Synthesis of Substituted Bicyclo[2.2.2]octatrienes

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An efficient route to bicyclo[2.2.2]octatriene, barrelene, and substituted versions of this molecule has been developed starting from the benzene equivalent *cis*-3,5-cyclohexadiene-1,2-diol. Following the Diels−Alder reaction of this molecule with an activated acetylene, conversion of the diol to the final olefin was accomplished through formation of a thiocarbonate intermediate and subsequent reaction with 1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine (DPD). The synthesis developed allows a variety of barrelenes to be prepared in as few as three steps from commercially available starting materials.

Introduction

Since the synthesis of bicyclo[2.2.2]octatriene, barrelene, was first reported by Zimmerman,[1,2] there has been considerable interest in the synthesis and study of this compound and its derivatives.[3] Several syntheses of barrelene have been subsequently reported that allow this compound to be prepared by shorter routes than the original procedure.[4−10] These routes have generally not been applied to the synthesis of substituted barrelenes, however. Conversely, methods employed for the synthesis of substituted barrelenes[11−20] have generally not been applied to the synthesis of unsubstituted barrelene.[21] One reason for this is that barrelenes such as dicyano- and bis(trifluoromethyl)barrelene are synthesized by the Diels−Alder reaction of highly activated acetylenes, dicyanoacetylene and hexafluoro-2-butyne, with benzene.[11−13,15] This same procedure has not been used to prepare unsubstituted barrelene since acetylene is not sufficiently activated to undergo an efficient Diels−Alder reaction with benzene. In fact, while dicyanobarrelene[15] is obtained in 63% yield by this procedure, bis(trifluoromethyl)barrelene[11−13] is produced in yields of only 8−10%.[22] Following this trend further, Diels−Alder addition of the less activated, diester-substituted acetylenes to benzene produces barrelene products only when the benzene derivative employed is also activated.[20,23,24]

Barrelene

Recently, we reported the synthesis of 2,3-diester-substituted barrelenes and the ring-opening metathesis polymerization (ROMP) of these molecules.[25] We now report that the synthesis developed for those barrelenes can be extended to the synthesis of unsubstituted barrelene and other disubstituted barrelenes. Since benzene is a poor diene for most dienophiles, we employed *cis*-3,5-cyclohexadiene-1,2-diol, or a protected form of this molecule, as a benzene equivalent. The route developed allows the preparation of a variety of barrelenes in as few as three steps from commercially available starting materials.

Results and Discussion

All syntheses were carried out in a similar manner with the Diels−Alder addition of an acetylene bearing electron-withdrawing groups to the benzene equivalent *cis*-3,5-cyclohexadiene-1,2-diol, **1**, or the acetonide-protected form of this molecule, **9**. The barrelenes were then obtained by conversion of the diol to the olefin. In cases where protection of the diol was not necessary, the Diels−Alder reaction was followed by conversion of the diol, **3**, to the thiocarbonate, **4**, using (thiocarbonyl)diimidazole (TCDI) as shown in Scheme 1. Conversion of **4** to barrelene was then accomplished using 1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine (DPD).[26,27] In the case

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(21) Reference 17 descibes a procedue for the synthesis of unsubstituted barrelene and substituted barrelenes in 3−8% yield. The procedure described in ref 18 allows the synthesis of ether-substituted barrelene by a route similar to that used for the synthesis of unsubstituted barrelene from bicyclo[2.2.2]oct-7-ene-2,5-dione.[6,7,8,10]
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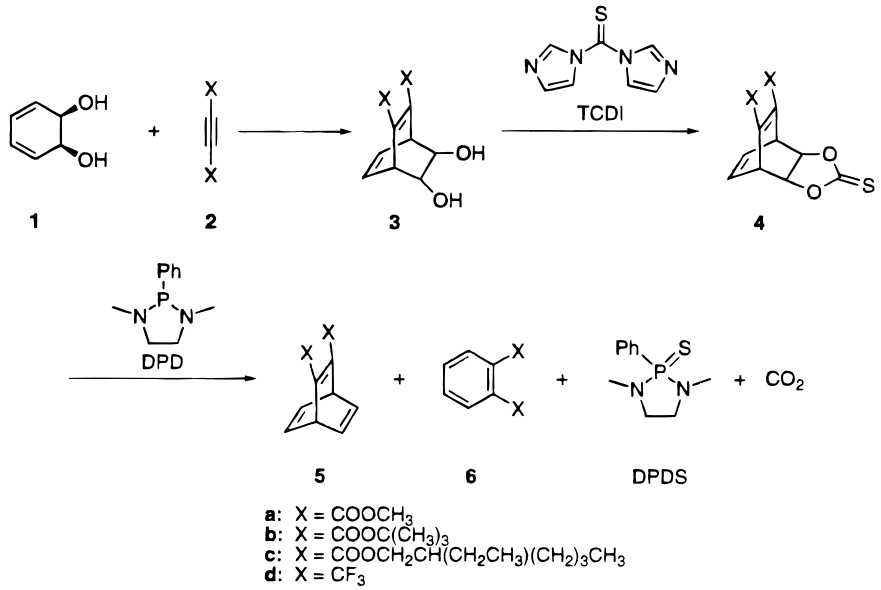
Scheme 1



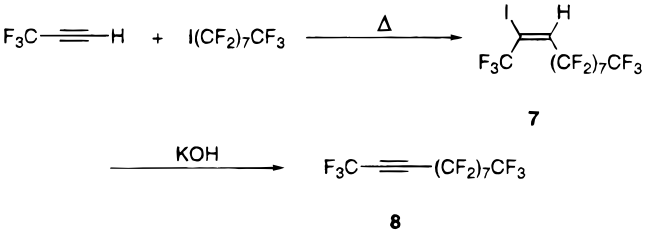
a: X = $COOCH_3$
b: X = $COOC(CH_3)_3$
c: X = $COOCH_2CH(CH_2CH_3)(CH_2)_3CH_3$
d: X = CF_3

of **5d**, the product is volatile and can be obtained in pure form by vacuum transferring it out of the reaction mixture. Purification of **5a**−**c** can be accomplished by column chromatography or by a combination of column chromatography and recrystallization.[25,27]

Other methods to generate the final double bond either directly from the diol[28,29] or by base-initiated thermal fragmentation of the benzaldehyde acetal as previously reported for benzobarrelene[30,31] failed. Fragmentation of the acetal using KDA led to complete decomposition of the starting material, and as previously observed for the synthesis of benzobarrelene, no reaction occurred when LDA was employed. In the case of direct reduction of the diol, only decomposition was observed when Ti^0 reagents were employed,[29] and the method reported by Barua et al.[28] produced only recovered starting material. An attempt to convert **4d** to **5d** using $Ni(COD)_2$[32] resulted in complete consumption of the starting material but yielded none of the desired product.

