature). As structural data for these molecules become available,[9] efforts will be directed toward developing an understanding of the quantitative relationships between torsional distortion of the bridgehead double bonds and their chemical reactivity.

Experimental Section

A nitrogen or argon atmosphere was employed for all reactions unless otherwise stated. Vertical and horizontal gas-phase thermolysis utilized dry oxygen free nitrogen gas obtained by passing N_2 through a glass-packed column of manganous oxide on vermiculite. Preparative solution-phase thermolysis utilized a high-temperature molten salt bath[24] and employed sealed glass Pyrex tubes (typical length = 17 cm, o.d. = 3.3 mm, i.d. = 2.5 mm).

The horizontal gas-phase thermolysis apparatus consists of a U tube of 5-mm glass fitted to a source of dry nitrogen on one end and a 33 cm × 1 cm hollow quartz tube on the other. The quartz tube is heated by a three-stage tube furnace. The effluent is trapped in a U tube by a −78 °C bath. Flow is monitored by a flow meter at the exit.

The vertical drop thermolysis apparatus consists of 35 cm × 1 cm quartz tube packed with quartz helices and heated by a tube furnace. Sample is introduced by dropwise addition of benzene solution through a pressure-equalizing funnel that is fitted with a source of dry nitrogen. Products are trapped by a −78 °C bath.

A. Synthesis of Diene Alcohols. Diene alcohols **6**[18] and **9**[16] were prepared by the literature procedures.

4-Methylene-5-hexenoic Acid (8). Silver(I) oxide (6.10 g, 26.3 mmol) was added to a solution of H_2O (70 mL), THF (40 mL), and NaOH (5.51 g, 137.8 mmol). The stirred suspension was cooled (0 °C), and a THF solution (20 mL) of aldehyde **7** (1.50 g, 13.6 mmol) was added dropwise. After 3 h at 0 °C the reaction mixture was treated with 6 M HCl (pH 3) and vacuum filtered and the aqueous layer extracted with ether (4 × 25 mL). The precipitate was washed with ether (7 × 25 mL), and the combined organic extracts were dried over anhydrous $MgSO_4$. The crude product was purified by flash column chromatography on silica gel (1:1 Skelly F/Et_2O) to give 1.63 g (94%) of diene carboxylic acid: IR (neat) 3500–2500, 3090, 1710, 1600, 1412, 895 cm^{-1}; ^1H NMR (80 MHz, $(CD_3)_2CO$) δ 7.5 (br s, 1 H, CO_2H), 6.35 (dd, J = 17.5, 10.9 Hz, 1 H, CH_2=CH), 5.38 (d, J = 17.5 Hz, 1 H, CH_2=CH), 5.03 (m, 3 H, C=CH_2), 2.51 (s, 4 H, CH_2CH_2); ^{13}C NMR (22.63 MHz, $(CD_3)_2CO$) δ 174.2, 145.5, 138.9, 115.9, 113.3, 32.4, 26.5.

4-Methylene-5-hexen-1-ol-*1,1-d*$_2$ (9d). An ethereal solution (20 mL) of the above diene carboxylic acid (1.40 g, 11.1 mmol) was added to lithium aluminum tetradeuteride (0.88 g, 21.1 mmol) in ether (20 mL) at a rate to sustain a mild reflux. After 3 h, the reaction mixture was treated with H_2O (10 mL) and 6 M HCl (pH 4). The crude product was isolated by extraction with ether (3 × 25 mL), and the combined extracts were washed with brine and dried over anhydrous $MgSO_4$. Purification by flash column chromatography on silica gel (3:1 Skelly F/ether) gives 0.765 g (62%) of dienol-*1,1-d*$_2$ **9d**: IR (CCl_4) 3650, 3100, 2940, 2200, 2100, 1600, 1100, 955, 905, 895 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 6.40 (dd, J = 17.6, 10.8 Hz, 1 H, CH_2=CH), 5.25 (d, J = 17.6 Hz, 1 H, CH_2=CH), 5.05 (m, 3 H, CH=CH_2), 2.32 (t, J = 7.7 Hz, 2 H, =CHCH_2), 1.76 (t, J = 7.7 Hz, 2 H, CH_2CD_2OH), 1.50 (s, 1 H, CD_2OH) [by ^1H NMR % deuterium incorporation ≥98%]; ^{13}C NMR (22.63 MHz, $CDCl_3$) δ 146.0, 138.9, 115.9, 113.4, 61.7 (pent), 30.9, 27.6; mass spectrum (100 eV, CI, 2-methylpropane), m/e (relative intensity) 115 (MH^+, 56), 98 (9.7), 97 (100), 96 (9), 83 (10).

B. Synthesis of Dienyne Ethers. 2-Propynyl 3-Methylene-4-pentenyl Ether (13). Sodium hydride (1.76 g, 50% oil dispersion, 36.6 mmol) was washed free of mineral oil, dissolved in DME (20 mL), and then heated to 50–55 °C. To the stirred suspension was added dropwise a DME solution (15 mL) of dienol **6** (3.10 g, 30.7 mmol). After being stirred at 50–55 °C for 2 h, the reaction was cooled (−10 °C) and treated dropwise with a toluene solution of propargyl bromide (4.79 g, 40.2 mmol). After 2 h at −10 °C the reaction mixture was permitted to warm to room temperature and then treated with H_2O (10 mL) and dilute HCl (pH 6). The crude product was isolated by extraction with ether (3 × 15 mL) and then purified by flash column chromatography on silica gel (15:1 Skelly F/Et_2O) to give 3.02 g (73%) of dienyne ether **13**: IR (CCl_4) 3320, 3095, 2960, 2900, 2870, 2120, 1600, 1445, 1360, 1105, 990, 900, 665, 625 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 6.40 (dd, J = 17.6, 10.3 Hz, 1 H, CH_2=CH), 5.28 (d, J = 17.6 Hz, 1 H, CH=CH_2), 5.08 (m, 3 H, =CH_2), 4.17 (d, J = 2.4 Hz, 2 H, OCH_2C≡), 3.69 (t, J = 6.7 Hz, 2 H, CH_2CH_2O), 2.55 (t, J = 6.7 Hz, 2 H, CH_2CH_2O), 2.43 (t, J = 2.4 Hz, 1 H, ≡CH); ^{13}C NMR (62.89 MHz, $CDCl_3$) δ 143.0 (s), 138.9 (d), 117.2 (t), 113.5 (t), 80.0 (s), 74.4 (d), 68.8 (t), 58.2 (t), 31.6 (t); mass spectrum, (100 eV, CI, 2-methylpropane), m/e (relative intensity) 137 (MH^+, 82), 123 (30), 119 (32), 109 (64), 107 (98), 95 (39), 93 (40), 85 (67), 83 (50), 81 (100), 79 (40); high-resolution mass spectrum (70 eV, EI), m/e calcd (M − H^+) 135.0810, obsd (M − H^+) 135.0811.

2-Propynyl 4-Methylene-5-hexenyl ether (14). **14** was obtained from dienol **9** and propargyl bromide (72%): IR (CCl_4) 3310, 3100, 2950, 2860, 1600, 1105, 895, 660, 620 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 6.39 (dd, J = 17.7, 10.7 Hz, 1 H, CH=CH_2), 5.25 (d, J = 17.7 Hz, 1 H, CH=CH_2), 5.06 (m, 3 H, C=CH_2), 4.16 (d, J = 2.3 Hz, 2 H, OCH_2C≡), 3.56 (t, J = 6.5 Hz, 2 H, CH_2CH_2O), 2.43 (t, J = 2.3 Hz, 1 H, C≡CH), 2.31 (t, J = 7 Hz, 2 H, =CCH_2CH_2), 1.80 (m, 2 H, $CH_2CH_2CH_2$); ^{13}C NMR (62.89 MHz, $CDCl_3$) δ 145.9 (s), 138.9 (d), 116.0 (t), 113.5 (t), 80 (s), 74.3 (d), 69.8 (t), 58.2 (t), 28 (t), 27.7 (t); mass spectrum (100 eV, CI, 2-methylpropane), m/e (relative intensity) 151 (MH^+, 21), 97 (9), 96 (9), 95 (100), 94 (8), 85 (18), 81 (11); high-resolution mass spectra (70 eV, EI), m/e calcd (M − H^+) 149.0966, obsd (M − H^+) 149.0968.

