Allenyl Allylic Ethers: Synthesis and Thermal Rearrangements

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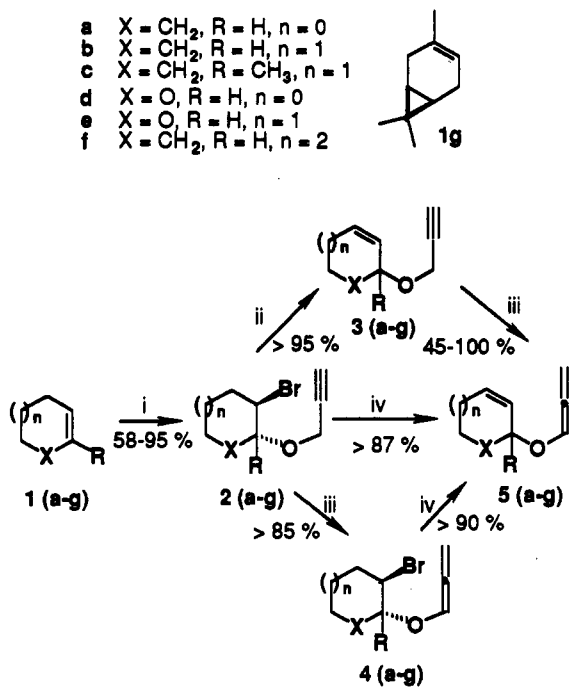
Application of the sequence halogenation/dehydrohalogenation/isomerization to alkenes **1a–g** affords allenyl allylic ethers **5a–g**. Thermal isomerizations of **5a,d,e** proceed by Claisen rearrangement, while **5b,c,f,g** are transformed by alternate modes of [2 + 2]cycloaddition involving biradical intermediates of type **19** to polycyclic structures; the variations in these thermal isomerizations are mainly a function of ring size.

In the course of developing the synthetic potential of vicinal β-bromo ethers obtained from the reaction of alkenes with *N*-bromosuccinimide (NBS) in the presence of functionalized alcohols,[1] we have uncovered a facile method for the preparation of allenyl allylic ethers.[2] Since these materials appeared to be suitable precursors of highly unsaturated aldehydes by Claisen rearrangement,[3] an examination of the thermal chemistry of a number of these allenyl ethers was undertaken. In this report, we detail the amazingly diverse thermal behavior of this class of compounds.[4]

Results

The conversion of cyclic olefins **1** to the corresponding propargyl β-bromo ethers **2** proceeded smoothly upon the addition of NBS in small portions at −20 °C in the presence of an excess of propargyl alcohol as reactant and solvent (Scheme I). In this manner, cyclopentene (**1a**), cyclohexene (**1b**), 1-methylcyclohexene (**1c**), cycloheptene (**1f**), dihydrofuran (**1d**), dihydropyran (**1e**), and (+)-Δ^3-carene (**1g**) were all transformed into the corresponding adducts, generally in excellent yield. In the case of **1g**, a single diastereomer was observed that is assigned as **2g** by analogy with the generation of the corresponding bromohydrin.[5] The dehydrobromination of bromides **2** to give the propargyl allylic ethers **3** could be effected cleanly by heating to 110 °C with 3 equiv of 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU). The regioselectivity of this method is undoubtedly a consequence of the preference for anti elimination. Interestingly, the propargyl unit was unaffected by this reagent. On the other hand, isomerization[6] of the propargyl group of **2** could be performed by treatment with 0.3–0.5 equiv of KO-*t*-Bu in the presence of 18-crown-6 in benzene at room temperature to give allenyl ethers **4** with an intact bromo substituent. (Furan **4d** could not be prepared in this fashion.) Subsequent dehydrobromination of allenyl ethers **4** was carried out with 1.2 equiv of KO-*t*-Bu at 60 °C to produce the allenyl allylic ethers **5**. Similar conditions with 1.5 equiv of KO-*t*-Bu sufficed to convert the initial adducts **2a**, **2b**, and **2f** more directly into **5a**, **5b**, and **5f**, respectively. Alternatively, the allylic propargyl ethers **3** could be isomerized to allenyl ethers **5** with 0.5 equiv of KO-*t*-Bu in pentane at reflux. Thus, the allenyl allylic ethers **5** and their precursors are readily available for use as synthetic intermediates.

Scheme I[a]



[a] Key: (i) NBS/propargyl alcohol, −20 °C; (ii) DBU (3 equiv), 110 °C, 5h; (iii) KO-*t*-Bu (0.5 equiv), pentane, 35 °C, 12 h; (iv) KO-*t*-Bu (1.2–1.5 equiv), benzene, 60 °C, 6 h.

The thermolysis of the cyclopentyl ether **5a** generated the expected Claisen product **6a** in 75% isolated yield after heating to reflux in benzene for 4 h (Scheme II). These conditions appear to be milder than those for the analogous vinyl allylic ethers.[7] The analogous five-membered heterocyclic system **5d** likewise underwent

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(1) (a) Okabe, M.; Abe, M.; Tada, M. *J. Org. Chem.* **1982**, *47*, 1775. (b) Moriya, O.; Okawara, M.; Ueno, Y. *Chem. Lett.* **1984**, 1437. (c) Dulcère, J.-P.; Rodriguez, J.; Santelli, M.; Zahra, J. P. *Tetrahedron Lett.* **1987**, *28*, 2009.

(2) Dulcère, J.-P.; Mihoubi, M. N.; Rodriguez, J. *J. Chem. Soc., Chem. Commun.* **1988**, 237. Note that the structures in Scheme 3 of this article are incorrect owing to a transcription error.

(3) For recent examples of more highly functionalized systems, see: Sleeman, M. J.; Meehan, G. V. *Tetrahedron Lett.* **1989**, *30*, 3345.

(4) For a preliminary communication, see: Dulcère, J.-P.; Crandall, J. K. *J. Chem. Soc., Chem. Commun.* **1990**, 561.

(5) Cocker, W.; Grayson, D. H. *Tetrahedron Lett.* **1969**, 4451.

(6) Brandsma, L.; Verkruijsse, H. D. *Synthesis of Acetylenes, Allenes and Cumulenes*; Elsevier: New York, 1981. Hoff, S.; Brandsma, L.; Arens, J. F. *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 916.

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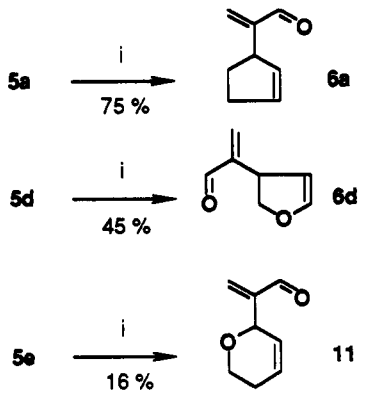
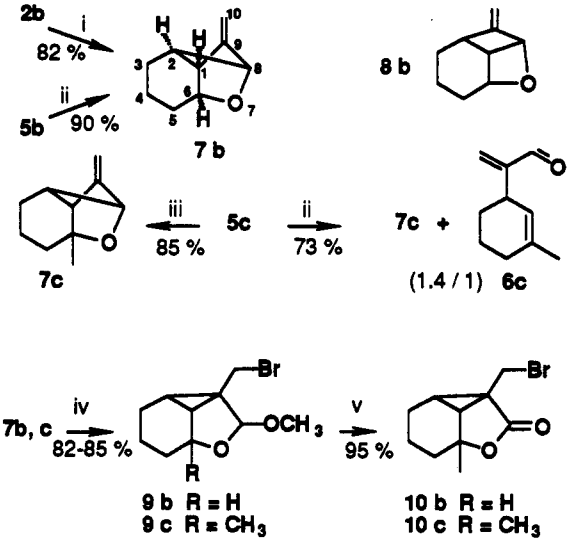
Scheme II[a]



[a] Key: (i) benzene, 80 °C, 4 h.

Scheme III[a]



[a] Key: (i) KO-*t*-Bu (1.8 equiv), 140 °C, xylene, 5 h; (ii) 140 °C, xylene, 3 h; (iii) 80 °C, benzene, 8 h; (iv) NBS/methanol, −20 °C; (vi) Jones' reagent.

rearrangement under these conditions, although the yield was lower here owing to the instability of furan derivative **6d**.