While the synthesis of **3a**−**d** was readily accomplished by direct reaction of an activated acetylene, **2**, with the unprotected diol, **1**, the synthesis of several other barrelenes was greatly improved by using a protected form of the diol, **9**. Using the acetonide has the dual advantage of protecting the diol from acid-catalyzed decomposition to phenol and also activating the diene so that less reactive dienophiles react more efficiently.[33−35] Protection of the diol by thiocarbonate was also attempted, but rapid exothermic decomposition occurred when either TCDI or thiophosgene[27] was employed.

Scheme 2



7

8

To prepare a barrelene bearing a perfluorooctyl chain, the acetylene, **8**,[36−38] was first synthesized as shown in Scheme 2, and this was then reacted with the acetal, **9**, as shown in Scheme 3. Use of **9** yielded the Diels−Alder adduct, **10**, in near-quantitative yield in contrast to the reaction with **1**, which resulted in decomposition to phenol, presumably due to the presence of residual hydrofluoric acid in **8**.[39] The acetonide protecting group was then removed under acidic conditions to yield the diol, **11**, in quantitative yield. To optimize the ease of performing and purifying this reaction and minimize reaction time, several deprotection methods were tested. The fastest conversion was achieved using the dimethyl acetal, **10a**, and a 1:1 mixture of 6 M HCl and dioxane. These conditions work well since the acetone generated boils off quickly, thus driving the reaction toward products. Methanol and pyridinium *p*-toluenesulfonate gave **11** in good yields, but these conditions required longer reaction times and periodic replenishment of methanol, which boiled off with the 2,2-dimethoxypropane produced. Deprotection of the benzaldehyde acetal, **10b**, required much longer reaction times since the benzaldehyde or benzaldehyde dimethyl acetal produced is much less volatile than the products of deprotection of **10a**. After the deprotection was complete, **11** was converted to barrelene **13** through the thiocarbonate, **12**.

Synthesis of unsubstituted barrelene and octylbarrelene also required use of the protected diol, **9a**. The

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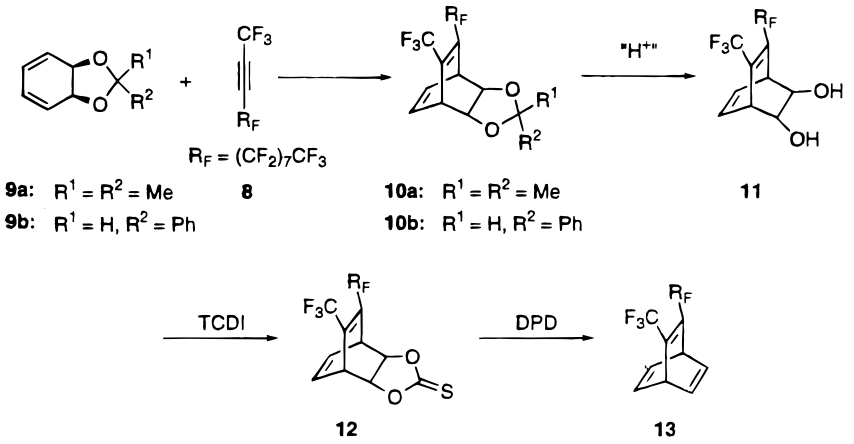
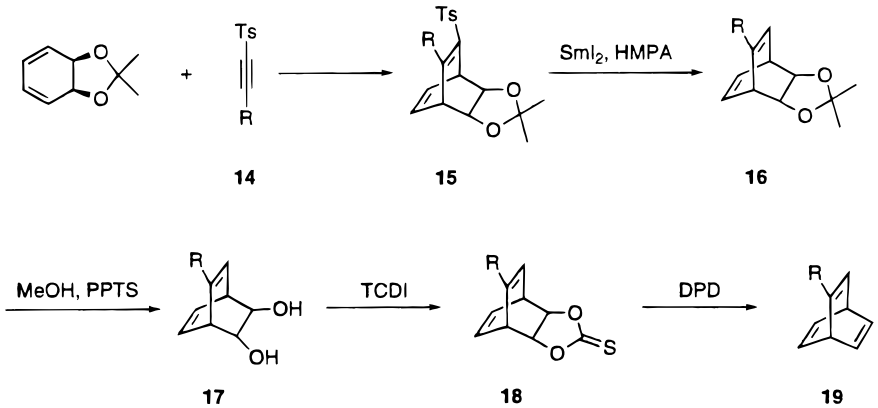
(39) Further evidence for hydrofluoric acid present in compound **8**, which is a liquid, was the ability of the neat liquid to etch glass when left in contact for extended periods. Because the acetonide, **9a**, is deprotected by acid, the success of the reaction of **8** with **9a** probably also relies on the fact that this Diels−Alder reaction is much faster than the reaction of **8** with **1**.

Scheme 3



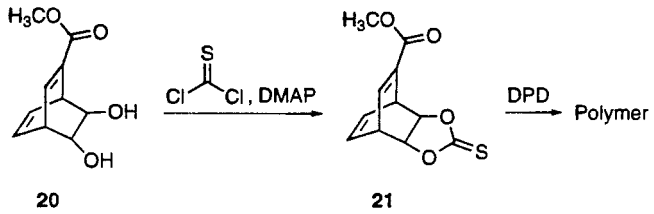
Scheme 4



acetylenes **14a**,**b**,[40,41] activated by a *p*-toluenesulfone group, underwent the Diels−Alder reaction with **9a** as shown in Scheme 4. After the *p*-toluenesulfone group was removed by reductive desulfonylation,[42] the diol was deprotected under acidic conditions as before, but in this case methanol and pyridinium *p*-toluenesulfonate were employed since the use of HCl resulted in decomposition. Using methanol was also an advantage since **17a** is rather soluble in water and is difficult to extract from the aqueous HCl. Formation of the final olefin bond was accomplished as previously described.

Attempts to synthesize a monoester-substituted barrelene by this route did not succeed. Starting from **9a** and methyl propiolate, the diol, **20**, was prepared by using the same procedure as for **17**. This intermediate, which was more heat sensitive than the other diols, was converted into the thiocarbonate, **21**, using thiophosgene and DMAP at 0 °C as shown in Scheme 5. Reaction of **21** with DPD under the same conditions employed for the other thiocarbonates produced only polymeric products, presumably by reaction of the acrylate functionality.

Scheme 5



Conclusions

The synthesis presented here affords an efficient route to several substituted barrelenes in as few as three steps from commercially available starting materials, as well as a route to unsubstituted barrelene. Reaction of activated acetylenes with *cis*-3,5-cyclohexadiene-1,2-diol or a protected form of this benzene equivalent generally afforded the Diels−Alder adduct in high yield. This intermediate was then converted to barrelene by formation of the thiocarbonate followed by elimination of this moiety to yield the final olefin bond.