2-Propynyl 4-Methylene-5-hexenyl-*1,1-d*$_2$ Ether (14d). **14d** was obtained from sodium hydride (0.335 g, 50% mineral oil dispersion 8.00 mmol), dienol-*1,1-d*$_2$ **9d** (0.720 g, 6.30 mmol), and propargyl bromide (1.12 g, 9.4 mmol). Purification by flash column chromatography on silica gel gives 0.682 g (72%) of dideuterio dienyne ether **14d**: IR (CCl_4) 3310, 3100, 2950, 2850, 2170, 2070, 1600, 1440, 1170, 1100, 1080, 890, 660, 620 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 6.35 (dd, J = 17.6, 10.7 Hz, 1 H, CH_2=CH), 5.24 (d, J = 17.6 Hz, 1 H, CH_2=CH), 5.04 (m, 3 H, C=CH_2), 4.12 (d, J = 2.6 Hz, 2 H, OCH_2C≡), 2.42 (t, J = 2.6 Hz, 2 H, ≡CH), 2.29 (t, J = 7.7 Hz, 2 H, =CHCH_2), 1.77 (t, J = 7.7 Hz, 2 H, CH_2CD_2O) [by ^1H NMR % deuterium incorporation ≥98%]; ^{13}C NMR (22.63 MHz, C_6D_6) δ 146.4, 139.5, 116.6, 114.0, 81.9, 75.5, 70.1 (pent), 59.5, 30.5, 30.3; mass spectrum (100 eV, CI, 2-methylpropane), m/e (relative intensity) 153 (MH^+, 18), 99 (8), 98 (9), 99 (100), 96 (12), 87 (22).

5-Methylene-6-hepten-1-ol (10). To refluxing THF (150 mL, 1.8 mol) was added dropwise aqueous HI (72 mL, 0.42 mol, 47%). After 2 h, the reaction mixture was cooled, poured into brine (100 mL), extracted three times with 1:1 pentane/ether (100 mL), and dried with anhydrous $MgSO_4$. Concentration and filtration through silica gel (Skelly F/Et_2O, 3:1) gave 23 g (27%) of 4-iodo-1-butanol, which was used immediately. To a solution of 4-iodo-1-butanol (10.0 g, 50 mmol) in THF (300 mL) at 0 °C was added Li_2CuCl_4/THF[25] (0.3 M, 5.0 mL, 1.5 mmol) followed by

(25) Nunomoto, S.; Yamashita, Y. *J. Org. Chem.* **1979**, *44*, 4788.

dropwise addition of chloroprene Grignard[15] (1.1 M THF, 100 mL, 100 mmol). After addition the reaction was warmed to 25 °C and stirred 1 h. The crude product was isolated by pouring into saturated NH_4Cl (100 mL), acidifying with 2 M HCl (pH 6), extracting three times with 1:1 pentanes/Et_2O (75 mL), and drying ($MgSO_4$). Purification by flash column chromatography on silica gel (3:1 pentanes/Et_2O) gave 4.98 g (79%) dienol **10**: IR (CCl_4) 3640, 3380 (br), 3080, 2930, 2860, 1595, 890 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 6.37 (dd, J = 17.6, 10.8 Hz, 1 H, C*H*=CH_2), 5.23 (d, J = 17.6 Hz, 1 H, CH=C*H*$_2$), 5.06 (d, J = 10.8 Hz, 1 H, CH=C*H*$_2$), 5.02 (s, 1 H, C=C*H*$_2$), 5.00 (s, 1 H, C=C*H*$_2$), 3.67 (t, J = 6.2 Hz, 2 H, CH_2CH_2OH), 2.25 (t, J = 6.7 Hz, 2 H, =CCH_2CH_2), 1.60 (m, 4 H, CH_2CH_2), 1.40 (br s, 1 H, CH_2OH); ^{13}C NMR (62.89 MHz, $CDCl_3$) δ 146.3, 139.1, 115.9, 113.3, 63.0, 32.8, 31.3, 24.4; mass spectrum (100 eV, CI, 2-methylpropane), m/e (relative intensity) 127 (MH^+, 13), 110 (11), 109 (100).

2-Propynyl 5-Methylene-6-heptenyl Ether (15). **15** was obtained in 76% yield from **11**: IR (CCl_4) 3320, 3095, 2950, 2870, 2120, 1600, 1440, 1360, 1110, 990, 900, 665, 625 cm^{-1}; ^1H NMR (250 MHz, C_6D_6) δ 6.33 (dd, J = 17.6, 10.7 Hz, 1 H, C*H*=CH_2), 5.17 (d, J = 17.6 Hz, 1 H, CH=C*H*$_2$), 4.96 (m, 3 H, =C*H*$_2$), 3.84 (d, J = 2.2 Hz, 2 H, $OCH_2C{\equiv}$), 3.32 (br t, 2 H, CH_2CH_2O), 2.12 (br t, 2 H, =CCH_2CH_2), 2.01 (t, J = 2.2 Hz, 1 H, C≡C*H*), 1.51 (m, 4 H, $CH_2CH_2CH_2O$); ^{13}C NMR (22.63 MHz, C_6D_6) δ 146.6, 139.3, 115.8, 113.2, 80.6, 74.2, 69.8, 58.0, 31.4, 29.7, 25.0; mass spectrum (100 eV, CI, 2-methylpropane), m/e (relative intensity) 163 ($M - H^+$, 0.1), 149 (1.3), 110 (8.6), 109 (100), 108 (20.1), 107 (16.4), 95 (34.7), 91 (13.6), 81 (46.9), 79 (50.2).

6-Methylene-7-octen-1-ol (12). 5-[(α-Tetrahydropyranyl)oxy]pentan-1-ol. To a stirred mixture of 1,5-pentanediol (37.0 g, 0.355 mol) and dihydropyran (15.0 g, 0.178 mol) at 0 °C was added dropwise concentrated HCl (300 μL). After being stirred at ≤5 °C for ~0.5 h, the reaction mixture was quenched by addition of K_2CO_3 (1 g, 0.010 mol) and poured into brine (100 mL)–3:1 pentanes/Et_2O (300 mL). The organic layer was washed with brine (100 mL), dried ($MgSO_4$), concentrated, and distilled 100–105 °C at 0.3 mmHg to yield 22 g (64%) of the monoprotected diol: ^1H NMR (250 MHz, $CDCl_3$) δ 4.56 ("t", J = 3.4 Hz, 1 H, OC*H*O), 3.79 (m, 2 H, CH_2O), 3.63 (t, J = 6.4 Hz, 2 H, CH_2OH), 3.42 (m, 2 H, CH_2O), 1.58 (m, 13 H, CH_2); ^{13}C NMR (62.89 MHz, $CDCl_3$) δ 98.8, 67.5, 62.3, 32.5, 30.6, 29.4, 25.5, 20.4.

5-[(α-Tetrahydropyranyl)oxy]-1-iodopentane. To a 0 °C solution of 5-[(α-tetrahydropyranyl)oxy]pentan-1-ol (1.41 g, 7.5 mmol) in CH_2Cl_2 (50 mL) was added dropwise NEt_3 (1.1 mL, 7.9 mmol) with stirring at 0 °C for 5 min. Methanesulfonyl chloride (0.61 mL, 7.9 mmol) was added and the reaction mixture allowed to stir an additional 0.5 h at 0 °C. The crude mesylate was isolated by pouring into ice–H_2O (25 mL), then washing with cold 2 M HCl (10 mL), cold saturated $NaHCO_3$ (10 mL), and cold brine (10 mL), and drying ($MgSO_4$). The mesylate was concentrated and immediately transferred to an acetone solution (50 mL) of NaI (2.20 g, 15.2 mmole). The reaction contents were refluxed for 10 h and then poured into H_2O (100 mL)/Skelly F (100 mL). The aqueous layer was extracted with Skelly F (100 mL) and then washed with saturated $Na_2S_2O_3$. Purification by flash column chromatography on SiO_2 (6:1 Skelly F/Et_2O) afforded 1.37 g (61%) of the THP-protected iodo alcohol (which was immediately used in the next reaction): ^1H NMR (250 MHz, $CDCl_3$) δ 4.57 ("t", J = 3.7 Hz, 1 H, OC*H*O), 3.80 (m, 2 H, CH_2O), 3.45 (m, 2 H, CH_2O), 3.20 (t, J = 7.0 Hz, 2 H, ICH_2CH_2), 1.60 (m, 12 H); ^{13}C NMR (62.89 MHz, $CDCl_3$) δ 98.9, 67.2, 62.4, 33.4, 30.9, 28.8, 27.4, 25.6, 19.7, 6.8.