Upon heating for 3 h in xylene at reflux, the cyclohexenyl ether **5b** gave a 90% yield of a totally different type of product with a tricyclic ring skeleton and an exocyclic methylene group (Scheme III). (Uncharacterized decomposition of **5b** was observed in refluxing benzene). The exact structure of this material was difficult to ascertain, even after extensive NMR examination including the determination of the one-bond C–H coupling constants and 2D DEPT, COSY, and HETCOR spectra. In particular, these data did not permit unequivocal differentiation between the two [2 + 2]-cycloaddition structures **7b** and **8b**. The possibility of large four-bond coupling constants[8] and small vicinal coupling constants in these rigid systems was a major point of ambiguity here. Final discrimination in favor of **7b** was secured by an INADEQUATE NMR experiment[9] that established carbon connectivities of the saturated carbons which are uniquely consistent with structure **7b**, when taken in conjunction with carbon connectivities to the oxygen supplied by the chemical shift data. In accord with this assignment, the two observed ^{13}C–^{13}C coupling constants between carbons that are part of the four-membered ring (Scheme III) are significantly smaller [$J(C_1–C_2)$ = 23.7 Hz, $J(C_2–C_8)$ = 28.9 Hz] than the others, which fall in the usual range of 30–40 Hz.[10] A more expeditious preparation of **7b** involved heating **2b** with 1.8 equiv of KO-*t*-Bu in refluxing xylene for 5 h. These conditions simultaneously performed both base-promoted and thermal conversions. Analogous compounds have been hypothesized as intermediates in the base-promoted chemistry of certain 3-(propargyloxy)-1-vinylcyclohexenes to account for the formation of polycyclic compounds that were proposed to arise from further [3,3]-sigmatropic rearrangement of these more highly unsaturated derivatives of structure **7**.[11] These transformations were in competition with the desired Diels–Alder reaction of the allenyl intermediate that predominated in most cases. Allenyl ethers were demonstrated in some cases, but [2 + 2]-cycloaddition products corresponding to structure **7** were never actually isolated or observed in this study.

In the course of this structural work, **7b** was treated with NBS in methanol to give the structurally rearranged acetal **9b**. This transformation of the strained methylenecyclobutane moiety of **7b** can be understood in terms of an electrophile-induced, cyclobutyl–cyclopropylcarbinyl rearrangement[12] with regiocontrol so as to give an oxygen-stabilized cation which is the precursor to the acetal center of **9b**. The assignment of structure **9b** is in accord with DEPT, COSY, and HETCOR NMR data. Furthermore, Jones oxidation of **9b** generated lactone **10b**, whose structure was secured by a single-crystal X-ray diffraction determination.[13] A curious feature of the NMR spectra of **9b** and **10b** is the very large difference in chemical shifts for the diastereotropic protons of the bromomethylene group ($\Delta\delta$ = 1.22 and 0.91 ppm, respectively).[14] This suggests a preferred conformation in which the two protons are in very different magnetic environments. This is consistent with the solid-state structure of **10b**, in which one of the hydrogens subtends the angle defined by the two adjacent carbon–carbon bonds of the cyclopropyl group and is located 1.97 Å above the plane defined by the three-membered ring, which places it in the shielding zone of this anisotropic unit.[15] The other hydrogen on the bromomethylene unit, which points toward the carbonyl oxygen of the lactone with an interatomic distance of 2.78 Å, may experience a deshielding influence owing to its proximity to this electronegative atom which enhances the difference in chemical shift between the diastereotopic

(7) For reviews of the Claisen rearrangement, see: Wipf, P. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: Oxford, 1991; Vol. 5, Chapter 7.2, Ziegler, F. E. *Chem. Rev.* **1988**, *88*, 1423. For kinetic data in solution, see: Gajewski, J. J.; Jurayi, J.; Kimbrough, D. R.; Gande, M. E.; Ganem, B.; Carpenter, B. K. *J. Am. Chem. Soc.* **1987**, *109*, 1170. Burrows, C. J.; Carpenter, B. K. *J. Am. Chem. Soc.* **1981**, *103*, 6983.

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(10) Marshall, J. L. *Carbon–Carbon and Carbon–Proton NMR Couplings*; Verlag Chemie: Deerfield Beach, FL, 1983.

(11) Hayakawa, K.; Aso, K.; Shiro, M.; Kanematsu, K. *J. Am. Chem. Soc.* **1989**, *111*, 5312. Kanematsu, K.; Nagashima, S. *J. Chem. Soc., Chem. Commun.* **1989**, 1029.

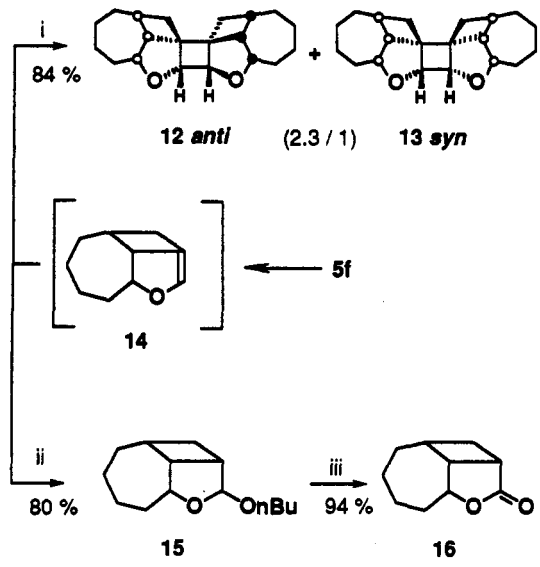
(12) Hesse, M. *Ring Enlargements in Organic Chemistry*: VCH: Weinheim, 1991.

(13) For access to X-ray crystallographic data, see ref 4.

(14) For a similar situation with a related compound, see: Ziegler, F. E.; Marino, A. F.; Petroff, O. A. C.; Studt, W. L. *Tetrahedron Lett.* **1974**, 2035.

(15) Williams, D. H.; Fleming, I. *Spectroscopic Methods in Organic Chemistry*, 4th ed.; Mc Graw-Hill Book Co.: New York, 1987; p 74.

Scheme IV[a]



[a] Key: (i) 140 °C, xylene, 4 h; (ii) 117 °C, *n*-butanol, 4h; (iii) Jones' reagent.

hydrogens. The conformation of acetal **9b** is probably very similar to that of **10b** with respect to the bromomethyl group.

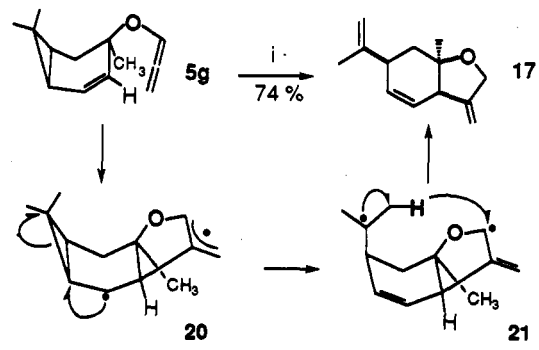
An interesting dichotomy was observed in the pyrolysis of **5c** (Scheme III), a methyl-substituted analog of **5b**. This tertiary allenyl ether was slowly isomerized in pentane at reflux to give an analogous tricyclic product **7c** in excellent yield when account is taken of the unreacted starting material. A more rapid and complete conversion to **7c** occurred in refluxing benzene. On the other hand, heating in refluxing xylene for 3 h gave a mixture of unsaturated aldehyde **6c** (30%) and tricyclic compound **7c** (43%). Under these thermal conditions **7c** is stable. The structure of **7c** follows from its spectroscopic properties, which closely parallel those of **7b**. Conversion to acetal **9c** was analogously effected with NBS in methanol, and subsequent Jones oxidation of **9c** led to lactone **10c**. Thus, it appears that the methyl substituent in **5c** somehow facilitates the Claisen rearrangement; indeed, heating **5b** from 40 to 80 °C still only leads to the cycloadduct **7c**, whereas at higher temperatures the Claisen rearrangement yielding **6c** occurs and becomes competitive with the cycloaddition process. This implies a much greater thermal dependence for the rate of the Claisen rearrangement.

Unfortunately, pyran analog **5e** (Scheme III) did not undergo such a well-behaved thermal conversion. The only product obtained from the complicated mixture arising from heating **5e** in refluxing benzene was 16% of an impure material which is tentatively assigned structure **11** on the basis of IR and ^{1}H and ^{13}C-NMR data. This structure is formally a [1,3]-sigmatropic rearrangement product. Conversions of this type are rare, although Grieco has recently found that similar transformations of vinyl allyl ethers are facilitated in concentrated solutions of $LiClO_4$ in ether.[16]

Yet another type of product was obtained on heating the cycloheptenyl derivative **5f** in xylene at reflux (Scheme IV). In this case, a mixture of two symmetrical dimers

(16) Grieco, P. A.; Clark, J. D.; Jagoe, C. T. *J. Am. Chem. Soc.* **1991**, *113*, 5488.