In addition to the barrelenes synthesized here, the route presented should allow the preparation of other related barrelenes and benzobarrelenes by using other dienophiles and/or any of the wide variety of substituted benzene equivalents similar to **1**.[43] We are currently exploring this possibility as well as the ring-opening metathesis polymerization of the compounds reported here.

Experimental Section

General Procedures. NMR spectra were recorded on a QE Plus-300 MHz (300.1 MHz ^{1}H; 75.49 MHz ^{13}C) spectrometer or a JEOL JNM-GX400 (399.78 MHz ^{1}H, 100.53 MHz ^{13}C,

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376.14 MHz ^{19}F) spectrometer as noted. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). Elemental analyses were performed by Caltech Analytical Labs or Mid-West Microlab. High-resolution mass spectra were obtained from UC Riverside Mass Spectrometry Facility.

Materials. THF and toluene were dried by passing through activated alumina columns. Acetylenes **2c**[44] and **14a**,**b**[40,41] and protected diols **9a**,**b**[30,31,35] were prepared according to literature procedures. Hexamethylphosphoramide (HMPA) was purchased from Aldrich and dried over calcium hydride and then distilled under reduced pressure prior to use. 3,3,3-Trifluoropropyne was purchased from PCR Inc. *cis*-3,5-Cyclohexadiene-1,2-diol was obtained from ICI. (Thiocarbonyl)diimidazole (TCDI), 1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine (DPD), 2,2-dimethoxypropane, perfluorooctyliodide, pyridinium *p*-toluenesulfonate (PPTS), methyl propiolate, 2-ethylhexanol, acetylenedicarboxylic acid, hexafluoro-2-butyne, and SmI_2 in THF were purchased from Aldrich and used without further purification except where noted otherwise. Compounds **3a**,**b**−**5a**,**b** were prepared as previously reported.[25]

Bis(2-ethylhexyl) 2,3-Dihydroxy-5,7-bicyclo[2.2.2]octa-5,7-diene-5,6-dicarboxylate (3c). A 100 mL round-bottom flask was charged with 10.43 g (30.81 mmol) of 2-ethylhexyl acetylenedicarboxylate and 15.00 g (150 mmol) of $CaCO_3$. After the mixture was stirred for 30 min under a flow of argon, 1.73 g (15.43 mmol) of *cis*-3,5-cyclohexadiene-1,2-diol and 2.13 mL of dry THF were added to the flask. The reaction was heated at 60 °C for 3 days and then filtered to remove $CaCO_3$. After the $CaCO_3$ was rinsed with $CHCl_3$, the solvent was removed under vacuum to yield a yellow oil. The yellow oil was loaded onto a column of silica gel and eluted with 10% ethyl acetate/hexane. Following removal of solvent, 5.03 g (11.16 mmol, 71.20%) of a mixture of syn and anti product isomers was obtained as a yellow oil. Note: Calcium carbonate was added to this reaction to decrease formation of phenol: ^{1}H NMR (300 MHz, C_6D_6) anti δ 6.21 (m, 2H), syn δ 5.72 (dd, J = 4.2, 3.3 Hz, 2H), 4.21 (m, 2H) 4.19−4.02 (m, 6H), 3.73 (bs, 2H), 2.37 (bs, 2H), 1.53 (m, 2H), 1.40−1.02 (m, 16H) 0.89−0.79 (m, 12H); ^{13}C NMR (75 MHz, C_6D_6) anti δ 166.1, 141.0, 132.3, 68.5, 67.8, 47.9, 39.5, 31.1, 29.6, 24.5, 23.7, 14.6, 11.5; syn δ 167.35, 140.3, 132.4, 68.3, 67.2, 47.3, 39.5, 31.1, 29.6, 24.5, 23.7, 14.6, 11.5; HRMS calcd for $C_{26}H_{42}O_6$ $(M + H)^+$ 451.30594, found 451.3070. Anal. Calcd for $C_{26}H_{42}O_6$: C, 69.30; H, 9.39. Found: C, 68.91; H, 9.34.

Bis(2-ethylhexyl) 2,3-(Thiomethylenedioxy)-5,7-bicyclo-[2.2.2]octa-5,7-diene-5,6-dicarboxylate (4c). Compound **3c** (3.98 g, 8.84 mmol) and 1.93 g (90% pure, 9.72 mmol) of (thiocarbonyl)diimidazole (TCDI) were loaded into a 50 mL flask purged with argon. Dry toluene (30 mL) was added to yield a solution containing undissolved TCDI. The solution was heated in an oil bath, which had been preheated to 135 °C, for 20 min. An additional 0.913 g of TCDI was loaded into the flask and the reaction was heated for 15 min. After cooling to room temperature, the yellow solution was poured onto a plug of silica gel and eluted with 50% ethyl acetate/hexane. Removal of solvent under vacuum yielded 4.01 g (8.15 mmol, 92.12%) of **4c** as a yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) anti δ 6.55 (dd, J = 4.2, 3.3 Hz, 2H), 5.00 (m, 2H), 4.55 (m, 2H), 4.12 (m, 4H), 1.60 (m, 2H), 1.4−1.29 (m, 16H), 0.90 (t, J = 7.2, 12H); syn δ 6.40 (dd, J = 4.5, 3.0 Hz, 2H), 4.91 (m, 2H), 4.55 (m, 2H), 4.14 (m, 4H), 1.64 (m, 2H), 1.46−1.23 (m, 16H), 0.90 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) anti δ 191.5, 164.3, 139.4, 131.3 81.4, 69.1, 43.0, 38.9, 30.8, 29.1, 24.0, 23.9, 14.3, 11.1; syn δ 191.6, 165.5, 139.6, 132.4, 80.7, 68.5, 43.4, 39.6, 31.0, 29.7, 24.4, 23.8, 14.6, 11.6; HRMS calcd for $C_{27}H_{40}O_6S$ $(M + H)^+$ 493.2624, found 493.2620. Anal. Calcd for $C_{27}H_{40}O_6S$: C, 65.82; H, 8.18. Found: C, 65.87; H, 8.21.