6-Methylene-7-octen-1-ol (12). To a solution of 5-[(α-tetrahydropyranyl)oxy]-1-iodopentane (20.57 g, 69.0 mmol) in THF (400 mL) at 25 °C was added Li_2CuCl_4 (0.3 M THF, 5.0 mL, 1.5 mmol) followed by dropwise addition of chloroprene Grignard (1.1 m THF, 72 mL, 76 mmol). After addition, the reaction contents were stirred an additional 0.5 h. The crude THP-protected diene alcohol was isolated by pouring onto cold saturated NH_4Cl (200 mL), acidifying with 2 M HCl (pH ~6), extracting the aqueous fraction three times with Skelly F (200 mL), washing organic fraction with brine (100 mL), and drying ($MgSO_4$). The THP-protected dienol was immediately concentrated, transferred to an absolute ethanol solution (400 mL) containing pyridinium *p*-toluenesulfonate[19] (1.2 g, 5.0 mmol), and heated to 40 °C for 3.5 h. The reaction mixture was then concentrated to 100 mL and poured into H_2O (100 mL)/Skelly F (50 mL)/Et_2O (50 mL) and the aqueous layer extracted three times with 1:1 Skelly F/Et_2O (50 mL). The combined organic fractions were washed with brine (50 mL) and dried ($MgSO_4$). Concentration and purification by flash column chromatography on SiO_2 (3:1 Skelly F/Et_2O) afforded 7.87 g (81%) of dienol **12**: IR (CCl_4) 3340, 3080, 2935, 2860, 1595, 1040, 985, 890 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 6.35 (dd, J = 17.6, 10.8 Hz, 1 H, C*H*=CH_2), 5.21 (d, J = 17.6 Hz, 1 H, CH=C*H*$_2$), 5.04 (d, J = 10.8 Hz, 1 H, CH=C*H*$_2$), 5.00 (s, 1 H, CH=C*H*$_2$), 4.97 (s, 1 H, C=C*H*$_2$), 3.62 (t, J = 6.5 Hz, 2 H, CH_2OH), 2.21 (t, J = 7.4 Hz, 2 H, =CCH_2), 1.95 (s, 1 H, CH_2OH), 1.54 (m, 6 H, CH_2); ^{13}C NMR (62.89 MHz, $CDCl_3$) δ 146.5, 139.1, 115.7, 113.2, 63.0, 34.5, 31.3, 27.9, 24.0.

2-Propynyl 6-Methylene-7-octenyl Ether (16). **16** was obtained in 76% yield from **12** and propargyl bromide: IR (CCl_4) 3315, 3085, 2940, 2855, 1595, 1100, 900, 890, 660, 620 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 6.36 (dd, J = 17.6, 10.8 Hz, 1 H, C*H*=CH_2), 5.22 (d, J = 17.6 Hz, 1 H, CH=C*H*$_2$), 5.05 (d, J = 10.8 Hz, 1 H, CH=C*H*$_2$), 5.00 (s, 1 H, C=C*H*$_2$), 4.98 (s, 1 H, C=C*H*$_2$), 4.14 (d, J = 2.4 Hz, 2 H, $OCH_2C{\equiv}CH$), 3.52 (t, J = 6.5 Hz, 2 H, OCH_2CH_2), 2.42 (t, J = 2.4 Hz, $CH_2C{\equiv}CH$), 2.22 (t, J = 7.3 Hz, 2 H, =CCH_2CH_2), 1.54 (m, 6 H, $CH_2CH_2CH_2$); ^{13}C NMR (62.89 MHz, $CDCl_3$) δ 146.5, 139.1, 115.7, 113.2, 80.2, 74.2, 70.2, 58.1, 31.4, 29.5, 28.1, 26.2; mass spectrum (100 eV, CI, 2-methylpropane), m/e relative intensity) 179 (MH^+, 18.5), 124 (12), 123 (100), 109 (11), 95 (11), 83 (51), 81 (24).

3-Butynyl 2-Methylene-3-butenyl Ether (18). Sodium hydride (1.00 g, 50% oil dispersion, 20.90 mmol) was washed free of mineral oil, then added to DME (25 mL), and heated to 50 °C. To the stirred suspension was added dropwise a DME solution (10 mL) of 3-butyn-1-ol (**17a**) (1.41 g, 20.1 mmol). After being stirred 1 h at 50 °C the reaction was cooled (0 °C) and treated dropwise with a DME solution (10 mL) of 2-(bromomethyl)-1,3-butadiene[20] (0.99 g, 6.74 mmol). After 2 h at 0 °C and 12 h at 25 °C the reaction was quenched by addition of H_2O (15 mL). The crude product was isolated by extraction with ether (3 × 25 mL) and then purified by flash column chromatography on silica gel to give 0.66 g (72%) of dienyne ether **18**: IR (CCl_4) 3315, 3100, 3020, 2955, 2925, 2875, 1600, 1378, 1128, 1104, 905, 630 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 6.36 (dd, J = 17.8, 11.0 Hz, 1 H, CH_2=C*H*), 5.31 (d, J = 17.8 Hz, 1 H, CH_2=CH), 5.26 (s, 1 H, C=C*H*$_2$), 5.17 (s, 1 H, C=C*H*$_2$), 5.09 (d, J = 11.0 Hz, CH=C*H*$_2$), 4.19 (s, 2 H, CH_2O), 3.55 (t, J = 7.0 Hz, 2 H, OCH_2CH_2), 2.46 (t, d, J = 7.0, 2.7 Hz, 2 H, OCH_2CH_2), 1.98 (t, J = 2.7 Hz, 1 H, ≡C*H*); ^{13}C NMR (62.89 MHz, $CDCl_3$) δ 142.3 (s), 136.6 (d), 117.4 (t), 114.6 (t), 81.4 (ns), 70.8 nt), 69.4 (d), 68.3 (t), 19.9 (t); mass spectrum (100 eV, CI, 2-methylpropane) m/e (relative intensity) 137 (MH^+, 26), 119 (37), 109 (33), 107 (100), 97 (27), 95 (22), 93 (36), 91 (34), 81 (18); high-resolution mass spectrum (70 eV, EI), m/e calcd ($M - H^+$) 135.0810, obsd ($M - H^+$) 135.0811.

4-Pentynyl 2-Methylene-3-butenyl Ether (19). **19** was obtained from 4-pentyn-1-ol (**17b**) (1.7 g, 20.5 mmol) and 2-(bromomethyl)-1,3-butadiene (2.0 g, 13.7 mmol). Purification by flash column chromatography gave 1.66 g (81%) of dienyne ether **19**: IR (CCl_4) 3320, 3090, 2940, 2860, 2120, 1600, 1440, 1110, 990, 910, 630 cm^{-1}; ^1H NMR (250 MHz, C_6D_6) δ 6.28 (dd, J = 17.6, 11.0 Hz, 1 H, C*H*=CH_2), 5.22 (m, 2 H, CH=C*H*$_2$), 4.99 (m, 2 H, CH=C*H*$_2$, C=C*H*$_2$), 3.95 (s, 2 H, =CCH_2O), 3.26 (t, J = 6.0 Hz, 2 H, OCH_2CH_2), 2.12 (td, J = 7.0, 2.6 Hz, $CH_2CH_2C{\equiv}CH$), 1.75 (t, J = 2.6 Hz, C≡C*H*), 1.62 (m, 2 H, $CH_2CH_2CH_2$); ^{13}C NMR (22.63 MHz, C_6D_6) δ 143.3, 137.1, 116.7, 114.2, 84.0, 70.1, 69.0, 68.6, 29.1, 15.5; mass spectrum (100 eV, CI, 2-methylpropane) m/e (relative intensity) 151 (MH^+, 58), 133 (74), 123 (31), 121 (21), 109 (61), 107 (74), 105 (100), 97 (91), 95 (32), 93 (27), 91 (59), 83 (90), 81 (71); high-resolution mass spectrum (70 eV, EI), m/e calcd ($M - H^+$) 149.0966, obsd ($M - H^+$) 149.0964.

