Thermal Rearrangements of Spiro[2.4]hepta-1,4,6-trienes

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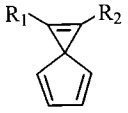
Thermolysis of spiro[2.4]hepta-1,4,6-triene (**1a**) at 50 °C yielded bicyclo[3.2.0]hepta-1,3,6-triene (**5**), which dimerized in two different fashions to form cyclobutanes. The 1,2-dimethyl and 1-propyl derivatives of **1a** also rearranged at 50 °C, but at a faster rate, each yielding a pair of cyclobutane dimers. The structures of these symmetrical dimers were investigated by 1D and 2D NMR and NOE difference spectroscopy. Ab initio calculations indicated that the two strained olefins **1a** and **5** had comparable energies about 50 kcal/mol lower than norborna-1(7),2,5-triene, which was thus excluded as a reaction intermediate.

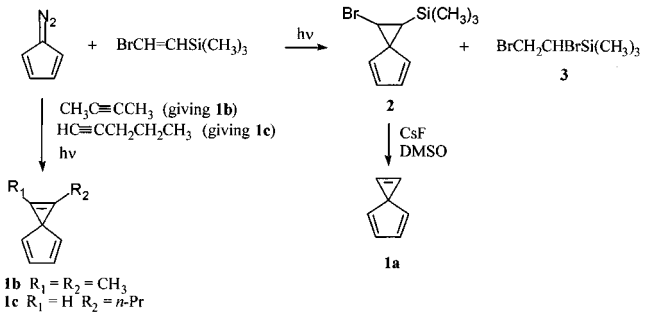
The possibility that double bonds arranged perpendicularly in space might interact by conjugation has generated considerable interest in the synthesis of molecules with geometry suitable for this interaction. The spiro[2.4]hepta-1,4,6-trienes are of interest in this regard since ground-state stabilization through spiroconjugation has been predicted on the basis of theoretical calculations.[1−6] The high strain energy of the cyclopropene ring suggests that facile low-temperature rearrangements might be expected. In this paper, we show that spirenes **1a**−**c** readily undergo [1,5]-sigmatropic reactions to yield bicyclo[3.2.0]hepta-1,3,6-trienes as reactive intermediates.



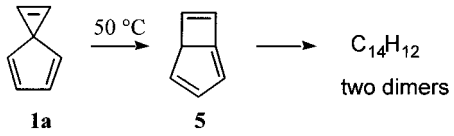
1a $R_1 = R_2 = H$
1b $R_1 = R_2 = CH_3$
1c $R_1 = H$ $R_2 = n$-Pr

The synthesis of spiro[2.4]hepta-1,4,6-triene **1a** is illustrated in Scheme 1. Photolysis of a solution of diazocyclopentadiene[7] in (2-bromovinyl)trimethylsilane yielded the desired precursor **2** as a mixture of trans and cis isomers.[8,9a] A coproduct identified as **3** was isolated by preparative gas chromatography. The origin of **3**, although formally the HBr addition product of the silane, has not been determined. Conversion to the spirene **1a** was accomplished by treating **2** with CsF in dimethyl sulfoxide.[9] Low-temperature distillation provided **1a** in 68% yield. Spirenes **1b** and **1c** were prepared by photolysis of diazocyclopentadiene in the presence of the appropriate alkyne (Scheme 1).[8]

Scheme 1



Scheme 2



When **1a** or its alkylated derivatives **1b** or **1c** was heated to 50 °C, a pair of dimeric products was formed cleanly in high yield. In formulating a pathway leading from spirene **1a** to the dimers, we considered the pathway shown in Scheme 2, a [1,5]-sigmatropic shift in which a cyclopropenyl carbon of **1a** migrates to an adjacent carbon of the cyclopentadienyl ring, leading to bicyclo[3.2.0]-