Scheme V[a]



[a] Key: (i) 140 °C, xylene, 8 h.

was formed in good yield. Once again it was necessary to resort to X-ray determinations[13] to define the structures of these crystalline dimers. They proved to be **12** and **13**, the two head-to-head structures formally derived from suprafacial [2 + 2]-cycloaddition of strained olefin **14**.[17] Supporting evidence for the actual intermediacy of alkene **14** was secured by performing the thermolysis of **5f** in refluxing *n*-butanol. This resulted in diversion of reactive olefin **14** to the *n*-butyl acetal **15** in good yield. The corresponding lactone **16** was readily prepared by Jones oxidation of **15**. Since our initial report, related stable olefinic products related to **14** have been observed in the thermolysis of analogous allenyl vinyl sulfones, where the sulfur geometry results in a much less strained system.[18]

Finally, the thermal behavior of the carene derivative **5g** provided valuable information concerning the mechanistic details of these reactions (Scheme V). Thus, heating **5g** in xylene at reflux gave a 74% yield of a bicyclic compound deduced as structure **17** on the basis of its characteristic spectroscopic data, particularly those associated with the three different double bonds.

Discussion

Recent studies on the mechanism of intermolecular cycloadditions of allenes and olefins has provided a growing body of information which strongly implicates the involvement of biradical intermediates.[19] This situation appears to be facilitated by the "strain" associated with cumulation of the double bonds in the allene moiety.[20] Accordingly, the involvement of related intermediates in the intramolecular reactions of olefinic allenes such as structure **5** can reasonably be anticipated. However, the Claisen rearrangement that takes place with several of the allenyl ethers **5** to generate unsaturated aldehydes of type **6** is most likely a concerted [3,3]-sigmatropic process. The bulk of the available evidence concerning the analogous vinyl allyl ethers indicates that they rearrange to unsaturated aldehydes in this manner.[3,21] Although the

(17) For similar dimerizations of strained trisubstituted olefins, see: Grant, D.; McKervey, R. A.; Rooney, J. J.; Samman, N. G.; Step, G. *J. Chem. Soc., Chem. Commun.* **1972**, 1186. Osterman, V. M.; Schulte, G.; Berson, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 8727.

(18) Kanematsu, K.; Sugimoto, N.; Kawaoka, M.; Yeo, S.; Shiro, M. *Tetrahedron Lett.* **1991**, *32*, 1351.

(19) (a) Pasto, D. J.; Yang, S-H. *J. Am. Chem. Soc.* **1984**, *106*, 152. (b) Pasto, D. J.; Sugi, K. D.; Malandra, J. L. *J. Org. Chem.* **1991**, *56*, 3781. (c) Pasto, D. J.; Sugi, K. D. *J. Org. Chem.* **1991**, *56*, 3795. (d) Pasto, D. J.; Benn, D. C. *J. Org. Chem.* **1991**, *56*, 6209. (e) Pasto, D. J.; Sugi, K. D. *J. Org. Chem.* **1991**, *56*, 6216.

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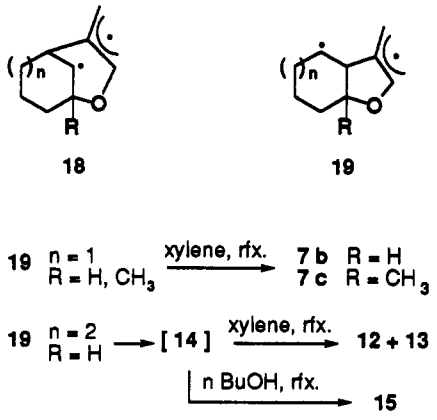
(21) Vittorelli, P.; Winkler, T.; Hansen, H.-J.; Schmid, H. *Helv. Chim. Acta* **1968**, *51*, 1457.

Scheme VI



observed product could, in principle, be achieved via cyclization to biradical **18** (Scheme VI) followed by fragmentation of this 1,4 biradical to aldehyde **6**, this alternative is considered to be less likely. The endo-type cyclization leading to **18** would not appear to be a favorable process if the nature of the transition state resembles that for simple radical cyclizations, since the preferred geometry, or approach trajectory,[22] would not be easily achieved. Indeed, the formation of biradical **19** by exo cyclization should be favored over endo attack to give **18**. Although this reaction pathway is clearly not competitive with the Claisen rearrangement for the five-ring allenyl ethers **5a** and **5b**, cyclization to **19** serves nicely as a key step toward the products observed with the six- and seven-membered ring compounds in this series. Thus, the tricyclic products **7b** and **7c** (Scheme III), which are found in the thermolysis reactions of the six-ring allenyl ethers **5b** and **5c**, respectively, are rationalized by bond formation between the simple radical site and the internal carbon of the allylic radical moiety of biradical **19**. On the other hand, with the larger seven-ring analog **5f** (Scheme IV), radical coupling occurs at the terminal carbon of the allylic radical unit of **19** to produce the strained olefin **14**. The ultimate fate of this unstable intermediate depends on the reaction conditions. It is converted to acetal **15** by the addition of *n*-butyl alcohol, when the latter is employed as the solvent for the thermal isomerization of **5f**. In the absence of an excess of a reactive solvent, the main reaction pathway involves dimerization of **14** to the heptacyclic compounds **12** and **13**. The selectivity of this dimerization process is notable, insofar as both regio- and stereochemistry are concerned, although this is not inconsistent with the known chemistry of similar strained trisubstituted olefins.[17]

Thus, the different types of products can be understood in terms of competition in the formation and subsequent reactivity of **19**, which is very sensitive to the size of the ring originally present in its precursor **5**. These subtle effects are not at all obvious, but appear to be a result of the closely balanced energetics of the relevant processes. The decreasing importance of the Claisen rearrangement for compounds other than **5a** and **5d** seems to be associated with destabilizing interactions between the allenyloxy group and transannular hydrogens in the transition-state geometry for this transformation for ring sizes other than nearly planar five-membered rings. The radical coupling regiochemistry of **19** is surely a result of the stereoelectronics in the respective transition states for the two different reaction modes, which are clearly influenced by the flexibility imparted by an additional methylene group in the original carbocycle of the starting material.

Finally, the reaction of the carene derivative **5g** serves to validate the radical mechanisms that have been proposed above. In this case, syn cyclization leads initially to biradical **20** (Scheme V), which is rapidly diverted to the isomeric species **21** by the thermodynamically favorable ring-opening of the cyclopropylcarbinyl radical moiety present in **20**.[23] From this point, an intramolecular 1,7-hydrogen shift generates the observed product **17**. This relatively uncommon type of intramolecular radical disproportionation is greatly facilitated by the bicyclic structure of **21**, which holds the two reactive centers in close proximity to each other.

In conclusion, thermal isomerizations of allenyl allylic ethers certainly proceed *via* the biradical intermediate **19** which accounts for the polycyclic structures obtained during these [2 + 2]-cycloadditions.

Experimental Section

General. Infrared (IR) spectra were determined on thin films between NaCl disks or on solutions in $CDCl_3$ on a Perkin-Elmer 298. Nuclear magnetic resonance (NMR) spectra were recorded on $CDCl_3$ solutions using Varian XL 200, Bruker AC 200, and Bruker AM-500 instruments. The multiplicities of ^{13}C signals were determined by APT or DEPT techniques. Mass spectra (MS) were obtained on a Varian MAT-311 spectrometer. Melting points were determined on a Buchi apparatus. Flash chromatography was performed using Merck silica gel 60 (250–400 mesh).

Preparation of Propargyl Ethers 2. To a mixture of 0.1 mol of olefin **1** and 18 mL (3 equiv) of freshly distilled propargyl alcohol in 10 mL of CH_2Cl_2 at −20 °C under argon was added 20 g (1.1 equiv) of NBS in small portions over 0.5 h. After the mixture was stirred for 2 h at −20 °C and a further 15 h at room temperature, 30 mL of water was added and the mixture was extracted three times with 50-mL portions of CH_2Cl_2. The extracts were washed with saturated $NaHSO_3$ solution, aqueous K_2CO_3, and water, dried ($MgSO_4$), and concentrated. The crude products were purified by distillation or chromatography to obtain pure materials for spectroscopic characterization, but they were usually pure enough to use directly in subsequent conversions. The following products were obtained in this manner. They all showed characteristic IR bands near 3300 and 2120 cm^{-1}.