4-[(3-Methylene-4-pentenyl)oxy]-2-butynoic Acid, Methyl Ester (22). A THF solution (100 mL) of dienyne ether **20** (3.02 g, 22.1 mmol) was cooled (−78 °C) and treated dropwise with a hexane solution of *n*-BuLi (22.9 mmol). After 0.5 h, methyl chloroformate (1.86 mL, 24.1 mmol) was added and the solution stirred at −78 °C for an additional 2 h and then allowed to warm

(26) Gordon, A. J.; Ford, R. A. *The Chemists' Companion*; Wiley: New York, 1972; p 450.
(27) Tamaura, M.; Kochi, J. *Synthesis* **1971**, *303*.

to room temperature. The solution was treated with H_2O (50 mL), then extracted with ether (4 × 25 mL), dried ($MgSO_4$), and purified by flash chromatography on silica gel (5:1 Skelly F/Et_2O) to give 3.9 g (90%) of dienyne ester **22**: IR (CCl_4) 3100, 2960, 2240, 1730, 1600, 1435, 1250, 1110, 1060, 900 cm^{-1}; ^1H NMR (250 MHz, C_6D_6) δ 6.36 (dd, J = 17.6, 11.0 Hz, 1 H, C*H*=CH_2), 5.17 (d, J = 17.6 Hz, 1 H, CH=C*H*$_2$), 5.02 (m, 3 H, C=C*H*$_2$), 3.75 (s, 2 H, O*CH*$_2$C≡), 3.47 (t, J = 7.0 Hz, 2 H, CH_2CH_2O) 3.31 (s, 3 H, CO_2CH_3), 2.45 (t, J = 7.0 Hz, 2 H, CH_2CH_2O); ^{13}C NMR (62.89 MHz, C_6D_6) δ 153.9 (s), 143.5 (s), 139.4 (d), 117.7 (t), 113.8 (t), 84.5 (s), 78.8 (s), 69.6 (t), 58.0 t), 52.4 (q), 32.1 (t); mass spectrum (100 eV, CI, 2-methylpropane), m/e (relative intensity) 195 (MH^+, 0.3), 177 (3), 163 (6), 135 (18), 105 (6), 97 (25), 81 (100), 79 (33); high-resolution mass spectra, (70 eV, EI), m/e calcd ($M^{\cdot+}$) 194.0943, obsd ($M^{\cdot+}$) 194.0970.

4-[(4-Methylene-5-hexenyl)oxy]-2-butynoic Acid, Methyl Ester (23). **23** was obtained from **14** in 79% yield: IR (CCl_4) 3100, 2960, 2240, 1730, 1435, 1250, 1110, 1060, 895 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 6.36 (dd, J = 17.6, 10.5 Hz, 1 H, C*H*=CH_2), 5.24 (d, J = 17.6 Hz, 1 H, CH=C*H*$_2$), 5.03 (m, 3 H, C=C*H*$_2$), 4.26 (s, 2 H, O*CH*$_2$C≡), 3.76 (s, 3 H, CO_2CH_3), 3.54 (t, J = 6.3 Hz, 2 H, CH_2CH_2O), 2.29 (t, J = 7 Hz, 2 H, =CC*H*$_2$CH$_2$), 1.78 (m, 2 H, $CH_2CH_2CH_2$); ^{13}C NMR (62.89 MHz, C_6D_6) δ 153.9 (s), 146.5 (s), 139.5 (d), 116.5 (t), 84.6 (s), 78.6 (se, 70.4 (t), 58.0 (t), 52.5 (q), 28.7 (t), 28.4 (t); mass spectrum (100 eV, CI, 2-methylpropane), m/e (relative intensity) 209 (MH^+ 0.2), 121 (4), 119 (5), 105 (4), 97 (12), 95 (100), 93 (12), 85 (14), 81(14), 79 (19); high-resolution mass spectra (70 eV, EI), m/e calcd ($M^{\cdot+}$) 208.1099, obsd ($M^{\cdot+}$) 208.1096.

4-[(5-Methylene-6-heptenyl)oxy]-2-butynoic Acid, Methyl Ester (24). **24** was obtained from **15** in 85% yield: IR (CCl_4) 3090, 2845, 2230, 1725, 1595, 1435, 1250, 1110, 1060, 890 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 6.32 (dd, J = 17.6, 10.8 Hz, 1 H, *H*C=CH_2), 5.18 (d, J = 17.6 Hz, 1 H, CH=C*H*$_2$), 5.01 (d, J = 10.8 Hz, 1 H, CH=C*H*$_2$), 4.98 (s, 1 H, C=C*H*$_2$), 4.95 (s, 1 H, C=CH$_2$), 4.22 (s, 2 H, O*CH*$_2$C≡), 3.74 (s, 3 H, CO_2CH_3), 3.51 (t, J = 6.0 Hz, 2 H, O*CH*$_2$CH$_2$), 2.20 (t, J = 7.0 Hz, 2 H, =CC*H*$_2$CH$_2$) 1.55 (m, 4 H, C*H*$_2$C*H*$_2$); ^{13}C NMR (62.89 MHz, $CDCl_3$) 153.5, 146.1, 138.9, 115.7, 113.2, 84.0, 77.6, 70.5, 57.8, 52.7, 31.1, 29.3, 24.6.

4-[(6-Methylene-7-octenyl)oxy]-2-butynoic Acid, Methyl Ester (25). **25** was obtained from **16** in 91% yield: IR (CCl_4) 3080, 2935, 2860, 2230, 1725, 1595, 1435, 1250, 1105, 1055, 890 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 6.36 (dd J = 17.6, 10.8 Hz, H, C*H*=CH_2), 5.22 (d, J = 17.6 Hz, 1 H, CH=C*H*$_2$), 5.05 (d, J = 10.8 Hz, 1 H, CH=C*H*$_2$), 5.01 (s, 1 H, CH=C*H*$_2$), 4.99 (s, 1 H, C=C*H*$_2$), 4.27 (s, 2 H, O*CH*$_2$C≡C), 3.79 (d, 2 H, CO_2CH_3), 3.53 (t, J = 6.5 Hz, 2 H, C*H*$_2$O), 2.22 (t, J = 7.4 Hz, 2 H, CH_2=cC*H*$_2$CH$_2$), 1.53 (m, 6 H, C*H*$_2$); ^{13}C NMR (62.89 MHz, $CDCl_3$) δ 153.2, 146.0, 138.7, 115.3, 112.7, 83.7, 76.5, 70.4, 57.5, 52.3, 31.0, 29.0, 27.6, 25.7; mass spectrum (100 eV, CI, 2-methylpropane), m/e (relative intensity) 237 (MH^+, 11), 141 (59), 123 (100), 81 (16).

6-[(2-Methylene-3-butenyl)oxy]-2-hexynoic Acid, Methyl Ester (27). **27** was obtained from **19** in 82% yield: IR (CCl_4) 3100, 2965, 2870, 2245, 1730, 1435, 1220, 1130, 1110, 1075, 905 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 6.37 (dd, J = 17.8, 11.0 Hz, 1 H, C*H*=CH_2), 5.30 (d, J = 17.8 Hz, 1 H, CH=C*H*$_2$), 5.25 (s, 1 H, C=C*H*$_2$), 5.18 (s, 1 H, C=C*H*$_2$), 5.12 (d, J = 11.0 Hz, 1 H, CH=C*H*$_2$), 4.16 (s, 2 H, =CC*H*$_2$O), 3.77 (s, 3 H, CO_2CH_3), 3.53 (t, J = 6.0 Hz, 2 H, O*CH*$_2$CH$_2$), 2.47 (t, J = 7.1 Hz, 2 H, ≡CC*H*$_2$CH$_2$), 1.86 (m, 2 H, $CH_2CH_2CH_2$); ^{13}C NMR (62.89 MHz, $CDCl_3$) δ 154.2, 142.6, 136.6, 117.2, 114.4, 89.2, 73.1, 70.7, 68.3, 52.5, 28.0, 15.9; mass spectrum (100 eV, CI, 2-methylpropane), m/e (relative intensity) 209 (MH^+, 100).