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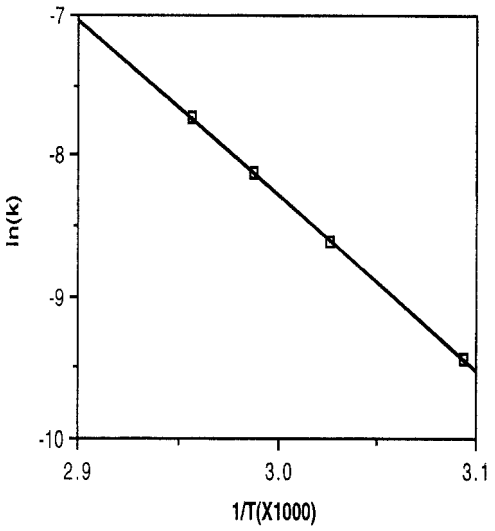

Figure 1. Arrhenius plot of the rearrangement of spiro[2.4]-hepta-1,4,6-triene.

hepta-1,3,6-triene **5**. The stereochemistry of this process is lost as the bridgehead double bond of **5** is formed. The calculated activation energy of this process is close to 30 kcal/mol. Calculations at the HF and CASSCF levels showed that **1a** is more stable than **5**, but at MP2, CCD, and CCSD(T), the opposite held. The calculated difference in energy is small:[10] **1a** is destabilized by the cyclopropene double bond and the spiro center, while **5** is destabilized by the bridgehead double bond. Because the two factors roughly cancel each other, the only driving force for the reaction is the depletion of **5** by irreversible dimerization. The possible conversion of **5** to **1a** has also been considered,[9d] and the activation energy has previously been estimated at ca. 25 kcal/mol in both directions.[11]

The rearrangement **1a** → **5** has the characteristics of a unimolecular reaction. Thermolysis was investigated over the temperature range 50−65 °C. The first-order rate constant is given by the expression $k = 10^{12} \cdot \exp(-24\,700/RT)$. The experimental activation energy (24.7 kcal/mol) is in remarkably good agreement with calculated values.[11] The results are shown as an Arrhenius plot in Figure 1. The reaction proceeded somewhat faster with **1b** and **1c**. In the case of the unsymmetrical spirene **1c**, apparently only the propyl-bearing cyclopropenyl carbon migrated in the [1,5]-sigmatropic shift,[12] resulting in the formation of a single pair of dimers (see below). Such preferential bond migration is a striking example of the topochemical rule formulated by Epiotis and Shaik[12a] that a thermal sigmatropic shift will preferentially take place via the path that couples the best donor−acceptor fragments. Preferential migration of one bond in a 1,5-sigmatropic rearrangement has been previously reported in a similar compound.[12b]

Under conditions of vacuum pyrolysis, the strained bicyclo[3.2.0]hepta-1,3,6-triene **5** can apparently attain the triplet state[13] and can undergo numerous rearrangements.[9d,11,13] At lower temperatures and higher concentrations, dimerization is the predominant fate of **5**. (Rearrangement of **5** to cycloheptatetraene is unfavorable, with a calculated activation energy of at least 35 kcal/mol.[11,13]) Although dimers of **5** and various derivatives have been described by several groups,[9d,14−18] the regio- and stereochemical structure of the products remains unclear. Cycloaddition of **5** at the strained bridgehead double bond,[19] as reported by Bauld et al.,[14] could in principle lead to the generation of four different isomers, **6**−**9**, analogous to those suggested for the dimerization of a benzo derivative of **5**.[15,20] However, our results and those of others[9d,14−18] indicated the formation of only two isomers from **5** or its derivatives. A crystal structure of the bis-benzo derivative of **6a** ($R_1 + R_2$ = benzo) has been reported[15] and one of the two dimers shown to have C_s symmetry, but no corresponding NMR characterization was given. Another study contains ^{1}H NMR data for dimers derived from **5** but no structure determinations.[14]

From thermolysis of **1a**−**c**, we isolated individual dimers by preparative TLC and characterized each isomer by ^{1}H and ^{13}C NMR and mass spectrometry. Additional NMR data, including DQF−COSY, HSQC, HMBC, and NOE difference spectra, were obtained for

(10) [1,3]-sigmatropic rearrangement of **1a** to norbornatriene **4** is ruled out since calculations at the MP2/6-311G* level showed that **4** is higher in energy than spirene **1a** by about 50 kcal/mol. Thus **4** would be unattainable by thermolysis of **1a**. Similar energy differences between **1a**, **4**, and **5** were reported previously.[11]