***trans*-1-Bromo-2-(2-propyn-1-yloxy)cyclopentane (2a):**[24] 95% yield: bp 83–85 °C (0.5 Torr); ^1H NMR δ 4.28 (m, 2), 4.19 (d, 2 J = 2.4 Hz), 2.45 (t, 1, J = 2.4 Hz), 2.4–1.6 (m, 6); ^{13}C NMR δ 87.2, 79.6, 74.6, 56.7, 53.7, 34.6, 29.7, 21.7. Anal. Calcd for $C_8H_{11}BrO$: C, 47.32; H, 5.46; Br, 39.35. Found: C, 47.28; H, 5.44; Br, 40.05.

***trans*-1-Bromo-2-(2-propyn-1-yloxy)cyclohexane (2b):**[24] 93% yield; ^1H NMR δ 4.27 (d, 2, J = 2.4 Hz), 3.95 (m, 1), 3.52 (m, 1), 2.40 (t, 1, J = 2.4 Hz), 2.4–1.2 (m, 8); ^{13}C NMR δ 80.9, 80.0, 74.2, 57.1, 54.9, 35.3, 30.7, 25.1, 23.1; HRMS calcd for $C_9H_{13}O^{79}Br$ 216.0150, found 216.0141. Anal. Calcd for $C_9H_{13}BrO$: C, 49.79; H, 6.04; Br, 36.80. Found: C, 49.83; H, 6.04; Br, 36.91.

***trans*-1-Bromo-2-methyl-2-(2-propyn-1-yloxy)cyclohexane (2c):** 94% yield; ^1H NMR δ 4.24 (dd, 1, J = 7.3, 4.5 Hz), 4.15 (d, 2, J = 2.4 Hz), 2.40 (t, 1, J = 2.4 Hz), 2.00–1.40 (m, 8), 1.37 (s, 3); ^{13}C NMR δ 81.3, 77.8, 73.3, 59.4, 50.2, 33.5, 33.1, 23.3, 21.8, 21.6; HRMS; calcd for M^+ $C_{10}H_{14}O^{79}Br$ 229.0228, found 229.0229. Anal. Calcd for $C_{10}H_{15}BrO$: C, 51.97; H, 6.54; Br, 34.57. Found: C, 51.48; H, 6.57; Br, 35.28.

***trans*-3-Bromo-2-(2-propyn-1-yloxy)tetrahydrofuran (2d):** 58% yield; ^1H NMR δ 4.20–4.00 (m, 4), 4.13 (d, 2, J = 2.4 Hz), 2.60 (m, 1), 2.40 (t, 1, J = 2.4 Hz), 2.18 (m, 1); ^{13}C NMR δ 106.7, 78.9, 74.6, 66.9, 53.8, 49.7, 33.6. This material decomposed rapidly on standing.

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(24) Torii, S.; Inokuchi, T.; Yukawa, T. *J. Org. Chem.* **1985**, *50*, 5875.

***trans*-3-Bromo-2-(2-propyn-1-yloxy)tetrahydropyran (2e)**: [25] 90% yield; ^{1}H NMR δ 4.71 (d, 1, J = 3.9 Hz), 4.21 (dd, 1, J = 15.7, 2.4 Hz), 4.13 (dd, 1, J = 15.7, 2.4 Hz), 3.89 (dt, 1, J = 6.0, 3.9 Hz); 3.76 (ddd, 1, J = 11.5, 8.4, 3.2 Hz), 3.48 (m, 1), 2.38 (t, 1, J = 2.4 Hz), 2.25 (m, 1), 1.85 (m, 2), 1.40 (m, 1); ^{13}C NMR δ 98.6, 78.6, 74.8, 61.9, 54.3, 48.4, 29.1, 22.3. Anal. Calcd for $C_8H_{11}BrO_2$: C, 43.86; H, 5.06; Br, 36.47. Found: C, 43.61; H, 4.97; Br, 36.59.

***trans*-1-Bromo-2-(2-propyn-1-yloxy)cycloheptane (2f)**: 90% yield; ^{1}H NMR δ 4.28 (dd, 1, J = 15.8, 2.4 Hz), 4.20 (dd, 1, J = 15.8, 2.4 Hz), 4.19 (dt, 1, J = 7.4, 3.4 Hz), 3.84 (ddd, 1, J = 7.4, 6.9, 2.9 Hz), 2.43 (t, 1, J = 2.4 Hz), 2.20–1.40 (m, 10); ^{13}C NMR δ 85.5, 80.0, 74.3, 58.8, 57.1, 34.8, 30.0, 28.0, 24.6, 22.2. Anal. Calcd for $C_{10}H_{15}BrO$: C, 51.97; H, 6.92; Br, 34.57. Found: C, 52.15; H, 6.43; Br, 34.69.

(1*R*,3*R*,4*R*,6*S*)-3-Bromo-4-(2-propyn-1-yloxy)-4,7,7-trimethylbicyclo[4.1.0]heptane (2g): 87% yield from Δ^3-carene with $[\alpha]^{22}_{578}$ +12.7 (*c* 1.2 $CHCl_3$); $[\alpha]^{22}_{578}$ −56 (*c*, 1.05 $CHCl_3$); ^{1}H NMR δ 4.17 (d, 2, J = 2.4 Hz), 4.02 (t, 1, J = 8.9 Hz), 2.42 (dd, 2, J = 4.9, 8.9 Hz), 2.39 (t, 1, J = 2.4 Hz), 2.24 (dd, 1, J = 14.4, 9.4 Hz), 1.49 (dd, 1, J = 14.4, 4.5 Hz), 1.40 (s, 3), 1.01 (s, 3), 0.98 (s, 3), 0.80 (dt, 1, J = 9.4, 4.5 Hz), 0.66 (dt, 1, J = 9.4, 4.9 Hz); ^{13}C NMR δ 81.3, 77.1, 73.4, 59.3, 50.3, 31.9, 30.6, 28.6, 21.6, 19.7, 18.3, 18.0, 15.6. Anal. Calcd for $C_{13}H_{19}BrO$: C, 57.58; H, 7.06; Br, 29.46. Found: C, 57.67; H, 7.12; Br, 29.04.

Preparation of Propargyl Allylic Ethers 3. A mixture of 20 mmol of **2** and 12 mL (5 equiv) of DBU was stirred for 5 h at 110 °C under an argon atmosphere. The mixture was cooled, 40 mL of anhydrous ether was added, and the mixture was stirred for 1 h. Filtration, concentration, and filtration through 10 g of silica gel with pentane–ether (30:70) gave the following products in nearly quantitative yields after chromatography. These compounds showed characteristic IR bands at 3300, 2120, 1650–1630, and 1120 cm^{-1}.

3-(2-Propyn-1-yloxy)cyclopentene (3a): 80% yield; ^{1}H NMR δ 6.02 (ddt, 1, J = 5.7, 2.1, 1.1 Hz), 5.86 (dq, 1, J = 5.7, 2.1 Hz), 4.72 (m, 1), 4.17 (dd, 1, J = 15.7, 2.4 Hz), 4.08 (dd, 1, J = 15.7, 2.4 Hz), 2.39 (t, 1, J = 2.4 Hz), 2.60–1.70 (m, 4); ^{13}C NMR δ 136.2, 130.2, 84.2, 80.4, 73.8, 55.6, 31.0, 29.6. Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.70; H, 8.20.

3-(2-Propyn-1-yloxy)cyclohexene (3b): 100% yield; ^{1}H NMR (60 MHz) δ 5.91 (m, 2), 4.25 (d, 2, J = 2.0 Hz), 4.15 (m, 1), 2.38 (t, 1, J = 2.0 Hz), 2.20–1.60 (m, 6); ^{13}C NMR δ 131.4, 127.1, 80.5, 73.8, 71.8, 55.2, 28.1, 25.2, 19.1. Anal. Calcd for $C_9H_{12}O$: C, 79.41; H, 8.82. Found: C, 79.37; H, 8.81.