Typical Thermolysis Procedures. Solution-Phase Thermolysis of Dienyne Ester 22. Preparation of 3-Oxabicyclo[4.3.1]deca-1(9),6(7)-diene-9-carboxylic Acid, Methyl Ester (37). A benzene solution (20 mL) of dienyne ester **32** (370 mg) was heated in a Carius tube at 209 °C for 0.5 h. GC analysis reveals two major components; these are dienyne ester **22**, 66%, and bridgehead diene ester **37**, 30%. The compounds were separated by rapid flash column chromatography on silica gel (Skelly F/Et_2O, 6:1). Bridgehead diene ester **37** was further purified by preparative VPC (5 ft × $^1/_4$ in. 10% SP2100): ^1H NMR (250 MHz, $CDCl_3$) δ 6.13 (m, 1 H, C*H*=C), 4.49 (s, 2 H, =CC*H*$_2$O), 4.14 (ddd, J = 11, 4, 2 Hz, 1 H, O*CH*$_2$CH$_2$), 3.74 (s, 3 H, CO_2CH_3), 3.65 (ddd, J = 17.7, 6.0, 1 Hz, 1 H, $H_2C(C{=}C)_2$), 3.57 (d, J = 9.2 Hz, 1 H, (C=C)$_2$CH$_2$), 3.16 (br d, J = 17.7 Hz, 1 H, $H_2C(C{=}C)_2$), 3.00 (dt J = 11, 2 Hz, 1 H, OCH_2CH$_2$), 2.73 (br "t", 1 H, OCH$_2$CH_2C=), 2.43 (br d, J = 9.2 Hz, 1 H, (C=C)$_2$CH_2), 2.00 (dd, J = 12.5, 2 Hz, 1 H, C=CCH_2); UV spectrum (hexanes), λ_{max} 298 (weak), 209 nm; ^{13}C NMR (62.89 MHz, C_6D_6) δ 169.1, 166.1, 155.6, 140.1, 132.9, 75.6, 70.9, 51.3, 42.4, 37.1, 34.3; mass spectrum (100 eV, CI, 2-methylpropane), m/e (relative intensity) 195 (MH^+, 77), 177 (100), 165 (22), 163 (15), 71 (17).

Gas-Phase Vertical Drop Thermolysis of Dienyne Ester 22. Preparation of 3-Oxabicyclo[4.3.1]deca-1(9),6(7)-diene-9-carboxylic Acid, Methyl Ester (37). A benzene solution (25.0 mL) of dienyne ester **22** (0.05 M) was thermolyzed at 315 °C with a flow of atmospheric N_2 (36 mL/min) and a drop rate of 0.25 mL/min. GC analysis revealed the presence of three compounds: dienyne ester **22** (69%), propellane **36** (2%), and bridgehead diene **37** (28%).

Propellane 36: IR (CCl_4) 2960, 2860, 1727, 1615, 1440, 1240, 1095, 1083 cm^{-1}; ^1H NMR (250 MHz, C_6D_6) δ 6.46 (t, J = 2.4 Hz, 1 H, CH_2CH=C), 4.64 (d, J = 11.6 Hz, 1 H, CH_2O), 4.18 (d, J = 11.6 Hz, 1 H, CCH_2O), 3.45 (s, 3 H, CO_2CH_3), 3.39 (m, 1 H, OCH_2CH$_2$), 2.96 (ddd, J = 11.3, 10.0, 4.6 Hz, 1 H, OCH_2CH$_2$), 2.36 (dd, J = 19.7, 2.4 Hz, 1 H, CCH_2C=), 2.10 (dd, J = 19.7, 2.4 Hz, 1 H, CCH_2C=), 1.83 (ddd, J = 13.5, 10.0, 5.7 Hz, 1 H, CCH_2CH$_2$), 1.39 (ddd, J = 13.5, 4.8, 4.8 Hz, 1 H, CCH_2CH$_2$), 1.11 (d, J = 4.0 Hz, 1 H, cyclopropyl C*H*), 0.30 (d, J = 4.0 Hz, 1 H, cyclopropyl C*H*); ^{13}C NMR (22.63 MHz, C_6D_6) δ 164.8, 142.2, 141.8, 68.5, 63.6, 51.3, 44.1, 31.1, 30.9, 27.0, 24.1; mass spectrum (100 eV, CI, 2-methylpropane), m/e (relative intensity) 195 (MH^+, 45), 177 (46), 164 (62), 163 (88), 145 (12), 135 (13), 105 (100), 91 (20), 79 (14), 77 (14).

Propellane 35: UV spectrum (heanes), λ_{max} 205 nm (sh); ^1H NMR (250 MHz, $CDCl_3$) δ 5.99 (d, d, J = 5.4, 2.2 Hz, 1 H, C=C*H*), 5.41 (dd, J = 5.4, 2.0 Hz, 1 H, *H*C=C), 4.22 (d, J = 11.4 Hz, 1 H, CCH_2O), 3.76 (d, J = 11.4 Hz, 1 H, CCH_2O), 3.70 (s, 4 H, C*H*CO$_2$C*H*CO$_2$CH$_3$), 3.55 (m, 1 H, CH_2CH_2O), 3.18 (ddd, J = 11.4, 8.6, 6.2 Hz, 1 H, CH_2CH_2O), 1.93 (m, 2 H, CCH_2CH$_2$O), 0.92 (d, J = 4.2 Hz, 1 H, cyclopropyl C*H*), 0.63 (d, J = 4.2 Hz, 1 H, cyclopropyl C*H*); ^{13}C NMR (62.89 MHz, $CDCl_3$) δ 173.4 (s), 140.7 (d), 125.7 (d), 71.9 (t), 63.8 (q), 56.8 (d), 52.0 (t), 32.4 (s), 26.2 (t), 26.0 (t), 24.7 (s); mass spectrum (100 eV, CI, 2-methylpropane), m/e (relative intensity) 195 (MH^+, 100), 194 (9), 177 (66), 165 (13), 164 (10), 135 (11).

Triene ester 34: UV spectrum (hexanes), λ_{max} 240 br, 221 (sh) nm; ^1H NMR (250 MHz, $CDCl_3$) δ 6.83 (t, J = 3.6 Hz, 1 H, *H*C=CCO$_2$CH$_3$), 5.58 (s, 1 H, C=C*H*$_2$), 5.10 (s, 1 H, C=C*H*$_2$), 4.85 (s, 1 H, C=C*H*$_2$), 4.81 (s, 1 H, C=CH$_2$), 3.79 (s, 3 H, CO_2CH_3), 3.08 (br s, 4 H, =CCH_2C=); mass spectrum (100 eV, CI, 2-methylpropane), m/e (relative intensity) 165 (MH^+, 100), 164 (16), 105 (9).

Triene ester 33: UV spectrum (hexanes), λ_{max} 227, 225 (sh) nm; ^1H NMR (250 MHz, $CDCl_3$) δ 6.33 (d, J = 10.2 Hz, 1 H, =CC*H*=), 5.83 (dd, J = 10.2, 5.0 Hz, 1 H, HC=C*H*CH), 5.00 (s, 1 H, =C*H*), 4.95 (br s, 3 H, =C*H*$_2$), 3.83 (d, J = 5.0 Hz, 1 H, *H*CCO$_2$CH$_3$), 3.72 (s, 3 H, CO_2CH_3), 3.36 (br d, J = 15.6 Hz, 1 H, CH_2(C=C)$_2$), 3.04 (d, J = 15.6 Hz, 1 H, CH_2(C=C)$_2$); mass spectrum, (100 eV, CI, 2-methylpropane), m/e (relative intensity) 165 (MH^+, 100), 164 (19), 121 (38), 105 (22).

Bridgehead diene ether 21: IR (CCl_4) 3030, 2940, 2860, 2810, 1460, 1350, 1075, 1050 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 6.11 (m, 1 H, C*H*=C), 5.82 (m, 1 H, C*H*=C), 4.38 (d, J = 11.7 Hz, 1 H, CH_2), 4.38 (d, J = 11.7 Hz, 1 H, CH_2O), 4.00 (d, J = 11.7 Hz, 1 H, CH_2O), 3.56 (dd, J = 12.5, 6.6 Hz, 1 H, CH_2CH_2O), 3.30 (dd, J = 12.5, 8.5 Hz, 1 H, CH_2CH_2O), 3.12 (dt, J = 12.0, 1.8 Hz, 1 H, (CH=C)$_2$CH_2), 2.93 (dt, J = 16.9, 6.6 Hz, 1 H, CH_2(CH=C)$_2$), 2.60 (m, 2 H), 2.38 (dt, J = 14, 8, Hz, 1 H, =CCH_2CH$_2$), 2.13 (m, 2 H), 1.7 (m, 1 H, OCH$_2$CH_2CH$_2$); ^{13}C NMR (62.89 MHz, $CDCl_3$) δ 149.2, 147.8, 134.2, 128.3, 73.8, 63.9, 35.6, 33.2, 31.0, 30.6; mass spectrum (100 eV, CI, 2-methylpropane), m/e (relative intensity) 151 (MH^+, 100), 133 (73), 105 (48), 91 (10); high-resolution mass spectrum (70 eV, EI), m/e calcd ($M^{\cdot+}$) 150.1045, obsd 150.1054.