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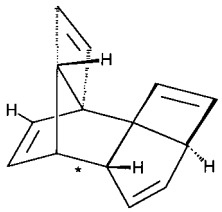
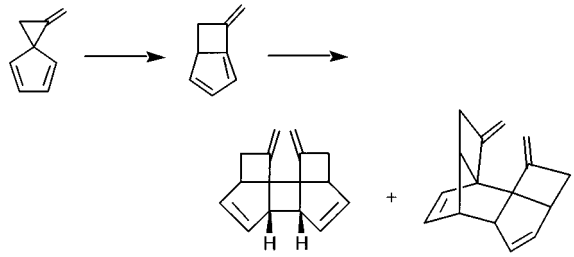
(19) Alternatively, dimerization might proceed via a Diels−Alder adduct proposed initially by Breslow and co-workers,[16] followed by a [1,3]-sigmatropic rearrangement within the norbornene framework of the bond marked by an asterisk.

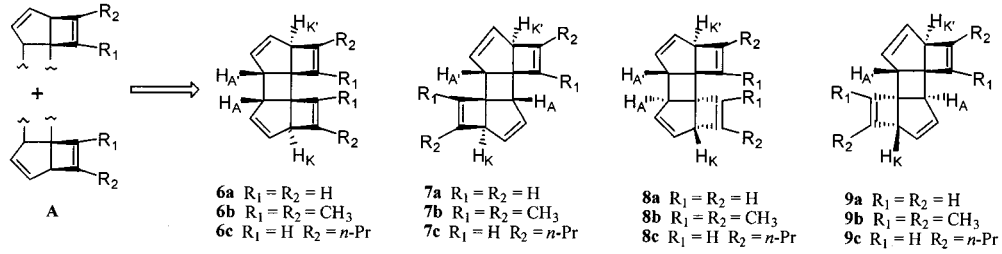


Note that after 1-methylenespiro[2.4]hepta-4,6-diene undergoes a bond-specific 1,5-sigmatropic rearrangement (migration of the allylic rather than the vinylic bond) to produce 7-methylenebicyclo[3.2.0]hepta-1,3-diene, this bicyclo analogue of **5** can undergo either [2 + 2]-dimerization at the strained bridgehead double bond to produce a derivative of **6a** or [2 + 4]-cycloaddition in a Diels−Alder fashion.[12b]



(20) High-energy isomers containing a trans fusion to a cyclobutane ring were not considered. Carbon multiplicities determined from DEPT spectra were incompatible with Diels−Alder dimerization[16] or another suggested isomer.[14]

Scheme 3



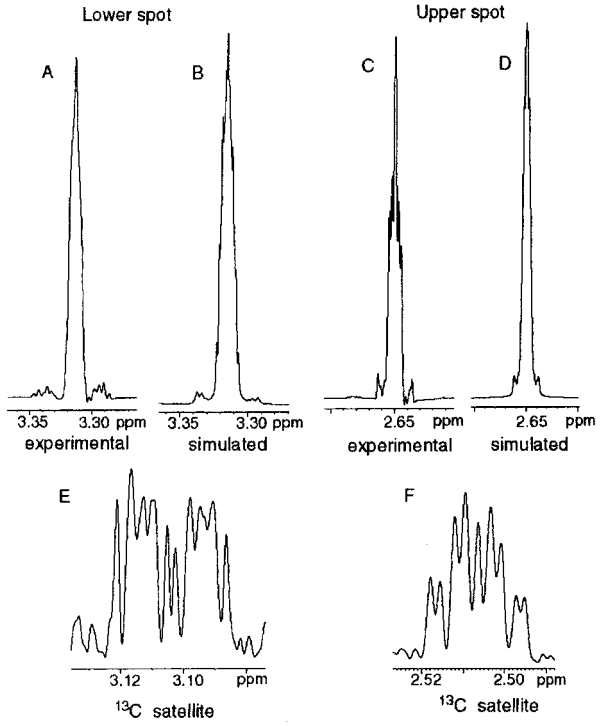


Figure 2. 500 MHz NMR spectra of the monoallylic methine resonances of the thermolysis products of **1b** (A and C) and their corresponding ^{13}C satellite signals (E and F). Analysis of the latter signals indicated approximate first-order coupling patterns of ddt (9.4, 3.7, 2.3 Hz) and dtd (4.4, 2.9, 1.2 Hz), respectively. These couplings were used to produce the simulated spectra (B and D).