3-Methyl-3-(2-propyn-1-yloxy)cyclohexene (3c): 100% yield; ^{1}H NMR δ 5.82 (dt, 1, J = 10.1, 3.6 Hz), 5.51 (br d, 1, J = 10.1 Hz), 4.01 (d, 2, J = 2.4 Hz), 2.31 (t, 1 J = 2.4 Hz), 2.0–1.4 (m, 6), 1.22 (s, 3); ^{13}C NMR δ 131.2, 131.1, 81.7, 72.8, 74.3, 50.6, 33.8, 26.7, 24.9, 19.7. Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 80.12; H, 9.31.

2-(2-Propyn-1-yloxy)-2,5-dihydrofuran (3d): 95% yield; ^{1}H NMR (C_6D_6) δ 6.06 (dq, 1, J = 4.3, 1.2 Hz), 5.67 (dq, 1, J = 6.1, 1.2 Hz), 5.58 (ddt, 1, J = 6.1, 2.4, 1.2 Hz), 4.41 (dddd, 1, J = 14.0, 4.3, 2.4, 1.2 Hz), 4.24 (dm, 1, J = 14.0 Hz), 4.23 (d, 2, J = 2.4 Hz), 2.20 (t, 1, J = 2.4 Hz); ^{13}C NMR δ 132.1, 126.1, 107.3, 80.5, 74.3, 74.1, 53.9. This material decomposed to furan and propargyl alcohol upon attempted chromatographic purification.

2-(2-Propyn-1-yloxy)-5,6-dihydro-2*H*-pyran (3e): 95% yield; ^{1}H NMR δ 6.05 (ddquint, 1, J = 10.1, 5.7, 1.1 Hz), 5.72 (ddt, 1, J = 10.1, 2.8, 1.1 Hz), 5.08 (m, 1), 4.27 (d, 2, J = 2.4 Hz), 3.88 (dt, 1, J = 11.2, 3.4 Hz), 3.71 (ddt, 1, J = 11.2, 6.2, 1.1 Hz), 2.42 (t, 1, J = 2.4 Hz), 2.30 (m, 1), 1.88 (dddt, 1, J = 18.0, 5.5, 3.4, 1.1 Hz); ^{13}C NMR δ 129.4, 125.4, 92.1, 79.7, 74.1, 57.4, 54.1, 24.6. Anal. Calcd for $C_8H_{10}O_2$: C, 69.55; H, 7.30. Found: C, 69.68; H, 7.24.

3-(2-Propyn-1-yloxy)cycloheptene (3f): 98% yield; ^{1}H NMR δ 5.85 (m, 1), 5.74 (m, 1), 4.23 (m, 1), 4.21 (dd, 1, J = 15.8, 2.4 Hz), 4.13 (dd, 1, J = 15.8, 2.4 Hz), 2.40 (t, 1, J = 2.4 Hz), 2.20–1.30 (m, 8); ^{13}C NMR δ 135.3, 131.5, 80.6, 78.3, 73.8, 55.7, 32.7, 28.6, 27.1, 26.7. Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.92; H, 9.34.

(25) Ueno, Y.; Chino, K.; Watanabe, M.; Moriya, O.; Okawara, M. *J. Am. Chem. Soc.* **1982**, *104*, 5564.

(1*S*,4*R*,6*S*)-4-(2-Propyn-1-yloxy)-4,7,7-trimethylbicyclo[4.1.0]hept-2-ene (3g): 95% yield; $[\alpha]^{20}_{578}$ −16.6 (*c* = 1.27 $CHCl_3$); ^{1}H NMR δ 5.74 (d, 1, J = 10.1 Hz), 5.59 (dd, 1, J = 10.1, 2.7 Hz), 4.00 (d, 2, J = 2.4 Hz), 3.64 (dd, 1, J = 14.3, 9.5 Hz), 2.32 (t, 1, J = 2.4 Hz), 1.66 (dd, 1, J = 14.3, 5.2 Hz), 1.27 (s, 3), 1.03 (s, 3), 0.9 (s, 3), 0.86 (m, 2); ^{13}C NMR δ 136.0, 126.9, 81.6, 77.7, 73.1, 50.8, 31.2, 27.8, 26.2, 26.2, 22.5, 20.6, 15.4. Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.01; H, 9.46.

Preparation of Allenyl Ethers 4. A mixture of 50 mmol of **2**, 0.3–0.5 equiv of potassium *tert*-butoxide, and 10 mg of 18-crown-6 in 100 mL of pentane was stirred for 20 h at reflux. The mixture was filtered through silica gel which was washed with 60 mL of 1:1 pentane–ether. Removal of the solvent gave **4** in adequate purity for further reaction. Pure samples for spectroscopic characterization were obtained by chromatography. The following materials were prepared in this manner (**4d** could not be isolated by this procedure). These compounds all showed characteristic IR bands near 1960 and 1100 cm^{-1}.

***trans*-1-Bromo-2-(1,2-propadienyloxy)cyclopentane (4a)**: 90% yield; ^{1}H NMR δ 6.55 (d, 1, J = 6.0 Hz), 5.44 (d, 2, J = 6.0 Hz), 4.31 (m, 2), 2.40–1.60 (m, 6); ^{13}C NMR δ 201.4, 119.9, 90.6, 86.4, 53.8, 34.7, 29.7, 22.1. Anal. Calcd for $C_8H_{11}BrO$: C, 47.32; H, 5.46; Br, 39.35. Found: C, 47.35; H, 5.42; Br, 39.45.

***trans*-1-Bromo-2-(1,2-propadienyloxy)cyclohexane (4b)**: 85% yield; ^{1}H NMR δ 6.45 (t, 1, J = 6.0 Hz), 5.28 (d, 2, J = 6.0 Hz), 4.05 (m, 1), 3.78 (m, 1), 2.40–1.40 (m, 8); ^{13}C NMR δ 201.0, 120.3, 90.6, 79.2, 53.0, 34.2, 29.3, 24.4, 22.5. Anal. Calcd for $C_9H_{13}BrO$: C, 49.79; H, 6.04; Br, 36.80. Found: C, 49.70; H, 5.98; Br, 36.88.

***trans*-1-Bromo-2-methyl-2-(1,2-propadienyloxy)cyclohexane (4c)**: 90% yield; ^{1}H NMR δ 6.47 (t, 1, J = 5.9 Hz), 5.26 (d, 2, J = 5.9 Hz), 4.28 (dd, 1, J = 7.3, 4.4 Hz), 2.20–1.50 (m, 8), 1.41 (s, 3); ^{13}C NMR δ 203.6, 113.3, 86.9, 79.6, 58.5, 33.4, 32.5, 22.7, 22.5, 21.5. Anal. Calcd for $C_{10}H_{15}BrO$: C, 51.97; H, 6.54; Br, 34.57. Found: C, 52.03; H, 6.51; Br, 34.49.

***trans*-3-Bromo-2-(1,2-propadienyloxy)tetrahydropyran (4e)**: 86% yield; ^{1}H NMR δ 6.58 (t, 1, J = 6.1 Hz), 5.41 (dd, 1, J = 9.0, 6.1 Hz), 5.34 (dd, 1, J = 9.0, 6.1 Hz), 4.88 (d, 1, J = 3.8 Hz), 4.02 (dt, 1, J = 5.7, 3.8 Hz), 3.90–3.60 (m, 2), 2.30–1.40 (m, 4); ^{13}C NMR δ 201.0, 117.9, 99.3, 89.3, 62.3, 47.9, 29.0, 22.2. Anal. Calcd for $C_8H_{11}BrO_2$: C, 43.86; H, 5.06; Br, 36.47. Found: C, 43.76; H, 5.03; Br, 36.57.

***trans*-1-Bromo-2-(1,2-propadienyloxy)cycloheptane (4f)**: 85% yield; ^{1}H NMR δ 6.74 (t, 1, J = 6.0 Hz), 5.52 (d, 2, J = 6.0 Hz), 4.36 (dt, 1, J = 6.9, 4.0 Hz), 4.12 (dt, 1, J = 7.2, 2.7 Hz), 2.30–1.60)m, 10); ^{13}C NMR δ 201.3, 120.2, 90.6, 84.3, 57.3, 34.8, 29.4, 28.2, 24.4, 22.1. Anal. Calcd for $C_{10}H_{15}BrO$: C, 51.97; H, 6.54; Br, 34.57. Found: C, 51.88; H, 6.50; Br, 34.68.