Aldehyde 20: IR (CCl_4) 3075, 2940, 2900, 2840, 1728, 1685, 1650, 1440, 1420, 1050, 885 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 9.76 (t, J = 1 Hz, 1 H, C*H*O), 5.47 (br s, 1 H, C*H*=C), 4.75 (s, 2 H, C=C*H*$_2$), 2.6 (s, 2 H, C*H*$_2$), 2.56 (td, J = 7, 1 Hz, 1 H, CH_2CH_2CHO), 2.4–2.1 (m, 6 H); ^{13}C NMR (22.63 MHz, $CDCl_3$)

δ 202, 146, 136, 122, 108, 42, 37, 32, 30, 28; mass spectrum (100 eV, CI, 2-methylpropane), *m/e* (relative intensity) 151 (MH^+, 100), 149 (10), 133 (60), 132 (10), 107 (12), 105 (12).

Aldehyde 7: IR (CCl_4) 3100, 2820, 2720, 1735, 1600, 900 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 9.81 (t, J = 1.3 Hz, 1 H, C*H*O), 6.40 (dd, J = 17.6, 10.7 Hz, 1 H, C*H*=), 5.24 (d, J = 17.6 Hz, 1 H, CH=CH_2), 5.07 (m, 3 H, =CH_2), 2.62 (m, 4 H, CH_2CH_2); ^{13}C NMR (22.63 MHz, $CDCl_3$) δ 201.8, 144.6, 138.5, 116.4, 113.7, 42.2, 23.7; mass spectrum (100 eV, CI, 2-methylpropane), *m/e* (relative intensity) 111 (MH^+, 5), 93 (100), 91 (14), 83 (12), 82 (26), 81 (27), 79 (13).

Bridgehead diene 21d: IR (CCl_4) 3040, 2930, 2860, 2810, 2200, 2100, 1625, 1350, 1117, 1075, 1055, 1040, 900 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 6.11 (m, 1 H, C*H*=C), 5.84 (m, 1 H, C*H*=C), 4.38 (d, J = 11.6 Hz, 1 H, CH_2O), 4.02 (d, J = 11.6 Hz, 1 H, CH_2O), 3.13 (dt, J = 12.1, 1.8 Hz, 1 H, (CH=C)$_2$CH_2), 2.49 (dt, J = 16.9, 6.6 Hz, 1 H, CH$_2$(CH=C)$_2$), 2.60 (m, 2 H), 2.38 (dt, J = 14, 8 Hz, 1 H, CH_2CH$_2$), 2.13 (m, 2 H), 1.7 (m, 1 H) [no signal at δ 3.8–3.3 (CH_2OCH$_2$) could be detected]; mass spectrum (100 eV, CI, 2-methylpropane), *m/e* (relative intensity) 153 (MH^+, 100), 152 (20), 135 (84), 106 (14), 105 (31).

Dienyne ether 14d (100 mg) was thermolyzed at 415 °C (17-s contact time). GC analysis revealed the presence of four major components; these were aldehyde **7d**, 22%, dienyne ether **14d**, 23%, bridgehead diene ether **21d**, 17%, and aldehyde **20d**, 17%. These compounds were isolated by preparative GC, and their spectral properties are listed below.

Aldehyde 7d: IR (CCl_4) 3100, 2910, 2060, 1725, 1600, 1410, 1090, 900 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 6.39 (dd, J = 17.6, 11.0 Hz, 1 H, C*H*=CH$_2$), 5.24 (d, J = 17.6 Hz, 1 H, CH=CH_2), 5.08 (m, 3 H, C=CH_2), 2.61 (m, 4 H, CH_2CH_2) [no signal at δ 9.81 (C*H*O could be detected]; mass spectrum (100 eV, CI, 2-methylpropane), *m/e* (relative intensity) 112 (MH^+, 5), 111 (3), 96 (6), 95 (10), 94 (100), 93 (10), 92 (11), 83 (24), 82 (13), 81 (21).

Dienyne ether 14d: identical spectroscopically with authentic sample.

Aldehyde 20d: IR (CCl_4) 3080, 3060, 2990, 2915, 2850, 2030, 1725, 1700, 1650, 1440, 1120, 1090, 1055, 885 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 5.48 (br s, 1 H, CH=C), 4.75 (s, 2 H, C=CH$_2$), 2.70 (s, 2 H, CH$_2$), 2.56 (t, J = 7.4 Hz, 2 H, CH$_2$CH$_2$CDO), 2.25 (m, 5 H) [no signal at δ 9.75 (C*H*O could be detected]; mass spectrum (100 eV, CI, 2-methylpropane) *m/e* (relative intensity) 153 (MH^+, 100), 152 (116), 135 (53), 134 (24), 108 (10), 106 (10).

Bridgehead diene ester 28: IR (CCl_4) 2955, 2880, 1712, 1615, 1435, 1335, 1225, 1200, 1080, 1055 cm^{-1}; UV spectrum (hexanes), λ_{max} 260 (weak), 230 (log ε 3.75), 199 (log ε 4.06) nm; ^1H NMR (250 MHz, $CDCl_3$) δ 5.97 (m, 1 H, C*H*=C), 4.83 (d, J = 14 Hz, 1 H, CH_2O), 4.39 (d, J = 14 Hz, 1 H, CH_2O), 3.85–3.50 (m, 6 H), 2.95 (m, 1 H), 2.65 (m, 2 H), 2.40 (m, 1 H), 2.13 (m, 2 H), 1.77 (m, 1 H); ^{13}C NMR (22.63 MHz, $CDCl_3$) δ 166.6, 162.2, 146.3, 135.7, 129.0, 71.3, 65.7, 51.5, 37.1, 32.0, 31.5, 29.8; mass spectrum (100 eV, CI, 2-methylpropane) *m/e* (relative intensity) 209 (MH^+, 15) 208 (6), 177 (66), 163 (100), 149 (36), 119 (62), 105 (50), 91 (55), 84 (64); high-resolution mass spectra (70 eV, EI), *m/e* calcd (M^+) 208.1099, obsd (M^+) 208.1113.

Bridgehead diene ester 29: IR ($CDCl_3$) 2950, 2925, 2860, 1690, 1605, 1430, 1260, 1085, 1055 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 6.15 (br m, 1 H, C*H*=C), 4.34 (dt, J = 11.8, 1.3 Hz, 1 H, C=CCH_2O), 4.04 (d, J = 11.8 Hz, 1 H, C=CCH_2O), 3.73 (s, 1 H, CO$_2$CH_3), 3.68 (dd, J = 17.1, 6.5 Hz, 1 H, CH_2(C=C)$_2$), 3.65–3.50 (m, 2 H, CH$_2$OCH_2CH$_2$CH$_2$CH_2CH$_2$), 3.28 (dd, J = 11.8, 1.7 Hz, 1 H, (C=C)$_2$CH_2), 3.20 (ddd, J = 12.9, 9.2, 1.8 Hz), 2.65 (br ddd, J = 17.1, 5.5, 2.8 Hz, 1 H, CH_2(C=C)$_2$), 2.50 (m, 1 H, =CHCH_2CH$_2$CH$_2$), 2.33 (dd, J = 11.8, 5.5 Hz, 1 H, (C=C)$_2$CH_2), 2.15 (m, 1 H, =CHCH$_2$CH_2CH$_2$O), 1.70 (m, 1 H, =CHCH$_2$CH_2CH$_2$O); ^{13}C NMR (62.89 MHz, $CDCl_3$) δ 167.4, 163.5, 145.6, 133.2, 130.6, 73.3, 64.8, 51.4, 40.3, 32.3, 32.0, 31.3; high-resolution mass spectrum (70 eV, EI), *m/e* calcd ($M^{\cdot+}$) 208.1099, obsd 208.1098.

Bridgehead diene ether 32: IR (CCl_4) 3130, 2940, 2920, 2860, 1630, 1065, 905 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 6.32 (br m, 1 H, C*H*=C), 5.96 (br "t", 1 H, C*H*=C), 4.42 (d, J = 11.5 Hz, 1 H, CH_2O), 4.04 (dt, J = 11.9, 3 Hz, 1 H, OCH_2CH$_2$), 3.82 (d, J = 11.5 Hz, 1 H, CH_2O), 3.30–3.00 (m, 4 H), 2.65 (br "t", J = 12 Hz, 1 H, CH_2CH$_2$O), 2.43 (br d, J = 10 Hz, 1 H, CH$_2$CH=C), 2.01 (dd, J = 12, 3 Hz, 1 H, CH_2CH$_2$O); ^{13}C NMR (62.89 MHz, $CDCl_3$) δ 159.7, 154.6, 139.5, 132.2, 74.9, 71.7, 40.0, 38.2, 33.5; mass spectrum (100 eV, CI, 2-methylpropane), *m/e* (relative intensity) 137 (MH^+, 28), 119 (100), 107 (72), 206 (35), 91 (26).