the two dimers derived from reaction of **1b**. Analysis of these NMR results led to substructure **A** (see the Supporting Information), two units of which can be joined to produce isomers **6b**−**9b** (Scheme 3), analogous to isomers proposed previously.[14,15] However, correlating the NMR data for the two dimers with candidate structures **6b**−**9b** proved to be nontrivial.

Isomers **6b**−**9b** have C_s, C_2, C_2, and C_i symmetry, respectively. This symmetry interfered with the usual application of 2D NMR correlation methods for determining regiochemistry and of NOE difference methods for determining stereochemistry. One intriguing consequence of the symmetry was the highly second-order nature of the ^1H NMR signal for the monoallylic methine H_A (Figure 2). The second-order character resulted from H_A being coupled to its isochronous, symmetrical counterpart $H_{A'}$. This represents the only significant $^1H-^1H$ scalar coupling between the two equivalent halves of each dimer **6b**−**9b**. The magnitude of the coupling between these chemically equivalent protons was not readily extracted from the $H_A/H_{A'}$ resonance, but examination of the ^{13}C satellites showed, as expected,[21] first-order resonances for both dimers (Figure 2). The observed 9.4- and 4.4-Hz splittings, which did not appear in other resonances, were assigned as the H_A–$H_{A'}$ couplings in the two dimers.

Knowledge of the critical H_A–$H_{A'}$ coupling, together with NOE difference data and molecular modeling, provided tentative structure assignments of the two dimers. Geometries derived from molecular mechanics calculations[22] were used to predict spin couplings and interatomic distances in dimers **6b**−**9b** for correlation with the observed NMR data. The thermolysis product showing a 9.4-Hz coupling could correspond to either dimer in which H_A and $H_{A'}$ are vicinal (**6b** or **8b**), whereas the 4.4-Hz coupling is likely a four-bond coupling in **7b** or **9b**.[23] Candidate isomers **8b** and **9b** were tentatively ruled out for both isomeric products by the absence of any NOE between protons only 2.3 Å apart.[24] Other evidence also supports the tentative correlations of the lower TLC spot to **6b** and the upper spot to **7b**. For example, the chemical shifts of the methyl protons of **7b** and **9b** (but not **6b** and **8b**) would be expected to be nearly the same on the basis of their remoteness from atoms in the other half of the dimer. Also, in a study of dimers obtained from the benzo derivative of **5**, one of the products was found by X-ray crystallography to have a structure analogous to that of **6b**.[15]

(21) When H_A coupled to a ^{13}C nucleus is observed without ^{13}C decoupling, the H_A resonance appears as a doublet ($J_{CH} \sim 140$ Hz). Because each line of the H_A doublet lies ca. 70 Hz from $H_{A'}$ bonded to ^{12}C, $\Delta\nu/J_{HH}$ is large, and the strong coupling condition between H_A and $H_{A'}$ is lifted: Simova, S. *Magn. Reson. Chem.* **1998**, *36*, 505 and references therein.

(22) Calculations in PCMODEL using the MM3 and MMX force fields gave similar geometries and relative energies. Density functional theory calculations for one dimer (**7b**) at the B3LYP/3-21G* level indicated interatomic distances within ca. 5−10% of those measured on the MM3 geometry. MM3 and MMX calculations for **7b**, **8b**, and **9b** gave structures with C_2, C_2, and C_i symmetry. These isomers had heats of formation within 0.8 kcal/mol of each other. Because the cyclobutane ring is nonplanar, the calculated structure for **6b** failed to show C_s symmetry, and the somewhat elevated heat of formation was not considered meaningful.