Bis(2-ethylhexyl) Bicyclo[2.2.2]octa-2,5,7-triene-2,3-dicarboxylate (5c). A 50 mL round-bottom flask was charged with 4.013 g (8.15 mmol) of compound **4c** and 4.50 mL of 1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine (DPD) to yield a brown mixture. The mixture was heated under argon in an oil bath at 40 °C for 7 days. The brown solution was then loaded onto a silica gel column and eluted with 10% ethyl acetate/hexane. After evaporation of solvent, 1.78 g (4.27 mmol, 52.5%) of the product was obtained as a yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.87 (m, 4H), 5.08 (m, 2H), 4.06 (dd, J = 6.0, 3.0 Hz, 4H), 1.59 (m, 2H), 1.39−1.28 (m, 16H), 0.88 (m, 12H); ^{13}C NMR (75 MHz, C_6D_6) δ 167.5, 149.7, 140.9, 68.2, 50.7, 39.5, 31.1, 29.6, 24.5, 23.7, 14.6, 11.5; HRMS calcd for $C_{26}H_{40}O_4$ M^+ 416.2926, found 416.2920. Anal. Calcd for $C_{26}H_{40}O_4$: C, 74.95; H, 9.68. Found: C, 74.87; H, 9.86.

5,6-Bis(trifluoromethyl)bicyclo[2.2.2]octa-5,7-diene-2,3-diol (3d). A Fischer−Porter bottle was charged with 9.16 g of *cis*-3,5-cyclohexadiene-1,2-diol (81.7 mmol) and purged with argon. Dry THF (40 mL) was then added to yield a colorless solution. The flask was then closed and pressurized to 65 psi with hexafluoro-2-butyne. As the pressure slowly decreased, more gas was admitted to maintain the initial pressure. After 1 week, the pressure was released, and solvent was removed by rotary evaporator to yield the product as 21 g (76.6 mmol, 94%) of a white solid. The crude product, which appeared clean by ^{1}H NMR, was used in the next reaction without further purification: ^{1}H NMR (300 MHz, $CDCl_3$) anti δ 6.50 (m, 2 H), 4.23 (br s, 2 H), 3.87 (br s, 2 H), 2.65 (br s 2 H); syn δ 6.32 (m, 2 H), 4.21 (m 2 H), 3.85 (br s, 2 H), 3.15 (br s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) anti δ 139.95m, 131.46, 120.94 (q, J = 275.47 Hz), 66.45, 45.19; syn δ 137.14m, 131.91, 121.22 (q, J = 272.60 Hz), 65.75, 45.03; ^{19}F NMR (376 MHz, $CDCl_3$) anti δ −61.49 s; syn δ −61.24 s; HRMS calcd for $C_{10}H_{12}F_6NO_2$ $(M + NH_4^+)$ 292.0769, found 292.0775. Anal. Calcd for $C_9H_{12}F_6O_2$: C, 43.81; H, 2.94; F, 41.58. Found: C, 44.03; H, 3.07; F, 41.75.

5,6-Bis(trifluoromethyl)bicyclo[2.2.2]octa-5,7-diene-2,3-thiocarbonate (4d). 3d (10.01 g, 36.5 mmol) and 7.53 g (90% pure, 38.0 mmol) of TCDI were put in a 500 mL round-bottom flask, and 150 mL of dry toluene was added. The flask was then put in an oil bath preheated to 130 °C. After 30 min, the reaction was cooled to rt and poured into a separatory funnel containing 10 mL of 1 M HCl. The aqueous layer was extracted with 3 × 100 mL ether. All organic layers were combined and dried over magnesium sulfate. After removal of solvent under vacuum, the product was obtained as a brown solid. This was dissolved in 100 mL of ethyl acetate, and 50 g of silica gel was added. Following evaporation of the solvent under vacuum, the free-flowing solid was loaded onto a column containing 750 g of silica gel and eluted with 20% ethyl acetate/hexane and then 50% ethyl acetate/hexane. The product was obtained as two isomers (total = 9.91 g, 31.33 mmol, 86%). The major isomer, anti (identified by comparison to similar previously characterized compounds[25]), was a white powder, and the minor isomer, syn, was a slightly yellow crystalline solid: ^{1}H NMR (300 MHz, $CDCl_3$) anti δ 6.61 (m, 2H), 4.98 (m, 2H), 4.61 (m, 2H); syn δ 6.50 (m, 2H), 4.97 (br s, 2H), 4.64 (m, 2H); ^{13}C (75 MHz, $CDCl_3$) anti δ 190.57, 137.28 m, 131.12, 120.17 (q, J = 272.1 Hz), 80.26, 41.631; syn δ 190.24, 137.01 m, 132.09, 120.36 (q, J = 273.95 Hz), 79.86, 41.54; ^{19}F NMR (376 MHz, $CDCl_3$) anti δ −61.47 s; syn δ −61.22 s; HRMS calcd for $C_{11}H_6F_6O_2S$ 315.99673, found 315.9985. Anal. Calcd for $C_{11}H_6F_6O_2S$: C, 41.78; H, 1.91, F, 36.05. Found: C, 41.82; H, 1.96; F, 36.13.

2,3-Bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5,7-triene (5d). A 450 mL Schlenk flask was loaded with 4.336 g (13.7 mmol) of **4d** and evacuated and then backfilled with argon three times. Next, 7.81 mL (97% pure, 41.1 mmol) of DPD, which was pumped down to 60 mTorr to remove volatile components, was added. This yielded a wet mixture, but most of the solid did not dissolve. The reaction was heated in an oil bath at 45 °C for 3 days. The flask was vented periodically to allow CO_2 formed by the reaction to escape. After being cooled to rt, the product was vacuum transferred out of the reaction mixture into a Schlenk flask in liquid nitrogen. A second vacuum transfer yielded 2.078 g (8.65 mmol, 63%) of the desired product as a clear colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.90 (m, 4 H), 5.092 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.18 m, 139.85, 122.07 (q, J = 272.07 Hz), 47.92; ^{19}F NMR (376 MHz, $CDCl_3$) δ −61.73 s; HRMS calcd

(44) Jeffery, G. H.; Vogel, A. I. *J. Chem. Soc.* **1948**, 674. Acetylene **2c** was purified on silica gel (10% ethyl acetate/hexane) rather than by distillation.

for $C_{10}H_6F_6$ 240.0372, found 240.0381. Anal. Calcd for $C_{10}H_6F_6$: C, 50.02; H, 2.52; F, 47.47. Found: C, 49.89; H, 2.48; F, 47.21.