Propellane 31: R_f 0.34; 23 mg; IR (CCl_4) 3060, 2920, 2850, 1090, 1030, 725 cm^{-1}; ^1H NMR (250 MHz, C_6D_6) δ 5.85, 5.76 (m, 1 H, C*H*=CH), 5.43, 5.34 (m, 1 H, CH=C*H*), 4.25, 4.09 (d, J= 11 Hz, 1 H, CH_2O), 3.85, 3.58 (d, J = 11 Hz, 1 H, CH_2O), 3.48, 3.37 (m, 1 H, OCH_2), 3.04, 2.98 (m, 1 H, OCH_2), 2.50, 2.27 (dt, J = 18.5, 5 Hz, 1 H, CH_2CH$_2$O), 2.25 (m, 1 H, CH$_2$), 2.02–1.5 (m, 2 H, CH$_2$), 1.09 ("t", J = 3 Hz, 1 H, cyclopropyl C*H*), 0.42, 0.36 (d, J = 3 Hz, 1 H, cyclopropyl C*H*); ^{13}C NMR (62.89 MHz, $CDCl_3$) δ 138.5, 135.6, 129.3, 127.4, 72.0, 68.7, 63.9, 63.7, 44.5, 40.6, 32.0, 31.9, 31.0, 28.0, 27.7, 26.9, 23.6, 23.3; mass spectrum (100 eV, CI, 2-methylpropane), *m/e* (relative intensity) 137 (MH^+, 5), 136 (8), 135 (5), 120 (10), 119 (100), 107 (16), 106 (35), 93 (24), 92 (12), 91 (47), 78 (18); high-resolution mass spectra (70 eV, EI), $C_9H_{12}O$ requires *m/e* 136.0889, found 136.0892.

Triene 30: IR (CCl_4) 3080, 3035, 1660, 1417, 882, 870, 710 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 6.17 (dt, J = 9.8, 2.1 Hz, 1 H, C*H*=CH), 5.80 (dt, J = 9.8, 3.8 Hz, 1 H, C*H*=CH), 4.77 (br m, 4 H, C=CH_2), 3.05 (br s, 2 H, CH_2), 2.86 (br s, 2 H, CH_2); ^{13}C NMR (62.89 MHz, $CDCl_3$) δ 143.5, 129.4, 129.0, 111.0, 108.7, 40.1, 34.7; mass spectrum, *m/e* (100 eV, CI, 2-methylpropane), *m/e* (relative intensity) 107 (MH^+, 100), 106 (48), 105 (33), 93 (40), 91 (68), 79 (17), 78 (47); high-resolution mass spectra (70 eV, EI), C_8H_{10} requires *m/e* 106.0793, found 106.0779.

Bridgehead diene 38: IR (CCl_4) 3060, 2960, 2940, 2860, 1410, 1340, 1110, 1090, 1075, 1045, 1010, 850 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 5.94 (d, "t", J = 6.5, 1.9 Hz, 1 H, C*H*=C), 5.66 (d "t", J = 6.4, 2.0 Hz, 1 H, C*H*=C), 4.37 (ddt, J = 11.8, 2.9, 1.4 Hz, 1 H, =CCH$_2$O), 3.88 (d, J = 11.8 Hz, 1 H, =CCH_2O), 3.36 (d"t" J = 16.5, 5.5 Hz, 1 H, CH$_2$CH_2O)$_2$ + =CCH_2), 3.25 (m, 2 H, CH_2(C=C)$_2$), 2.43 (m, 2 H, CH_2(C=C)$_2$ + =CCH_2), 2.20 (m, 2 H, =CCH_2CH$_2$CH), 2.0 (m, 1 H, CH_2(C=C)$_2$), 1.55 (m, 3 H, CH$_2$); ^{13}C NMR (62.89 MHz, $CDCl_3$) δ 147.4, 145.0, 130.7, 123.7, 72.5, 64.3, 34.6, 30.8, 29.3, 29.1; mass spectrum (100 eV, CI, 2-methylpropane), *m/e* (relative intensity) 165 (MH^+, 8), 147 (67), 131 (20), 105 (100), 91 (21); high-resolution mass spectrum (70 eV, EI), *m/e* calcd ($M^{\cdot+}$) 164.1202, obsd 164.1203.

Bridgehead diene 40: IR (CCl_4) 2942, 1712, 1615, 1442, 1338, 1330, 1255, 1192, 1162, 1094, 1088, 1071 cm^{-1}; UV spectrum (hexanes), λ_{max} 229, 196 nm; ^1H NMR (250 MHz, C_6D_6) δ 5.70 (d"t", J = 6.5, 2.1 Hz, 1 H, C*H*=C), 5.14 (dt, J = 14.4, 1.3 Hz, 1 H, =CCH_2O), 4.49 (ddd, J = 14.4, 3.4, 1.5 Hz, 1 H, =CCH_2O), 3.76 (dd, J = 17.2, 6.6 Hz, 1 H, CH_2(C=C)$_2$), 3.70 (dd, J = 12.6, 1.9 Hz, 1 H, CH_2(C=C)$_2$), 3.48 (m, 4 H, CO$_2$CH_3 + OCH_2CH$_2$), 3.04 (ddd, J = 11.3, 7.4, 3.9 Hz, 1 H, OCH_2CH$_2$), 2.5 (m, 1 H, CH_2(C=C)[$_2$), 2.35 (m, 1 H, =CCH_2(CH$_2$), 2.15 (m, 2 H, =CCH_2CH$_2$), 1.80 (m, 1 H, CH_2(C=C)$_2$), 1.45 (m, 2 H, CH$_2$CH_2CH$_2$CH$_2$), 1.20 (m, 1 H, CH$_2$CH_2CH$_2$); ^{13}C NMR (62.89 MHz, $CDCl_3$) δ 166.7, 159.5, 145.3, 131.6, 124.2, 69.7, 67.8, 51.6, 33.7, 32.5, 30.6, 27.9, 22.7; high-resolution mass spectrum (70 eV, EI), *m/e* calcd ($M^{\cdot+}$) 222.1256, obsd 222.1263.

Bridgehead diene 41: IR (CCl_4) 3025, 2920, 2845, 1450, 1440, 1430, 1350, 1185, 1170 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 5.73 (br d, J = 4.4 Hz, 1 H, C*H*=C), 5.58 (br d, J = 5.6 Hz, 1 H, C*H*=C), 4.30 (ddd, J = 12.7, 3.3, 1.6 Hz, 1 H, =CCH_2O), 3.79 (d, J = 12.7 Hz, 1 H, =CCH_2O), 3.58 (ddd, J = 11.5, 9.4, 2.4 Hz, 1 H, OCH_2CH$_2$), 3.26 (ddd, J = 11.5, 5.6, 2.9 Hz, 1 H, OCH_2CH$_2$), 3.15 (d, J = 15.7 Hz, 1 H, CH_2(C=C)$_2$), 2.77 (dtd, J = 18.4 Hz, 6.4 Hz, 2.2 Hz, 1 H, CH_2(C=C)$_2$), 2.50 (m, 1 H, CH_2(C=C)$_2$), 2.30 (m, 2 H, =CCH_2), 2.10 (m, 1 H, CH_2(C=C)$_2$), 1.90 (m, 1 H, CH$_2$), 1.4 (m, 5 H, CH_2); ^{13}C NMR (62.89 MHz, $CDCl_3$) δ 144.3, 142.6, 124.4, 121.6, 73.4, 69.8, 35.8, 32.2, 30.6, 29.5, 28.4, 24.0; mass spectrum (100 eV, CI, 2-methylpropane), *m/e* (relative intensity) 179 (MH^+, 4), 161 (34), 105 (100); high-resolution mass spectrum (70 eV, EI), *m/e* calcd ($M^{\cdot+}$) 178.1358, obsd ($M^{\cdot+}$) 178.1353.