(23) Predicted $H_A-H_{A'}$ couplings for **6b** and **8b** were 9.7 and 8.5 Hz, respectively, for the MM3 structures (or 10.5 and 7.1 Hz for the MMX structures). The observed 9.4-Hz coupling matches both MM3 values well but would be unusually large for a four-bond coupling. The 4.4-Hz coupling of the second dimer probably corresponds to an allylic or W-type four-bond coupling (**7b** or **9b**), whose magnitude depends on the extent of overlap by the rear lobes of the relevant C−H orbitals: (a) Smith, W. B.; Barfield, M. *Magn. Reson. Chem.* **1993**, *31*, 696. (b) Schaefer, T. Stereochemistry & Long-Range Coupling Constants. In *Encyclopedia of Nuclear Magnetic Resonance*; Grant, D. M., Harris, R. K., Eds.; 1996; Vol. 7, p 4571. Minor differences in the fit between the observed and simulated spectra in Figure 2 are attributable to our uncertainty about the sign of the long-range couplings and to the lack of any iterative optimization.

(24) The data in Tables S1 and S2 indicate reasonable correlations between NOE response and interatomic distances. The MM3 structure of **9b** shows that the monoallylic methine proton on one five-membered ring and the bis-allylic methine proton on the other five-membered ring are fixed in close proximity, and the MM3 structure of **8b** shows similarly close proximity for the bis-allylic methine and one of the methyl groups. However, no NOE was observed in either case. Further discussion is given in the Supporting Information.

Table 1. Comparison of ^{1}H and ^{13}C NMR Chemical Shifts for Methine Groups among thermolysis products of 1a (dihydro), 1b (dimethyl), and 1c (*n*-propyl)[a]

substituents	NMR chemical shifts (δ)			
	H_A	H_K	C_A	C_K
Lower TLC Spots				
dihydro (**6a**)	3.39	3.67	50.4	59.7
dimethyl (**6b**)	3.32	3.39	48.6	59.3
n-propyl (**6c**)	3.28	3.53	50.6	60.3
Upper TLC Spots				
dihydro (**7a**)	2.73	3.63	53.4	58.6
dimethyl (**7b**)	2.65	3.55	51.5	57.6
n-propyl (**7c**)	2.61	3.47	53.3	59.0

[a] Definitions of H_A, H_K, and their corresponding carbon atoms (C_A and C_K) are shown in Scheme 3, as are the location of dihydro ($R_1 = R_2 = H$), dimethyl ($R_1 = R_2 = Me$), and *n*-propyl ($R_1 = H$, $R_2 = n$-Pr) substituents.

Comparison of the NMR spectra of the thermolysis products of **1a**−**c** indicated distinctive patterns of chemical shifts (Table 1).[25] For example, in the chromatographically less mobile dimers, both methines resonated at δ 3.3−3.7, whereas the monoallylic methine was shifted upfield to ca. δ 2.6−2.7 in the more mobile dimer. These patterns indicate that the dimeric products from **1a** and **1c** have structures analogous to those from **1b**. Thus, the products of lower TLC mobility can tentatively be assigned as **6a**−**c** and those of higher mobility as **7a**−**c**.

In conclusion, the thermal rearrangements of spiro[2.4]hepta-1,4,6-trienes may be explained in terms of [1,5]-sigmatropic rearrangements to yield bicyclo[3.2.0]hepta-1,3,6-trienes, which then dimerize by formal cycloaddition across the strained bridgehead double bond. At the present level of understanding, neither free radical nor thermally forbidden concerted mechanisms account persuasively for the observed formation of only two of the four possible dimers. Finally, we note that at much higher temperatures, bicyclo[3.2.0]hepta-1,3,6-trienes can undergo gas-phase reactions other than dimerization.[9d,11,13] Studies on the direct observation of bicyclo[3.2.0]hepta-1,3,6-triene using low-temperature NMR spectroscopy are contemplated.