1-Iodo-1-(trifluoromethyl)-2-(perfluorooctyl)ethylene (7). Under argon, 23.75 g (43.5 mmol) of perfluorooctyl iodide was loaded into a steel bomb, and the bomb was then sealed and cooled to −78 °C. Approximately 4.8 g (51.0 mmol) of trifluoropropyne was condensed into the reaction vessel, which was then sealed and warmed to rt; the pressure increased to 100 psi. The reaction was then heated for 24 h at 210 °C. The pressure initially increased to ∼250 psi and then gradually decreased to <150 psi. After the reaction was allowed to cool to room temperature, the pressure was released and the product mixture was seen to be a reddish-purple liquid with some white precipitate. Distillation of two combined reactions at 86 °C/14 Torr yielded 43.79 g of product as a clear colorless liquid. ^{19}F NMR revealed this liquid to be 96% pure with some perfluorooctyl iodide impurity. Redistillation of this mixture at 94 °C/19 Torr yielded 37.9 g (59.2 mmol, 65%) of pure **7**: ^{1}H NMR (300 MHz, $CDCl_3$) δ major 7.15 (t, J = 12.3 Hz); minor 6.893 (t, J = 14.6 Hz); ^{19}F (376 MHz, $CDCl_3$) δ −66.89 (s, 3F), −80.91 (t J = 9.2 Hz, 3F), −111.06 (d J = 11.4 Hz, 2F), −121.57 (s, 2F), −121.96 (br s, 4F), −122.89 (br s, 4F), −126.23 (s, 2F); HRMS calcd for $C_{11}HF_{20}I$ 639.8803, found 639.8787. Anal. Calcd for $C_{11}HF_{20}I$: C, 20.58; H, 0.16; F, 59.18. Found: C, 20.32; H, 0.15; F, 59.32.

Perfluoro-2-undecyne (8). Inside a nitrogen-filled drybox, 17 g (88% pure, 267 mmol) of powdered KOH was loaded into a 250 mL round-bottom flask. Outside the box, under argon, 38 g (59 mmol) of **7** was added to the KOH to produce a slightly yellow slurry. A 15 cm Vigreux column and short-path distillation condenser were placed on the flask, and the pressure was reduced to 30 Torr. The flask was put in an oil bath at 67 °C, and then the temperature of the bath was raised to 90 °C over 10 min. When the temperature reached 85 °C the reaction began to reflux, and at 90 °C the reaction began refluxing vigorously and the distillation temperature was 76 °C. Redistillation of the mixture that collected in the receiver flask yielded 13.19 g (25.8 mmol, 44%) of the desired product and 8.3 g of recovered **7**: ^{13}C (100 MHz, neat w/C_6D_6 tube to lock) 121.82 (t J = 36.0 Hz), 118.96 (t J = 32.9 Hz), 116.11 (t J = 32.9 Hz), 114.45−106.00 m, 104.35 (t J = 33.3 Hz), 76.88 (q J = 56.7 Hz), 71.29 (t J = 38.5 Hz); ^{19}F NMR (376 MHz neat w/C_6D_6 tube to lock) −55.66 (s, 3F), −83.05 (t J = 10.3 Hz, 3F), −103.72 (s, 2F), −122.44 (s, 2F), −123.16 (br s, 4F), −123.83 (s, 2F), −124.08 (s, 2F), −127.80 (s, 2F); HRMS calcd for $C_{11}F_{20}$ 511.9680, found 511.9667. Anal. Calcd for $C_{11}F_{20}$: C, 25.80; F, 74.20. Found: C, 24.95; F, 74.22. The high level of fluorine in this compound reportedly interfered with the carbon determination, thus producing the low carbon value found. **Caution**: The reaction can become extremely rapid and explode. Best results were obtained with the pressure reported. Using higher pressures to try to improve the reaction yield usually resulted in an explosion. Use necessary precautions.

5-(Perfluorooctyl)-6-(trifluoromethyl)-5,7-bicyclo[2.2.2]-octa-5,7-diene 2,3-Dimethyl Acetal (10a). Under argon, 18.72 g (36.5 mmol) of compound **8** and 5.56 g (34.9 mmol) of **9a** were loaded into a 100 mL round-bottom flask, and 13 mL of dry THF was added to yield two clear liquid phases. The reaction vessel was sealed with a Kontes valve and heated at 45 °C overnight. The reaction, which was now one clear colorless phase, was then cooled to room temperature, and solvent was removed to yield **10a** as a slightly cloudy liquid in quantitative yield. ^{1}H NMR showed clean product with mainly one isomer. This crude material was used in the next reaction without further purification: ^{1}H NMR (300 Hz, $CDCl_3$) δ 6.42 (m, 2H), 4.38−4.30 (m, 3H), 4.24 (br m, 2H) 1.33 (s, 3H), 1.27 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −61.08 (m, 3F), −80.70 (s, 3F), −108.54 (dd J = 102.4 Hz, 2F), −120.13 (s, 2F), −121.74 (s, 6F), −122.67 (s, 2F), −126.07 (s, 2F); HRMS calcd for $C_{20}H_{13}F_{20}O_2$ 665.0596, found 665.0586. Anal. Calcd for $C_{20}H_{12}F_{20}O_2$: C, 36.16; H, 1.82; F, 57.20. Found: C, 36.28; H, 1.93; F, 57.23

5-(Perfluorooctyl)-6-(trifluoromethyl)bicyclo[2.2.2]octa-5,7-diene-2,3-diol (11). Method A. 10a (1.29 g, 1.94 mmol) was dissolved in 30 mL of dioxane, and 30 mL of freshly prepared 6 M HCl was added to yield a slightly cloudy solution that separated into two clear phases when stirring was stopped. After the reaction was heated at 65 °C for 1 day in an open flask, the solution turned brown and about half of the solvent evaporated. ^{1}H NMR showed complete reaction and clean product. The reaction mixture was extracted with 4 × 100 mL of ether. Combined organic layers were extracted with 10 mL of brine and 5 mL of distilled water and then dried over sodium sulfate. Residual water was removed by dissolving the mixture in chloroform and evaporating this by rotary evaporator. The crude material (1.1 g, 1.78 mmol, 92%) was used in the next reaction.

Method B. 10a (1.29 g, 1.94 mmol) was dissolved in 9 mL of methanol, and 97 mg of pyridinium *p*-toluenesulfonate was added to yield a clear colorless solution. The reaction was heated at 60 °C in an open flask. Methanol was added periodically to maintain the total volume around 9 mL. After 4 days, ^{1}H NMR showed complete reaction of the major isomer, but the minor isomer had not reacted much, so 11 mL of dioxane and 11 mL of 6 M HCl was added. After heating 1 day at 60 °C, the reaction was complete. The reaction was purified as in method A to yield 1.1 g (1.78 mmol, 92%) of a brown oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.52 (m, 2H), 4.29 (br m, 1H), 4.22 (br m, 1H), 3.89 (s, 2H), 2.52 (br s, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −61.12 (m, 3F), −80.83 (t, 3F, J = 9.2 Hz), −108.67 (m, 2F), −120.26 (br s, 2F), −121.83 (br s, 6F), −122.76 (br s, 2F), −126.19 (br s, 2F). HRMS calcd for $C_{17}H_6F_{20}O_2S$ 665.9687, found 665.9766. Anal. Calcd for $C_{17}H_8F_{20}O_2$: C, 32.71; H, 1.29; F, 60.87. Found: C, 32.60; H, 1.27; F, 60.85.