Metacyclophane 42: IR (CCl_4) 3050, 3020, 2925, 2845, 1460, 1450, 1435, 1070, 700 cm^{-1}; UV spectrum (hexanes), λ_{max} 221 (sh), 201 nm; ^1H NMR (250 MHz, $CDCl_3$) δ 7.74 (s, 1 H, phenyl C*H*), 7.23 ("t", J = 7.4 Hz, 1 H, phenyl C*H*), 7.04 (dt, J = 7.4, 1.8 Hz, 2 H, phenyl C*H*), 4.54 (br s, 2 H, CH_2O), 3.43 (br s, 2 H, CH_2O), 2.70 (t, J = 6.0 Hz, 2 H, CH_2), 1.45 (m, 4 H, CH_2), –0.13 (br s, 2 H, CH_2); ^{13}C NMR (62.89 MHz, $CDCl_3$) δ 142.6, 141.0, 132.9, 129.4, 126.9, 125.5, 74.9, 71.7, 37.2, 31.3, 30.3, 23.1; mass spectrum (100 eV, CI, 2-methylpropane), *m/e* (relative intensity) 177 (MH^+,

100), 161 (23), 159 (33), 147 (20); high-resolution mass spectrum (70 eV, EI), m/e calcd ($M^{\cdot+}$) 176.1201, obsd ($M^{\cdot+}$) 176.1199.

Bridgehead diene ester 43: IR (CCl_4) 2920, 2850, 1710, 1430, 1245, 1080, 750 cm^{-1}; UV spectrum (hexanes), λ_{max} 226, <195 nm; ^1H NMR (250 MHz, $CDCl_3$) δ 5.65 (br d, J = 6.3 Hz, 1 H, $HC{=}C$), 4.83 (d, J = 14.7 Hz, 1 H, $=CCH_2O$), 4.26 (ddd, J = 14.7, 3.5, 1.6 Hz, 1 H, $=CCH_2O$), 3.76 (s, 3 H, CO_2CH_3), 3.63 (ddd, J = 11.7, 5.8, 5.8 Hz, OCH_2CH_2), 3.52 (d, J = 16.3 Hz, 1 H, $CH_2(C{=}C)_2$), 3.42 (ddd, J = 18.4, 6.5, 1.7 Hz, 1 H, $CH_2(C{=}C)_2$), 3.19 (ddd, J = 11.7, 4.3, 4.3 Hz, 1 H, CH_2OCH_2), 2.55 (m, 1 H), 2.35 (m, 2 H), 2.12 (m, 1 H), 1.90 (m, 1 H), 1.78 (m, 1 H), 1.45 (m, 3 H), 1.2 (m, 1 H); ^{13}C NMR (62.89 MHz, $CDCl_3$) δ 167.5, 155.5, 143.0, 127.0, 121.8, 71.4, 69.8, 51.6, 35.7, 33.7, 30.3, 29.7, 28.9, 24.9; mass spectrum (100 eV, CI, 2-methylpropane), m/e (relative intensity) 237 (MH^+, 36), 205 (100); high-resolution mass spectra (70 eV, EI), m/e calcd ($M^{\cdot+}$) 236.1412; obsd ($M^{\cdot+}$) 236.1405.

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Registry No. **6**, 27974-99-8; **7**, 17844-21-2; **7d**, 111772-56-6; **8**, 59550-45-7; **9**, 17844-23-4; **9d**, 111772-43-1; **10**, 74785-37-8; **11**, 55305-32-3; **12**, 82865-60-9; **13**, 94499-41-9; **14**, 111772-44-2; **14d**, 111772-54-4; **15**, 111772-45-3; **16**, 97751-96-7; **17a**, 927-74-2; **14b**, 5390-04-5; **18**, 111772-46-4; **19**, 111772-47-5; **20**, 111772-48-6; **20d**, 111772-58-8; **21**, 111772-49-7; **21d**, 111772-57-7; **22**, 94499-42-0; **23**, 86532-33-4; **24**, 106111-48-2; **25**, 106111-49-3; **26**, 111772-50-0; **27**, 111772-51-1; **28**, 86532-36-7; **29**, 111772-52-2; **30**, 38461-17-5; **31** (isomer 1), 94499-43-1; **31** (isomer 2), 94499-45-3; **32**, 94499-39-5; **33**, 94517-65-4; **34**, 94517-64-3; **35**, 94499-46-4; **36**, 94499-44-2; **37**, 94499-40-8; **38**, 111772-53-3; **40**, 97752-01-7; **41**, 97751-97-8; **42**, 97751-98-9; **43**, 97751-99-0; $HC{\equiv}CCH_2Br$, 106-96-7; $I(CH_2)_4OH$, 3210-08-0; $H_2C{=}CHC(=CH_2)MgCl$, 32657-89-9; $CH_2{=}CHC(=CH_2)(CH_2)_5OTHP$, 111772-55-5; $HO(CH_2)_5OH$, 111-29-5; $THPO(CH_2)_5OH$, 76102-74-4; $MeSO_2O(CH_2)_5OTHP$, 76102-75-5; $BrCH_2C(=CH_2)CH{=}CH_2$, 23691-13-6; $ClCO_2Me$, 79-22-1.

Photochemistry of α,β-Unsaturated Thiones: Addition to Electron-Rich Olefins from T_1

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1,1,3-Trimethyl-2-thioxo-1,2-dihydronaphthalene (1) adds to electron-rich olefins upon excitation to either S_2 ($\pi\pi^*$) or S_1 ($n\pi^*$) states. Excitation to S_2 level resulted in the same mixture of products, namely thietane and 1,4-dithiane, as on excitation to S_1 level. Addition occurs to the thiocarbonyl function and not to the carbon–carbon double bond. The addition is site-specific, and the formation of thietane is regiospecific. The ratio of thietane to 1,4-dithiane in the product mixture is dependent on the concentration of the thioenone. The addition is suggested to originate from the lowest triplet state (T_1) and involves diradical intermediates.

It was shown recently[1] that 1,1,3-trimethyl-2-thioxo-1,2-dihydronaphthalene (1) undergoes cycloaddition to electron-deficient olefins from the second excited singlet state to yield thietanes and also that the thietane formation is stereospecific and regioselective. In continuation of these studies, we have investigated the photochemical behavior of 1 toward electron-rich olefins, and the results of such an investigation are discussed in this paper.

Results and Discussion

(1) Photophysical Properties of 1 in Solution at Room Temperature. Absorption and emission characteristics of 1 were discussd in our earlier paper,[1] and the results of a time-resolved study of 1, based on nanosecond laser flash photolysis, are presented below.[2] Since the absorption bands corresponding to transitions in $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ of thioenone 1 are well separated from one another, different laser pulses were used to flash photolyze these absorption bands. High-intensity laser pulses at 532 nm (10–100 mJ, 6 ns, Quanta-Ray ND-YAG laser, 2nd harmonic) were used to flash photolyze 1 into its $n\pi^*$ band while laser pulses at 337.1 nm (ca. 3 mJ, 8 ns, Molectron UV 400 nitrogen laser) were used to flash photolyze into $\pi\pi^*$ band. The extinction coefficients at these two wavelengths vary by 3 orders of magnitude. Therefore, laser intensities were adjusted so that, in experiments at different wavelengths, the excited-state and the ground-state concentrations were comparable to one another.

A short-lived transient assignable as a triplet was observed upon 337.1-nm laser flash photolysis of benzene solution ($0.2–5 \times 10^{-3}$ M) of thioenone 1. The triplet assignment is based on efficient self-quenching (characteristic of thioketone triplets),[3] quenching by oxygen, di-*tert*-butyl nitroxide (DTBN), and ferrocene, and sensitization of *all-trans*-1,6-diphenyl-1,3,5-hexatriene (DPH) triplets when the thioenone is subjected to laser flash photolysis at 532 nm in the presence of DPH.

Self-Quenching Behavior of Thioenone Triplet. By use of 337.1-nm laser excitation, the self-quenching behavior of thioenone triplet was examined. The triplet decay lifetime (τ_T) was measured as a function of ground-state thioenone concentration ([ET]) in the limit of the low laser intensities (337.1 nm, 0.2–0.8 mJ $pulse^{-1}$). The self-quenching rate constant (k_{sq}^T) and the intrinsic triplet lifetime were calculated from the plot of the reciprocal of the observed lifetime against the ground-state thioenone concentration. The values of τ_T and k_{sq}^T thus obtained are 0.08×10^{-6} s and 3×10^9 M^{-1} s^{-1}, respectively.

Triplet-Quenching Studies. Quenching behavior of thioenone triplet toward O_2 and DTBN was examined by using 337.1-nm laser excitation. The decay of the thioenone triplet absorbance was followed by varying the con-

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