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Synthesis of the Bicyclopropenyls

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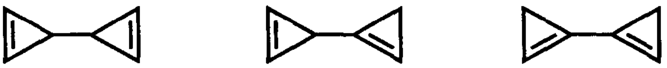
Abstract: Bicyclopropenyls 1-3 have been synthesized by the vacuum gas-phase elimination of β-halocyclopropylsilane precursors over solid fluoride. Bicycloprop-2-enyl 1 and bicycloprop-1,2'-enyl 2 were isolated and characterized using standard spectroscopic techniques whereas bicycloprop-1-enyl 3 could only be generated *in situ* and trapped by cyclopentadiene.

The bicyclopropenyls **1-3** are of interest from a modern theoretical, conceptual and mechanistic standpoint as well as from a historical standpoint.[1-4] Bicycloprop-2-enyl **1** occupies the most important position in this family since it is one of only four isomers of benzene in which each carbon is bound to a single

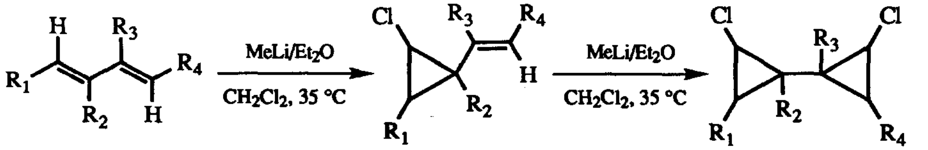


1 **2** **3**

hydrogen atom.[4] Bicycloprop-1-enyl **3** is of interest as a possible synthon to aryl compounds.[5] We have reported the synthesis of **1** and **2** in a recent preliminary account[6] and the structure of **1** has been established by x-ray crystallography.[7] Although two derivatives of **3** have been reported,[5,8] evidence for the parent hydrocarbon is less conclusive. In this paper we report experimental details on the synthesis of **1** and **2** as well as a new route to **3** which demonstrates that this isomer can be generated as a discrete species in high yield.

The starting materials **4a-c** used in these syntheses were prepared by the addition of chlorocarbene to the appropriate bis(trimethylsilyl)buta-1,3-dienes[9] **5a-c** as illustrated in Scheme 1. The intermediate vinylcyclo-

Scheme 1



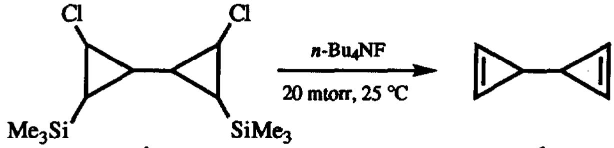
5a-c
5a: $R_1=R_4=SiMe_3$; $R_2=R_3=H$
5b: $R_1=R_3=SiMe_3$; $R_2=R_4=H$
$R_1=R_3=H$; $R_2=R_4=SiMe_3$
5c: $R_1=R_4=H$; $R_2=R_3=SiMe_3$

6a-d

4a-c
4a: $R_1=R_4=SiMe_3$; $R_2=R_3=H$
4b: $R_1=R_3=SiMe_3$; $R_2=R_4=H$
4c: $R_1=R_4=H$; $R_2=R_3=SiMe_3$

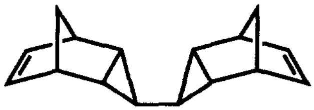
propanes **6a-d** were usually isolated without characterization and then exposed to a large excess of chlorocarbene. The resulting bicyclopropyl derivatives were isolated as mixtures of stereoisomers in most instances.

The vacuum gas-solid reaction (VGSR) procedure described previously[10] was used to convert the β-halocyclopropylsilane precursors to the bicyclopropenyls. The introduction of **4a** into the VGSR apparatus containing tetra-*n*-butylammonium fluoride adsorbed on glass helices yielded **1**, a moderately stable compound below about -10 °C. Above this temperature polymerization to yield a solid yellow mass was observed.