5-(Perfluorooctyl)-6-(trifluoromethyl)bicyclo[2.2.2]octa-5,7-diene-2,3-thiocarbonate (12). The procedure was essentially the same as for compound **4d**. Column chromatography was done on silica gel by eluting first with 10% ethyl acetate/hexane to obtain the major isomer and then 35% ethyl acetate/hexane to obtain the minor isomer. Both isomers were white solids (82%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.62 (m, 2H), 4.99 (m, 2H), 4.66 (br m, 1H), 4.59 (br m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −60.99 (s, 3F), −80.68 (s, 3F), −108.59 (s, 2F), −119.99 (s, 2F), −121.68 (br s, 4F), −121.82 (br s, 2F), −127.67 (br s, 2F), −126.08 (br s, 2F); HRMS calcd for $C_{18}H_{10}F_{20}NO_2S$ ($M + NH_4^+$) 642.0545, found 642.0552. Anal. Calcd for $C_{18}H_6F_{20}O_2S$: C, 32.45; H, 0.91; F, 57.03. Found: C, 32.22; H, 1.03; F, 57.13.

2-(Perfluorooctyl)-3-(trifluoromethyl)bicyclo[2.2.2]octa-2,5,7-triene (13). The major, anti isomer of compound **12** (3.3 g, 4.95 mmol) was put in a 25 mL round-bottom flask, and the flask was purged with argon. Addition of 3 mL (97% pure, 3.07 g, 15.8 mmol) of DPD only wetted the solid; none appeared to dissolve. The reaction was heated in an oil bath at 45 °C, and after 1 day the reaction was a brown liquid. After 3 days, the reaction mixture was loaded onto a plug of silica gel and eluted with 40% ethyl acetate/hexane. Removal of solvent yielded 1.9 g (3.22 mmol, 65%) of **13** as a slightly yellow oil. Note: This reaction has been done on larger scale to produce 11.5 g of **13**. The yield was reduced to 54% in this case: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.90 (m, 4H), 5.1415 (m, 1H), 5.1049 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ −61.50 (m, 3F), −80.70 (t, J = 9.2 Hz, 3F), −108.61 (br d, 2F), −193.04 (br s, 2F), −121.80 (br s, 6F), −122.67 (br s, 2F), −126.08 (br s, 2F); HRMS calcd for $C_{17}H_6F_{20}$ 590.0068, found 590.0170. Anal. Calcd for $C_{17}H_6F_{20}$: C, 34.60; H, 1.02; F, 64.38. Found: C, 34.40; H, 0.93; F, 64.24.

5-(*p*-Toluenesulfonyl)bicyclo[2.2.2]octa-5,7-diene 2,3-Dimethyl Acetal (15a). A 250 mL round-bottom flask was charged with 8.22 g (45.6 mmol) of ethynyl *p*-toluenesulfonate, **14a**, and then purged with argon. Dry benzene (40 mL) was added to yield a colorless solution. In a separate flask, 6.94 g (45.6 mmol) of **9a** was dissolved in 10 mL of dry benzene, and this solution was then added to the first solution. The flask was sealed with a Kontes valve, and the reaction was heated to 80 °C and stirred for 14 h. After this time, some white crystals had formed in the reaction mixture. The reaction was then cooled to rt, and more crystals formed. Removal of solvent under vacuum yielded a white solid that was then

recrystallized by dissolving it in hot acetone (250 mL) and then cooling the solution to −50 °C overnight. The white crystals obtained were rinsed with −78 °C acetone and dried under vacuum to yield 13.38 g (40.3 mmol, 88%) of **15a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, J = 8.32 Hz, 2H), 7.32 (d, J = 8.12 Hz, 2H), 7.15 (dd, J = 1.89, 6.47, 1H), 6.27 (m, 1H), 6.20 (m, 1H), 4.25 (dd, J = 6.81, 3.36 Hz, 1 H), 4.12 (m, 1H), 4.07 (m, 1H), 4.00 (m, 1H), 2.43 (s, 3H), 1.28 (s, 3H), 1.21 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.32, 144.53, 141.95, 135.39, 131.28, 130.95, 129.87, 127.83, 113.50, 78.35, 78.02, 43.45, 41.98, 25.60, 25.39, 21.54; HRMS calcd for $C_{18}H_{21}O_4S$ $(M + H)^+$ 333.1161, found 333.1160. Anal. Calcd for $C_{18}H_{20}O_4S$: C, 65.04; H, 6.06. Found: C, 64.75; H, 6.07. **Caution**: **14a** can contain acidic impurities that cause rapid exothermic decomposition of **9a**. This decomposition is especially violent if the two reactants are combined neat. Acid impurities were removed from **14a** by eluting it through a plug of silica gel (20% ethyl acetate/hexane).

Bicyclo[2.2.2]octa-5,7-diene 2,3-Dimethyl Acetal (16a). Compound **15a** (10.68 g, 32.1 mmol) was put in a 2000 mL round-bottom flask, and the flask was evacuated and then backfilled with argon three times. The flask was then put in a bath at −20 °C, and 1.6 L of SmI_2 solution (0.1 M in THF) was added while the bath temperature was maintained at or below −20 °C. HMPA (90 mL) that had been dried over calcium hydride and then distilled was then added to the solution, and the color changed from blue-green to dark purple. The reaction was stirred under argon for 90 min at a temperature of −20 °C, and then 150 mL of a saturated solution of aqueous NH_4Cl was added. After the mixture was stirred for 1 h, over which time the solution was allowed to warm to rt, THF was removed under vacuum. The remaining mixture was diluted with 50 mL of water, and the aqueous layer was then extracted with (3 × 500) mL of ether. The combined organic layers were then extracted with (2 × 200) mL of brine and (2 × 200) mL 0.1 M NaOH. These aqueous layers were then extracted with (3 × 200) mL of ether. The combined organic layers were dried over $MgSO_4$, and solvent was then removed under vacuum to yield a pink liquid. This was loaded onto a plug of silica gel and eluted first with hexane until all HMPA was eluted and then with 10% ethyl acetate/hexane. Removal of solvent yielded **16a** as a light pink solid. Further purification was accomplished using a silica gel column eluted with 10% ethyl acetate/hexane to yield the product as 4.2 g (23.6 mmol, 73%) of a white waxy solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.32 (m, 2H), 6.26 (m, 2H), 4.21 (m, 2H), 3.83 (m, 2H), 1.33 (s, 3H), 1.26 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.65, 131.91, 112.51, 78.44, 41.91, 25.90, 25.45; HRMS calcd for $C_{11}H_{15}O_2$ $(M + H)^+$ 179.1069, found 179.1077. Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.94; H, 8.02.