Experimental Section

Compounds are numbered under the assumption that **6a**−**c** and **7a**−**c** are the structures of the lower and upper TLC spots of the dimers from thermolysis. ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ [50−100 mM, 25 °C for **6b** and **7b** and referenced to Me_4Si, residual $CHCl_3$ (^{1}H, 7.26 ppm), or $CDCl_3$ (^{13}C, 77.0 ppm)]. NOE difference spectroscopy was done on nondegassed samples on the 500 MHz spectrometer with a 90° read pulse. PCMODEL (version 7, MMX and MM3 force fields) and Gaussian 98 were used to determine energies and geometries of the dimers. Vicinal ^{1}H NMR coupling constants were predicted in PCMODEL using a Karplus relationship applied to MM3 or Gaussian 98 structures. Spin simulation was done with Bruker Daisy software. Mass spectra (MS) were acquired at 70 eV on a sector instrument. High-resolution mass spectra were recorded using perfluorokerosene as the standard. Chemical reagents were used without further purification. Preparative gas chromatography was carried out using a thermal conductivity detector and a 2 m × 5 mm column (20% Carbowax 1450 on 80/100 Chromosorb W Acid Washed) using prepurified (99.999%) helium as the carrier gas. Column chromatography was performed using reagent-grade silica gel (230−400 mesh). All reactions were monitored by thin-layer chromatography (TLC) carried out on precoated silica gel 60 A plates (layer thickness 250 μm) with detection by UV light ($\lambda = 254$ nm) and iodine exposure. Purification by preparative TLC was carried out using 2 mm silica gel plates. Diazocyclopentadiene, prepared as described previously,[7] was vacuum distilled through a Vigreaux column, bp 52−53 °C/50 mm, and could be stored at −25 °C for several months.

Reaction of Diazocyclopentadiene with (2-Bromovinyl)trimethylsilane. A solution of diazocyclopentadiene (600 mg, 6.52 mmol) dissolved in commercially available (2-bromovinyl)trimethylsilane (10 mL) was purged with argon for 15 min. The solution was then irradiated for 2.5 h with a 450-W lamp in a quartz immersion apparatus (Pyrex filter). The temperature of the reaction mixture was kept at 0−5 °C. The excess (2-bromovinyl)trimethylsilane was removed and the black residue chromatographed quickly through a Florisil column using pentane as eluent. The solvent was removed under reduced pressure, and the crude mixture was separated by means of preparative gas chromatography (injector temperature, 180 °C; column temperature, 160 °C; detector temperature, 150 °C; carrier gas pressure, 120 kPa). The retention time was 4.6 min for **2** and 8.14 min for the coproduct identified as **3**. The desired adduct **2** was isolated as a colorless liquid (90 mg, 5.7%). Spectral data for *trans*-**2**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.51 (m, 2H), 6.34 (m, 1H), 6.12 (m, 1H), 3.85 (d, 1H, $J = 8.0$ Hz), 1.73 (d, 1H, $J = 8$ Hz), 0.09 (s, 9H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 139.04 (CH), 134.88 (CH), 131.60 (CH), 130.27 (CH), 46.23 (C), 30.12 (CH), 25.38 (CH), −1.19 (Me_3Si); HRMS (EI) *m/z* 244.0104, 242.0124, calcd for $C_{10}H_{15}{}^{81}BrSi$ 244.0106, calcd for $C_{10}H_{15}{}^{79}BrSi$ 242.0126. The corresponding signals of the cyclopropanyl protons $CHSiMe_3$ and CHBr of the cis isomer appear at δ 1.41 (d, $J = 10$ Hz) and 4.20 (d, $J = 10$ Hz). Spectral data for **3**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.98 (dd, AB system, 1H, $J = 11.1$, 4.6 Hz), 3.72 (t, 1H, $J = 11.1$ Hz), 3.49 (dd, AB system, 1H, $J = 11.1$, 4.6 Hz), 0.21 (s, 9H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 42.88 (CH), 36.48 (CH_2), −2.51 (Me_3Si); HRMS (CI) *m/z* 260.9124, 258.9166, calcd for $C_5H_{12}{}^{79}Br^{81}BrSi$ 260.9133, calcd for $C_5H_{12}{}^{79}Br_2Si$ 258.9154. Prolonged photolysis resulted in a higher yield of this product.