(1*R*,3*R*,4*R*,6*S*)-3-Bromo-4-(1,2-propadienyloxy)-4,7,7-trimethylbicyclo[4.1.0]heptane (4g): 88% yield; $[\alpha]^{20}_{578}$ −86.1 (*c* 3.1, $CHCl_3$); ^{1}H NMR δ 6.48 (t, 1, J = 6.0 Hz), 5.27 (d, 2, J = 6.0 Hz), 4.17 (t, 1, J = 8.9 Hz), 2.41 (dd, 2, J = 8.9, 4.6 Hz), 2.23 (dd, 1, J = 14.5, 9.4 Hz), 1.55 (dd, 1, J = 14.5, 5.1 Hz), 1.43 (s, 3), 0.98 (s, 3), 0.95 (s, 3), 0.80 (dt, 1, J = 9.4, 5.1 Hz), 0.67 (dt, 1, J = 9.4, 4.6 Hz); ^{13}C NMR δ 203.6, 113.3, 86.9, 78.9, 58.1, 31.6, 30.5, 28.5, 21.4, 19.5, 19.0, 17.9, 15.6. Anal. Calcd for $C_{13}H_{19}BrO$: C, 57.58; H, 7.06; Br, 29.46. Found: C, 57.65; H, 7.11; Br, 29.68.

Preparation of Allenyl Allylic Ethers 5. Three different methods were used to obtain these materials.

A. The combined dehydrobromination and isomerization of **2a**, **2b**, and **2f** was performed by stirring a mixture of 3.4 g (1.5 equiv) of potassium *tert*-butoxide, 10 mg of 18-crown-6, and 0.02 mol of **2** in 200 mL of benzene at 60 °C for 6 h under argon. The reaction mixture was filtered through silica gel, and the silica gel was washed with 100 mL of 1:2 pentane–ether. The solvent was removed from the filtrate under reduced pressure, and the residue was purified by chromatography to give **5a** (87%), **5b** (95%), and **5f** (90%).

B. Dehydrobromination of 0.02 mol of **4a**, **4b**, and **4f** was performed by stirring with a solution of 2.7 g (1.2 equiv) of potassium *tert*-butoxide and 10 mg of 18-crown-6 in 120 mL of benzene at 60 °C for 6 h under argon. Processing as described above gave **5a** (90%), **5b** (92%), and **5f** (90%).

C. The isomerization of 0.02 mol of **3** was performed by stirring with a mixture of 1.12 g (0.5 equiv) of potassium *tert*-butoxide and 10 mg of 18-crown-6 in 80 mL of pentane at reflux under

argon for 12 h. The reaction mixture was filterecd through silica gel, and the silica gel was washed with 50 mL of 1:1 pentane–ether. Removal of the solvent under reduced pressure gave the following products which could be used without further purification. Pure samples were prepared by flash chromatography: **5a** (92%), **5b** (100%), **5c** (98%), **5d** (45%), **5e** (85%), **5f** (100%), and **5g** (87%). These compounds gave characteristic IR bands at 1960–1955 and 1630–1653 cm^{-1}.

3-(1,2-Propadienyloxy)cyclopentene (5a): 87% yield; ^1H NMR δ 6.66 (t, 1, J = 6.0 Hz), 6.07 (m, 1), 5.88 (m, 1), 5.42 (d, 2, J = 6.0 Hz), 4.84 (m, 1), 2.60–1.80 (m, 4); ^{13}C NMR δ 202.1, 136.5, 130.4, 120.3, 89.6, 83.7, 31.3, 30.1. Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.59; H, 8.19.

3-(1,2-Propadienyloxy)cyclohexene (5b): 95% yield; ^1H NMR δ 6.66 (t, 1, J = 6.0 Hz), 5.92 (m, 1), 5.79 (m, 1), 5.41 (d, 2, J = 6.0 Hz), 4.22 (m, 1), 2.20–1.50 (m, 6). ^{13}C NMR δ 201.7, 131.6, 126.7, 120.1, 89.9, 71.5, 28.3, 25.1, 19.0. Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.47; H, 8.83.

3-Methyl-3-(1,2-propadienyloxy)-1-cyclohexene (5c): 98% yield; ^1H NMR δ 6.57 (t, 1, J = 5.9 Hz), 5.92 (br d, 1, J = 10.1 Hz), 5.63 (br d, 1, J = 10.1 Hz), 5.27 (d, 2, J = 5.9 Hz), 2.10–1.50 (m, 6), 1.36 (s, 3); ^{13}C NMR δ 203.6, 131.4, 131.2, 115.2, 86.7, 76.5, 34.8, 27.0, 25.1, 19.8. Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 80.10; H, 9.32.

2-(1,2-Propadienyloxy)-2,5-dihydrofuran (5d): 45% yield; ^1H NMR δ 6.66 (t, 1, J = 6.0 Hz), 6.32 (dq, 1, J = 6.1, 1.2 Hz), 6.06 (dq, 1, J = 4.1, 1.2 Hz), 5.87 (ddt, 1, J = 6.1, 2.5, 1.2 Hz), 5.46 (dd, 1, J = 8.8, 6.0 Hz), 5.38 (dd, 1, J = 8.8, 6.0 Hz), 4.78 (dddd, 1, J = 14.2, 4.1, 2.5, 1.2 Hz), 4.60 (dm, 1, J = 14.2 Hz); ^{13}C NMR δ 201.5, 132.8, 125.5, 118.0, 107.6, 89.4, 75.1.

2-(1,2-Propadienyloxy)-5,6-dihydro-2*H*-pyran (5e): 85% yield; ^1H NMR δ 6.63 (t, 1, J = 6.0 Hz), 6.05 (ddquint, 1, J = 10.1, 5.7, 1.1 Hz), 5.71 (ddt, 1, J = 10.1, 2.8, 1.1 Hz), 5.38 (dd, 1, J = 8.8, 6.0 Hz), 5.30 (dd, 1, J = 8.8, 6.0 Hz), 5.14 (m, 1), 3.88 (dt, 1, J = 11.3, 3.5 Hz), 3.73 (ddt, 1, J = 11.3, 6.3, 1.1 Hz), 2.27 (m, 1), 1.86 (dddt, 1, J = 18.0, 5.5, 3.5, 1.1 Hz); ^{13}C NMR δ 201.4, 130.0, 124.8, 118.4, 93.0, 89.5, 58.0, 24.5. Anal. Calcd for $C_8H_{10}O_2$: C, 69.55; H, 7.30. Found: C, 69.70; H, 7.24.

3-(1,2-Propadienyloxy)cycloheptene (5f): 90% yield; ^1H NMR δ 6.63 (t, 1, J = 6.0 Hz), 5.77 (m, 2), 5.39 (d, 2, J = 6.0 Hz), 4.34 (br d, 1, J = 9.4 Hz), 2.30–1.20 (m, 8); ^{13}C NMR δ 201.8, 135.5, 130.3, 120.0, 89.9, 78.2, 32.6, 28.5, 26.8, 26.7. Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.92; H, 9.32.

(1*S*,4*R*,6*S*)-4-(1,2-Propadienyloxy)-4,7,7-trimethylbicyclo[4.1.0]hept-2-ene (5g): 87% yield; $[\alpha]^{20}_{578}$ −157 (*c*, 11.8, $CHCl_3$); ^1H NMR δ 6.45 (t, 1, J = 6.0 Hz), 5.84 (d, 1, J = 9.9 Hz), 5.66 (dd, 1, J = 9.9, 2.1 Hz), 5.27 (d, 2, J = 6.0 Hz), 1.99 (dd, 1, J = 14.5, 8.6 Hz), 1.78 (dd, 1, J = 14.5, 5.5 Hz), 1.37 (s, 3), 1.06 (s, 3), 0.96 (s, 3), 0.94 (m, 2); ^{13}C NMR δ 202.9, 135.5, 126.90, 115.0, 87.3, 78.4, 32.0, 27.8, 27.2, 26.5, 22.2, 20.4, 15.5. Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.94; H, 9.47.

2-(Cyclopenten-3-yl)propenal (6a). A solution of 500 mg of **5a** was heated to reflux for 4 h in 15 mL of benzene. The solvent was removed, and the residue was purified by chromatography to give 375 mg (75%) of **6a** as an oil: IR ($CDCl_3$) 3060, 2700, 1680, 850 cm^{-1}; ^1H NMR δ 9.60 (s, 1), 6.19 (s, 1), 5.96 (s, 1), 5.93 (m, 1), 5.63 (m, 1), 3.75 (m, 1), 2.40–2.20 (m, 2), 1.60–1.40 (m, 2); ^{13}C NMR δ 194.6, 153.8, 133.1, 132.6, 131.5, 43.0, 31.9, 30.7. Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.60; H, 8.21.