Bicyclo[2.2.2]octa-5,7-diene-2,3-diol (17a). In a 250 mL round-bottom flask, **16a** (3.75 g, 21.04 mmol) was dissolved in 80 mL of methanol, and 1.09 g of pyridinium *p*-toluenesulfonate was added. The reaction, which was left open to the air, was heated at 70 °C, and the methanol was replenished periodically as it boiled off. After 1 week, the remaining methanol was removed under vacuum and the reaction was purified on a silica gel column eluted with 40% ethyl acetate/hexane. Removal of solvent under vacuum yielded 1.9 g (13.75 mmol, 66%) of **17a** as a white crystalline solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.42 (m, 2H), 6.24 (m, 2H), 3.82 (m, 2H), 3.70 (m, 2H), 2.30 (br s or m, 2H, −OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.93, 132.40, 67.22, 44.33; HRMS calcd for $C_8H_{14}NO_2$ $(M + NH_4^+)$ 156.1021, found 156.1023.

Bicyclo[2.2.2]octa-5,7-diene-2,3-thiocarbonate (18a). Under argon, 1.64 g (11.87 mmol) of **17a** was dissolved in 40 mL of dry toluene in a 250 mL round-bottom flask, and 2.5 g (90% pure, 12.62 mmol) of TCDI was added. The flask was put in an oil bath that had been preheated to 130 °C, and the reaction was stirred for 10 min. TCDI (0.12 g, 0.61 mmol) was then added, and the reaction was stirred for an additional 5 min at 130 °C. After the solvent was removed under vacuum, the solid was redissolved in ethyl acetate, and 18 g of silica gel was added. Solvent was removed to produce a free-flowing powder that was then loaded onto a column of 600 g of silica gel and eluted with 40% ethyl acetate/hexane. Removal of solvent under vacuum yielded 1.73 g (9.60 mmol, 81%) of **18a** as a white crystalline solid: ^{1}H (300 MHz, $CDCl_3$) δ 6.45 (m, 2H), 6.33 (m, 2H), 4.87 (m, 2H), 4.20 (m, 2H). ^{13}C (75 MHz, $CDCl_3$) δ 192.42, 132.61, 131.58, 81.87, 40.42; HRMS calcd for $C_9H_9O_2S$ $(M + H)^+$ 181.0321, found 181.0323. Anal. Calcd for $C_9H_8O_2S$: C, 59.98; H, 4.47. Found: C, 59.64; H, 4.53.

Bicyclo[2.2.2]octa-2,5,7-triene (19a). A 250 mL Schlenk flask was charged with 1.8 g (9.99 mmol) of **18a** and was then evacuated and filled with argon three times. Under argon, 6 mL (97% pure, 6.13 g, 31.6 mmol) of DPD that had been pumped down to remove all volatile components was added to yield a mixture containing a lot of undissolved **18a**. The flask was sealed, and the reaction mixture was heated at 40 °C for 5 days. The flask was vented periodically to allow CO_2 formed by the reaction to escape. **19a** (0.70 g, 6.72 mmol, 67.3%) was then vacuum transferred out of the reaction mixture as a colorless liquid: ^{1}H (300 MHz, $CDCl_3$) δ 6.78 (m, 6H), 4.842 (m, 2H); ^{13}C (75 MHz, $CDCl_3$) δ 140.60, 48.23; HRMS calcd for C_8H_8 104.0624, found 104.0627. Anal. Calcd for C_8H_8: C, 92.26; H, 7.74. Found: C, 92.20; H, 7.74.

5-(*p*-Toluenesulfonyl)-6-octylbicyclo[2.2.2]octa-5,7-diene 2,3-Dimethyl Acetal (15b). **14b** (100 mg, 0.342 mmol) and 52 mg (0.342 mmol) of **9a** were heated neat under argon for 3 days. Flash chromatography on silica gel (10% ethyl acetate/hexane) yielded **15b** (106 mg, 0.24 mmol, 70%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 6.19 (m, 2H), 4.19 (m, 2H), 4.07 (m, 1H), 3.82 (m, 1H), 2.73 (t, J = 6.9 Hz, 2 H), 2.42 (s, 3H), 1.26 (br d, 17H), 1.20 (s, 3H), 0.88 (t, J = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.4, 144.1, 138.0, 136.6, 131.9, 130.8, 129.8, 127.4, 113.1, 78.7, 78.0, 50.4, 44.0, 31.8, 31.4, 29.6, 29.4, 29.2, 27.4, 25.7, 25.6, 22.7, 21.6, 14.1; HRMS calcd for $C_{26}H_{36}O_4S$ $(M + H)^+$ 445.2413, found 445.2426. Anal. Calcd for $C_{26}H_{36}O_4S$: C, 70.24; H, 8.16. Found: C, 70.12; H, 8.16.

5-Octylbicyclo[2.2.2]octa-5,7-diene 2,3-Dimethyl Acetal (16b). To 3.6 g (8.1 mmol) of **15b**, dissolved in 4 mL of dry THF, was added under argon 420 mL of SmI_2 solution (0.1 M in THF). The mixture was cooled to −20 °C, and 26.5 mL of HMPA was added to yield a dark purple solution. The reaction was kept at − 20 °C for 1.5 h, treated with 42 mL of saturated NH_4Cl solution, and allowed to warm to rt, during which time the solution turned yellow and a white precipitate formed. The precipitate was filtered off and washed with diethyl ether several times, and then solvent was removed under vacuum. Brine (20 mL) was added to the remaining mixture, and it was then extracted with diethyl ether. The ether was removed under reduced pressure and the product purified by passing through a plug of silica gel. HMPA was removed first by eluting with hexane and then **16b** was eluted using 10% ethyl acetate/hexane. Removal of solvent yielded 1.57 g (5.43 mmol, 67%) of **16b** as a colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.30 (m, 2H), 5.72 (dd, J = 6.3, 1.8 Hz, 1H), 4.19 (m, 2H), 3.69 (m, 1H), 3.54 (m, 1H), 2.06 (td, J = 7.5, 0.75 Hz, 2 H), 1.31 (s, 3H), 1.24 (br d, 15H), 0.86 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.8, 132.8, 131.7, 124.7, 112.5, 79.4, 78.7, 46.4, 42.0, 34.0, 31.9, 29.43, 29.32, 29.27, 27.2, 26.0, 25.6, 22.7, 21.6, 14.1; HRMS calcd for $C_{19}H_{30}O_2$ $(M + H)^+$ 291.2324, found 291.2317.