Preparation of Spiro[2.4]hepta-1,4,6-triene (1a). Dry CsF (225 mg, 1.48 mmol) was placed in a 50-mL two-neck round-bottom flask connected to a series of three cold traps maintained at −45 °C and liquid nitrogen temperature. The system was then evacuated so that the vacuum reached ∼10 mTorr. Dry dimethyl sulfoxide (5 mL) was added to the flask via a syringe, followed by a solution of **2** (120 mg, 0.49 mmol) in DMSO (5 mL). The volatile products were condensed into the liquid nitrogen trap over a period of 30 min. The triene was condensed as a slightly yellowish solid (30 mg, 68%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (s, 2H), 6.57 (m, 2H), 6.09 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.51 (CH), 131.06 (CH), 117.95 (CH), 40.07 (C); IR 1718 cm^{-1} (cyclopropenyl stretching); UV (MeOH) λ_{max} 254 nm.

Thermolysis of Spiro[2.4]hepta-1,4,6-triene (1a). The spirene was heated in an NMR tube at 50 °C for 8 h as the reaction was monitored by ^{1}H NMR spectroscopy. Two isomeric dimers, corresponding to a 2:3 mixture of faster and slower moving components (**7a** and **6a**), were isolated by preparative TLC (hexane) in 80% combined yield and characterized by ^{1}H and ^{13}C NMR (Table S3 and Figures S9 and S10 of the Supporting Information). ^{1}H NMR spectra (recorded in $CDCl_3$) for the dimers showed that they are identical to the dimers of bicyclo[3.2.0]hepta-1,3,6-triene **5** reported earlier by Bauld et al.[14]

Preparation of 1,2-Dimethylspiro[2.4]hepta-1,4,6-triene (1b).[8] A solution of diazocyclopentadiene (1 g, 0.0109 mol) in 2-butyne (30 mL) was cooled to 0 °C in a Pyrex tube and purged with argon for 15 min. The contents of the tube were irradiated at 0 °C for 2 h using a 450-W lamp in a quartz immersion apparatus (Diaza filter, $\lambda = 366$ nm). During this time, 90% of the theoretical amount of nitrogen was evolved. The excess 2-butyne was removed in vacuo, and the black crude product was passed through a silica gel column using dichloromethane/pentane (30:70) as eluent. Evaporation of the

(25) Table S3 of the Supporting Information shows a full comparison of ^{1}H and ^{13}C NMR chemical shifts for the six dimeric products.

solvent afforded the triene as a pale yellow liquid (625 mg, 45%): ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.54 (m, 2H), 6.10 (m, 2H), 2.14 (s, 6H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 139.57 (CH), 129.46 (CH), 114.45 (C), 48.81 (C), 11.48 (Me); HRMS (EI) *m/z* 118.0780, calcd for C_9H_{10} 118.0782.

Thermolysis of 1,2-Dimethylspiro[2.4]hepta-1,4,6-triene (1b). A solution of the spirene (200 mg, 1.56 mmol) in chloroform (2 mL) was heated in an oil bath at 50 °C for 1 h. Monitoring of the reaction by TLC indicated a 3:2 mixture of upper and lower spots. Preparative TLC (hexane) afforded two isomeric dimers **7b** and **6b** (3:2 ratio) in 82% total yield. Spectral properties of **7b**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.98 (m, 2H), 5.90 (m, 2H), 3.55 (m, 2H), 2.65 (m, 2H), 1.64 (m, 12H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 145.64 (C), 138.62 (C), 136.23 (CH), 133.96 (CH), 62.15 (C), 57.66 (CH), 51.55 (CH), 12.02 (Me), 11.34 (Me); EI MS *m/z* 236 ([M]$^+$), 221 ([M − Me]$^+$), 206 ([M − 2Me]$^+$), 191 ([M − 3Me]$^+$); HRMS (EI) *m/z* 236.1567, calcd for $C_{18}H_{20}$ 236.1565. Spectral properties of **6b**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.97 (m, 2H), 5.69 (m, 2H), 3.39 (m, 2H), 3.32 (m, 2H), 1.72 (m, 6H), 1.58 (m, 6H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 145.01 (C), 139.52 (C), 135.17 (CH), 135.04 (CH), 61.26 (C), 59.30 (CH), 48.59 (CH), 12.18 (Me), 11.40 (Me); EI MS *m/z* 236 ([M]$^+$), 221 ([M − Me]$^+$), 206 ([M − 2Me]$^+$), 191 ([M − 3Me]$^+$); HRMS (EI) *m/z* 236.1565, calcd for $C_{18}H_{20}$ 236.1565.