2-(2,3-Dihydrofuran-3-yl)propenal (6d): Heating a solution of 600 mg of **5d** in 20 mL of refluxing benzene for 4 h gave, after purification as described above, 270 mg (45%) of **6d** as an oil: IR 3055, 2690, 1675 cm^{-1}; ^1H NMR δ (C_6D_6) 9.69 (s, 1), 6.40 (s, 1), 6.19 (s, 1); ^{13}C NMR δ (C_6D_6) 193.1, 152.5, 147.9, 132.7, 100.8, 74.8, 40.2. This material decomposes rapidly on standing.

2-(5,6-Dihydro-2*H*-pyran-2-yl)propenal (11). Heating a solution of 120 mg of **5e** in 6 mL of refluxing benzene for 4 h gave after purification 19 mg (16%) of **11** as an oil: IR 2700, 1670, 1165, 1150 cm^{-1}; ^1H NMR δ 9.52 (s, 1), 6.46 (s, 1), 6.08 (s, 1), 5.85 (m, 1), 5.65 (m, 1), 5.00 (m, 1), 3.90–3.60 (m, 2), 2.50–1.80 (m, 2); ^{13}C NMR δ 192.9, 149.1, 134.2, 127.3, 125.3, 69.9, 62.9, 25.0.

(1*R,2*R**,6*S**,8*R**)-9-Methylene-7-oxatricyclo[4.3.0.0^{2,8}]nonane (7b)). A.** Heating 500 mg of **5b** in 30 mL of refluxing xylene for 3 h gave, after concentration and chromatography, 450 mg (90%) of **7b**.

B. This product was also obtained by heating 1.0 g of **2b** with 930 mg (1.8 equiv) of potassium *tert*-butoxide in 100 mL of refluxing xylene for 5 h. Filtration through silica gel and purification as above gave 820 mg (82%) of **7b**: IR 3080, 1700, 920, 875 cm^{-1}; ^1H NMR (Scheme III) δ 4.49 (H_{10a}, s, 1), 4.40 (H_{10b}, s, 1), 4.31 (H_8, d, 1, J = 5.7 Hz), 4.09 (H_6, t, 1, J = 2.8 Hz), 2.8 (H_1, dd, 1, J = 5.7, 3.2 Hz), 2.10 (H_2, dt, 1, J = 6.4, 3.2 Hz), 1.77 (H_{5a}, ddt, 1, J = 14.0, 7.0, 2.8 Hz), 1.66 (H_{4a}, dquint, 1, J = 14.0, 7.0 Hz), 1.53 ($H_{3a,3b,5b}$, m, 3), 1.10 (H_{4b}, dquint, 1, J = 14, 7.0 Hz); ^{13}C NMR δ 150.0 (C_9), 91.8 (C_{10}, J = 159 Hz), 81.1 (C_8, J = 173 Hz), 71.8 (C_6, J = 155 Hz), 47.2 (C_1, J = 160 Hz), 40.4 (C_2, J = 145 Hz), 27.0 (C_5, J = 125 Hz), 20.6 (C_3, J = 130 Hz), 16.8 (C_4, J = 130 Hz). Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.43; H, 8.83.

The 2-D NMR INADEQUATE[9] Spectrum of 7b. The two-dimensional ^{13}C-^{13}C double-quantum coherence spectrum of **7b** was acquired on a Bruker AM-200 spectrometer using a spectral width of 5000 Hz, 32-step phase cycling, and data acquisition of 1024 × 128 increments in t_1 to provide, after zero filling in the F_1 dimension, a matrix of 4096 × 256 [$S(t_1,t_2)$]. Data files were processed using exponential broadening in both dimensions. The delay for the creation of the double-quantum coherence was 7.1 ms corresponding to coupling of 35 Hz, and the relaxation delay was 1s. The total performance time for the experiment was 54 h. The following one-bond ^{13}C–^{13}C coupling constants were observed (Scheme III): $J(C_1–C_2)$ = 23.7 Hz; $J(C_1–C_6)$ = 33.5 Hz; $J(C_2–C_3)$ = 34.5; $J(C_2–C_8)$ = 28.9 Hz; $J(C_3–C_4)$ = 32.3 Hz; $J(C_4–C_5)$ = 34.5 Hz; $J(C_5–C_6)$ = 37.0 Hz.

Thermolysis of 5c. Heating 310 mg of **5c** in 20 mL of refluxing pentane for 30 h gave, after purification as described above, 77 mg (25%) of recovered **5c** and 223 mg (72%) of (1*R**,2*R**,6*S**,8*R**)-9-methylene-6-methyl-7-oxatricyclo[4.3.0.0^{2,8}]nonane (**7c**) as a colorless liquid: IR 3080, 1700, 955, 880 cm^{-1}; ^1H NMR δ 4.59 (s, 1), 4.49 (s, 1), 4.40 (d, 1, J = 6.0 Hz), 2.63 (dd, 1, J = 6.0, 3.0 Hz), 2.15 (m, 1), 2.00–1.30 (m, 6), 1.28 (s, 3); ^{13}C NMR δ 150.4, 93.1, 82.7, 76.6, 53.3, 43.8, 33.6, 25.4, 21.7, 19.5. Anal. Calcd for $C_{10}H_{14}O$: C, 80.0; H, 9.33. Found: C, 80.10; H, 9.32. A similar experiment in benzene at 80 °C for 8 h effected complete conversion to **7c** (85%). However, heating 670 mg of **5c** in 30 mL of refluxing xylene for 3 h gave 288 mg (43%) of **7c** and 200 mg (30%) of 2-(1-methylcyclohexen-3-yl)propenal (**6c**): IR 3055, 2700, 1670 cm^{-1}; ^1H NMR δ 9.57 (s, 1), 6.23 (s, 1), 6.04 (s, 1), 5.20 (m, 1), 3.32 (m, 1), 2.00–1.80 (m, 2), 1.71 (s, 3), 1.60–1.20 (m, 4); ^{13}C NMR δ 194.1, 154.6, 136.5, 134.0, 122.2, 33.8, 30.1, 28.2, 23.9, 20.7. Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 80.10; H, 9.34. Heating **7c** in refluxing xylene for 5 h gave only recovered starting material.

Thermolysis of 5f. Heating a solution of 1.1 g of **5f** in 80 mL of refluxing xylene for 3 h gave, after removal of the solvent, a crystalline product which was resolved by chromatography into 649 mg (59%) of *anti*-2,5-dioxaheptacyclo[14.4.1.1^{6,11}.0^{3,14}.0^{4,13}.0^{13,22}.0^{14,21}]docosane (**12**),[13] mp 151–153 °C, and 275 mg (25%) of *syn*-2,5-dioxaheptacyclo[14.4.1.1^{6,11}.0^{3,14}.0^{4,13}.0^{13,22}.0^{14,21}]docosane **13**,[13] mp = 130–132 °C. *Anti* dimer **12** showed: IR ($CDCl_3$) 2960, 1110, 990 cm^{-1}; ^1H NMR δ 4.16 (s, 1), 4.10 (t, 1, J = 5.2 Hz), 2.53 (ddd, 1,J = 8.3, 5.2, 1.2 Hz), 2.27 (m, 1), 2.22 (m, 1), 2.11 (dd, 1, J = 11.6, 9.3 Hz), 1.8 (m, 1), 1.72 (m, 1), 1.68 (m, 1), 1.50 (m, 2), 1.59 (m, 1), 1.28 (dt, 1, J = 11.6, 1.2 Hz), 1.01 (m, 1); ^{13}C NMR δ 87.9, 81.8, 51.2, 46.5, 34.1 (2), 30.8, 29.7, 27.2, 25.4. *Syn* dimer **13** showed: IR ($CDCl_3$) 2920, 1100, 990 cm^{-1}; ^1H NMR δ 4.51 (dt, 1, J = 5.4, 1.4 Hz), 4.43 (s, 1), 2.70 (dd, 1, J = 8.0, 5.4 Hz), 2.27 (m, 1), 2.19 (m, 1), 2.13 (dd, 1, J = 11.3, 9.2 Hz), 1.77 (m, 1), 1.70 (m, 2), 1.56 (m, 1), 1.46 (m, 1), 1.42 (m, 1), 1.31 (dt, 1, J = 11.3, 1.4 Hz), 0.97 (m, 1); ^{13}C NMR δ 85.5, 84.6, 54.5, 48.7, 34.5 (2), 31.8, 29.6, 28.2, 25.3.