5-Octylbicyclo[2.2.2]octa-5,7-diene-2,3-diol (17b). **16b** (1.57 g, 5.43 mmol) and pyridinium *p*-toluenesulfonate (0.3 g, 1.1 mmol) were dissolved in 100 mL of methanol and heated to 60 °C in an open flask for 3 days. Methanol was removed under reduced pressure and the product purified by flash column chromatography on silica gel (50% ethyl acetate/hexane). Removal of solent under vacuum yielded 1 g of **17b** (4 mmol, 74%) as a colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.39 (m, 2H), 5.72 (m, 1H), 3.68 (m, 3H), 3.54 (m, 1H), 2.64 (s, 2H), 2.08 (t, J = 7.8 Hz, 2 H), 1.25 (br d, 12H), 0.87 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.2, 133.3, 132.6, 124.1, 68.4, 67.8, 48.9, 44.6, 33.9, 31.9, 29.47, 29.35, 29.30, 27.2, 22.7, 14.2; HRMS calcd for $C_{16}H_{26}O_2$ $(M + H)^+$ 249.1855, found 249.1859.

5-Octylbicyclo[2.2.2]octa-5,7-diene-2,3-thiocarbonate (18b). **17b** (1 g, 4 mmol) and TCDI (0.87 g, 4.4 mmol) were refluxed in 20 mL toluene for 30 min. The reaction mixture was eluted through a plug of silica with 30% ethyl acetate/

hexane to afford 1.15 g (3.9 mmol, 98%) of **18b** as a white crystalline solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.42 (m, 2H), 5.79 (dd, J_1=6.3 Hz, J_2 =1.5 Hz, 1H), 4.85 (m, 2H), 4.06 (m, 1H), 3.90 (m, 1H), 2.12 (t, J = 7.5 Hz, 2 H), 1.24 (br d, 12H), 0.86 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.64, 147.4, 132.6, 131.6, 128.2, 123.8, 82.6, 82.2, 45.0, 40.7, 33.9, 31.9, 29.3, 29.2, 27.0, 22.7, 14.1; HRMS calcd for $C_{17}H_{24}O_2S$ 292.1497, found 292.1504.

2-Octylbicyclo[2.2.2]octa-2,5,7-triene (19b). 18b (1.15 g, 3.9 mmol) was suspended in DPD (0.76 g, 11.7 mmol) and heated at 40 °C under argon for 5 days. The reaction mixture was purified by flash column chromatography on silica gel (10% ethyl acetate/hexane) to yield 168 mg (0.78 mmol, 25%) of **19b** as a colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.76 (m, 4H), 6.17 (dd, J = 6.1, 1.8 Hz, 1H), 4.68 (m, 1H), 4.49 (m, 1H), 2.06 (td, J =7.1, 1.8 Hz, 2 H), 1.25 (br d, 12H), 0.88 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.4, 141.0, 139.9, 131.5, 52.5, 47.8, 33.7, 31.9, 29.5, 29.3, 29.1, 27.2, 22.7, 14.1; HRMS calcd for $C_{19}H_{30}O_2$ $(M + H)^+$ 216.1877, found 216.1878.

5-(Methoxycarbonyl)bicyclo[2.2.2]octa-5,7-diene 2,3-Dimethyl Acetal. 9a (6.7 g, 44 mmol) and 7.2 g (85.7 mmol) of methyl propiolate were refluxed in 70 mL of dry benzene overnight. Removal of solvent and excess methyl propiolate under vacuum yielded 10.4 g (44 mmol, 100%) of the desired product: ^{1}H NMR (300 MHz, C_6D_6) δ 6.93 (dd, J = 6.3, 1.8 Hz, 1H), 6.25 (t, J = 6.0 Hz, 1H), 6.09 (t, J = 6.0 Hz, 1H), 4.51 (m, 1H), 3.98 (m, 1H), 3.80 (m, 1H), 3.54 (m, 1H), 3.37 (s, 3H), 1.34 (s, 3H), 1.11 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.9, 143.9, 138.1, 131.9, 130.4, 112.6, 78.0, 77.8, 50.7, 42.9, 41.6, 25.5, 24.9; HRMS calcd for $C_{13}H_{16}O_4$ $(M + H)^+$ 237.1127, found 237.1128. Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83. Found: C, 66.07; H, 6.73.

Methyl 2,3-Dihydroxybicyclo[2.2.2]octa-5,7-diene-5-carboxylate. The procedure was similar to that described for **17b** (60%): ^{1}H NMR (300 MHz, C_6D_6) δ 6.90 (dd, J = 6.3, 1.8 Hz, 1H), 6.27 (t, J = 6.0 Hz, 1H), 6.14 (t, J = 6.0 Hz, 1H), 4.46 (m, 1H), 3.50 (m, 2H), 3.30 (m, 1H), 3.22 (s, 3H), 2.85 (br d, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.1, 143.9, 137.3, 132.6, 131.4, 66.9, 67.0, 52.0, 45.7, 43.9; HRMS calcd for $C_{10}H_{16}NO_4$ $(M + NH_4^+)$ 214.1075, found 214.1076. Anal. Calcd for $C_{10}H_{12}O_4$: C, 61.21; H, 6.17. Found: C, 60.95; H, 6.16.

Methyl 2,3-(Thiomethylenedioxy)bicyclo[2.2.2]octa-5,7-diene-5-carboxylate (20). 3-(Methoxycarboxy)-7,8-dihydroxy[2.2.2]bicyclo-3,5-octadiene was reacted with thiophosgene and DMAP in analogy to the literature procedure[10] to yield **20** as a light yellow solid following column chromatography (71%): ^{1}H NMR (300 MHz, C_6D_6) δ 6.36 (dd, J_1 = 6.3, 1.8 Hz, 1H), 5.85 (t, J = 6.0 Hz, 1H), 5.70 (t, J = 6.0 Hz, 1H), 4.31 (m, 1H), 3.82 (m, 1H), 3.59 (m, 1H), 3.24 (s, 3H), 3.14 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.0, 163.7, 142.2, 137.5, 132.3, 131.0, 81.7, 81.5, 52.4, 41.8, 40.4; HRMS calcd for $C_{11}H_{14}NO_4S$ $(M + NH_4^+)$ 239.0375, found 239.0373. Anal. Calcd for $C_{11}H_{10}O_4S$: C, 64.00; H, 4.85. Found: C, 63.94; H, 4.75.

2-Methylbicyclo[2.2.2]octa-2,5,7-triene-2-carboxylate (21). Using a procedure analogous to the one for preparation of **19b** yielded a very viscous brown mixture. The same result was obtained when THF was used to dilute the reaction and when radical inhibitors, 4-methoxyphenol and BHT, were added to the THF solution in concentrations of 10 mol % and 100 mol % versus **20**. Under all conditions decomposition occurred after 3 h to 3 days.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for compounds **17a** and **16b**−**19b** (13 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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