Preparation of 1-*n*-Propylspiro[2.4]hepta-1,4,6-triene (1c). The spirene was synthesized from diazocyclopentadiene and 1-pentyne as described above for 1,2-dimethylspiro[2.4]-hepta-1,4,6-triene. The crude product was passed through a column of silica gel followed by vacuum distillation at 45 °C to afford **1c** (yellow liquid) in 55% yield: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.16 (t, 1H, J = 1.2 Hz), 6.55 (m, 2H), 6.11 (m, 2H), 2.58 (dt, 2H, J = 7.3, 1.2 Hz), 1.54 (sextet, 2H, J = 7.3 Hz), 0.94 (t, 3H, J = 7.3 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 140.76 (CH), 130.25 (C), 130.00 (CH), 105.90 (CH), 41.16 (C), 28.65 (CH_2), 20.72 (CH_2), 13.46 (Me); MS (EI) *m/z* 132 ([M]$^+$), 117 ([M − Me]$^+$), 103 ([M − Et]$^+$); HRMS (EI) *m/z* 132.0937, calcd for $C_{10}H_{12}$ 132.0939.

Thermolysis of 1-*n*-Propylspiro[2.4]hepta-1,4,6-triene (1c). A solution of the spirene (200 mg, 1.51 mmol) in chloroform (2 mL) was heated in an oil bath at 50 °C for 1 h. Monitoring of the reaction by TLC indicated two components in a 3:2 ratio of upper and lower spots. Preparative TLC (hexane) afforded individual isomeric dimers **7c** and **6c** (3:2 ratio) in 84% combined yield. Spectral data for **7c**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.91 (m, 4H), 5.80 (s, 2H), 3.47 (m, 2H), 2.61 (m, 2H), 2.05 (dt, 4H, J = 7.4, 1.0 Hz), 1.46 (sextet, 4H, J = 7.4 Hz), 0.91 (t, 6H, J = 7.4 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 159.69 (C), 136.40 (CH), 133.65 (CH), 128.32 (CH), 59.81 (C), 58.95 (CH), 53.28 (CH), 32.15 (CH_2), 20.20 (CH_2), 14.02 (Me); EI MS *m/z* 264 ([M]$^+$), 235 ([M − Et]$^+$), 221 ([M − Pr]$^+$); HRMS (EI) *m/z* 264.1875, calcd for $C_{20}H_{24}$ 264.1878. Spectral data for **6c**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.95 (m, 2H), 5.91 (m, 2H), 5.69 (m, 2H), 3.53 (m, 2H), 3.28 (m, 2H), 1.99 (t, 4H, J = 7.3 Hz), 1.43 (sextet, 4H, J = 7.3 Hz), 0.89 (t, 6H, J = 7.3 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 158.21 (C), 135.43 (CH), 134.55 (CH), 129.99 (CH), 60.28 (CH), 58.54 (C), 50.62 (CH), 32.18 (CH_2), 20.23 (CH_2), 14.05 (Me); MS (EI) *m/z* 264 ([M]$^+$), 249 ([M − Me]$^+$), 235 ([M − Et]$^+$), 221 ([M − Pr]$^+$); HRMS (EI) *m/z* 264.1876, calcd for $C_{20}H_{24}$ 264.1878.

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Supporting Information Available: Further information documenting the structure elucidation of dimers from thermolysis of **1a**−**c**, including tables and figures of NMR and mass spectral data for compounds **6a**−**c**, **7a**−**c**, and their synthetic precursors. This material is available free of charge via the Internet at http://pubs.acs.org.

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