(1*R*,3*S*,6*R*)-1-Methyl-3-isopropenyl-7-methylene-9-oxabicyclo[4.3.0]non-4-ene (17). Heating 875 mg of **5g** in 50 mL of refluxing xylene for 8 h gave, after removal of the solvent and chromatography, 647 mg (74%) of **17** as a colorless oil: $[\alpha]^{20}_{578}$ +30.3 (*c* 20.4, $CHCl_3$); IR 3080, 1630, 1090 cm^{-1}; ^1H NMR δ 5.87 (dm, 1, J = 10.0 Hz), 5.58 (dm, 1, J = 10.0 Hz), 4.91 (q, 1, J = 2.5 Hz), 4.86 (dt, 1, J = 2.5, 2.1 Hz), 4.73 (m, 2), 4.48 (ddt, 1, J = 13.3, 2.3, 1.3 Hz), 4.35 (dq, 1, J = 13.3, 2.1 Hz), 2.76 (m, 2), 1.67 (dd, 3, J = 1.3, 1.1 Hz), 1.52 (d, 2, J = 8.9 Hz), 1.32 (s, 3); ^{13}C NMR δ 152.7, 147.9, 129.9, 125.4, 110.4, 104.6, 81.6, 69.3, 49.1, 43.6, 35.6,

24.3, 20.2. Anal. Calcd for $C_{13}H_{18}O$: C, 82.10; H, 9.47. Found: C, 82.02; H, 9.48.

(1*R,2*S**,6*R**,8*S**,9*R**)-9-(Bromomethyl)-8-methoxy-7-oxatricyclo[4.3.0.0^{2,9}]nonane (9b).** To a solution of 1.81 g of **7b** in 30 mL of methanol under argon at −20 °C was added 2.4 g of NBS. After being stirred for 2 h at −20 °C, the mixture was concentrated and filtered to remove the solid succinimide which was washed with 1:1 pentane–ether. The solvent was removed, and the product was chromatographed to give 2.8 g (85%) of **9b**: IR 1150 cm^{-1}; ^{1}H NMR δ 4.76 (s, 1), 4.58 (m, 1), 4.21 (d, 1, *J* = 9.9 Hz), 3.44 (s, 3), 2.98 (d, 1, *J* = 9.9 Hz), 1.81 (m, 1), 1.76 (m, 1), 1.65 (m, 1), 1.56 (m, 1), 1.50 (m, 1), 1.40 (m, 1), 1.30 (m, 2); ^{13}C NMR δ 103.8, 74.4, 55.1, 38.5, 36.2, 26.9, 23.9, 22.1, 17.8, 14.9. Anal. Calcd for $C_{10}H_{15}BrO_2$: C, 48.60; H, 6.12; Br, 32.39. Found: C, 48.51; H, 6.06; Br, 32.34.

(1*R,2*S**,6*R**,8*S**,9*R**)-9-(Bromomethyl)-8-methoxy-6-methyl-7-oxatricyclo[4.3.0.0^{2,9}]nonane (9c).** In a similar manner 812 mg of **7c** was converted to 1.16 g (82%) of **9c**: IR 1080, 1050, 625 cm^{-1}; ^{1}H NMR δ 4.67 (s, 1), 4.23 (d, 1, *J* = 9.8 Hz), 3.36 (s, 3), 2.94 (d, 1, *J* = 9.8 Hz), 1.32 (s, 3), 1.80–1.10 (m, 8); ^{13}C NMR δ 103.5, 75.8, 54.8, 39.1, 36.6, 31.7, 30.9, 28.7, 23.1, 19.7, 14.8. Anal. Calcd for $C_{11}H_{17}BrO_2$: C, 50.59; H, 6.56; Br, 30.60. Found: C, 50.58; H, 6.50; Br, 30.61.

(1*R,2*R**,7*R**,9*R**,10*S**)-9-*n*-Butoxy-8-oxatricyclo[5.3.0.1^{2,10}]undecane (15).** A solution of 3.42 g of **5f** in 35 mL of 1-butanol was heated to reflux for 4 h. Concentration and chromatography purification gave 4.63 g (80%) of **15**: IR 2910, 1090, 1040 cm^{-1}; ^{1}H NMR δ 4.91 (s, 1), 4.15 (m, 1), 3.62 (dt, 1, *J* = 9.6, 6.7 Hz), 3.30 (dt, 1, *J* = 9.6, 6.7 Hz), 2.80 (m, 1), 2.61 (m, 1), 2.34–2.22 (m, 2), 2.06 (m, 1), 1.72–1.25 (m, 12), 0.83 (t, 3, *J* = 7.2 Hz); ^{13}C NMR δ 109.6, 79.6, 66.7, 43.4, 42.3, 34.7, 34.2, 31.8, 29.8, 28.0, 27.6, 25.8, 19.3, 13.8. Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 74.90; H, 10.72.

(1*R,2*S**,6*R**,9*R**)-9-(Bromomethyl)-7-oxatricyclo[4.3.0.0^{2,9}]nonan-8-one (10b).** A solution of 0.5 g of CrO_3 and 0.5 mL of concentrated H_2SO_4 in 1.5 mL of water was added slowly to 700 mg of **9b** in 10 mL of acetone at 0 °C. After being stirred for 2 h, the reaction mixture was filtered through silica gel, which was then washed with 20 mL of ether. The filtrate was washed with water, dried ($MgSO_4$), and concentrated. Chromatographic purification gave 622 mg (95%) of **10b** as a white solid:[13] mp 51–53 °C; IR ($CDCl_3$) 1770, 1080 cm^{-1}; ^{1}H NMR δ 4.9 (dt, 1, *J* = 5.7, 2.8 Hz), 4.09 (d, 1, *J* = 11.1 Hz), 3.18 (d, 1, *J* = 11.1 Hz), 2.37 (dd, 1, *J* = 8.1, 5.9 Hz), 2.01 (m, 1), 1.85 (m, 1), 1.76 (dt, 1 *J* = 7.8, 3.1 Hz), 1.60 (m, 3), 1.41 (m, 1); ^{13}C NMR δ 174.1, 72.9, 37.0, 32.4, 28.9, 28.7, 24.2, 18.1, 14.5. Anal. Calcd for $C_9H_{11}BrO_2$: C, 46.78; H, 4.80; Br, 34.58. Found: C, 46.82; H, 4.76; Br, 34.57.

(1*R,2*S**,6*R**,9*R**)-9-(Bromomethyl)-6-methyl-7-oxatricyclo[4.3.0.0^{2,9}]nonan-8-one (10c).** In a similar manner 157 mg of **9c** in 5 mL of acetone was oxidized with 100 mg of CrO_3 and 0.1 mL of concentrated H_2SO_4 in 0.3 mL of water to give 141 mg (96%) of **10c** as an oil: IR 1770, 1080 cm^{-1}; ^{1}H NMR δ 4.22 (d, 1, *J* − 11.0 Hz), 3.11 (d, 1, *J* = 11.0 Hz), 2.13 (d, 1, *J* = 8.2 Hz), 2.05–1.54 (m, 7), 1.56 (s, 3); ^{13}C NMR δ 173.4, 80.0, 38.7, 34.4, 32.9, 31.1, 30.5, 27.5, 18.1, 16.4. Anal. Calcd for $C_{10}H_{13}BrO_2$: C, 49.00; H, 5.35; Br, 32.60. Found: C, 49.02; H, 5.31; Br, 32.59.

(1*R,2*R**,7*R**,10*S**)-8-Oxatricyclo[5.3.0.1^{2,10}]undecan-9-one (16).** In a similar fashion 1.24 g of **15** in 20 mL of acetone was converted by a solution of 1.0 g of CrO_3 and 2 mL of concentrated H_2SO_4 in 3 mL of water to give 870 mg (94%) of **14** as a colorless oil: IR 1765, 1170, 970 cm^{-1}; ^{1}H NMR δ 4.66 (m, 1), 3.03 (m, 1), 2.94 (m, 1), 2.56–2.43 (m, 2), 2.22 (m, 1), 1.81–1.72 (m, 2), 1.61 (m, 2), 1.52 (m, 1), 1.45–1.35 (m, 2); ^{13}C NMR δ 181.4, 82.3, 41.8, 38.0, 37.5, 34.8, 31.1, 28.5, 28.2, 25.0. Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.22; H, 8.41.

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