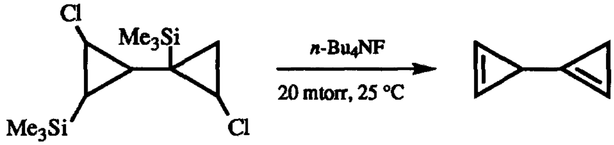
4a **1**

The Diels-Alder adduct **7**, mp 104-105 °C, was formed when **1** was isolated in a cold trap containing cyclopentadiene and stirred for 3 hours at -50 °C. The symmetry of **7** is apparent from the ^{13}C NMR spectrum which exhibits five lines at 19.3, 31.2, 42.8, 63.0, and 131.2 ppm.



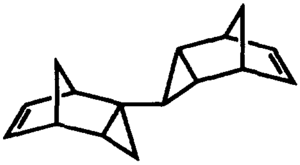
7

Bicycloprop-1,2'-enyl **2** was isolated when **4b** was eliminated over solid fluoride. Although **2** could be characterized readily by NMR spectroscopy at -50 °C, it was not possible to obtain a single crystal for x-ray structural analysis as described earlier for **1**.[7] The ^{1}H NMR spectrum of **2** exhibits the expected four signals at δ 0.83 (d, 2H, J=1.8), 2.59 (t, 1H, J=1.3), 6.38 (t, 1H, J=1.8), and 7.29 (d, 2H, J=1.3). ^{13}C NMR signals were observed at 3.5, 11.2, 95.5, 109.4, and 123.6 ppm.



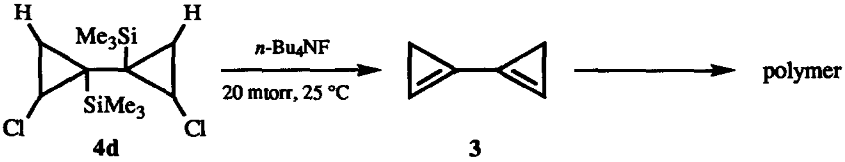
4b **2**

Isolation of **2** with cyclopentadiene as described above for **1** gave the Diels-Alder adduct **8**. Fifteen of the expected sixteen ^{13}C NMR signals could be observed. Four narrowly spaced olefinic carbon signals were observed at 131.3, 131.4, 131.7, and 132.7 ppm.



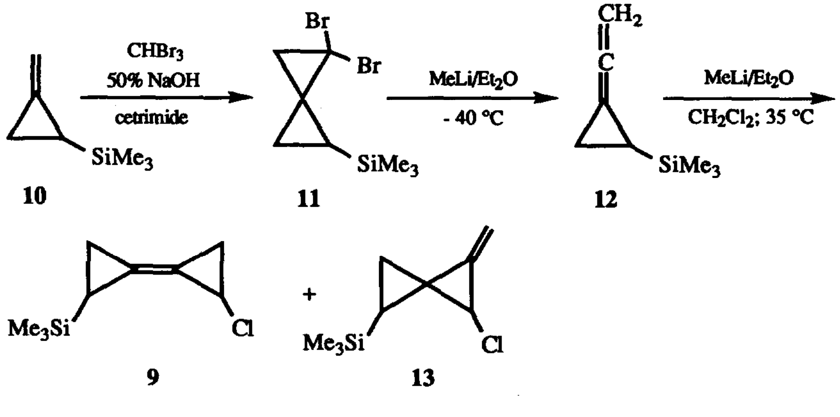
8

In contrast to 1 and 2, bicycloprop-1-enyl 3 proved to be an extremely labile compound. A white solid thought to be 3 was observed in a liquid N_2 trap at -196 °C when 4c was introduced slowly into the VGSR apparatus containing solid tetra-*n*-butylammonium fluoride. However, upon warming to -90 °C, the trap was found to contain mostly insoluble polymeric material. It was not possible to isolate a Diels-Alder adduct of 3 under the same conditions used to synthesize 7 and 8. In one experiment a small amount of material was extracted from the insoluble polymeric material at -90 °C. This compound exhibited ^{1}H NMR signals at δ 0.71 (d, 4H, J = 1.8 Hz) and 7.36 (t, 4H, J = 1.8 Hz). The ^{13}C NMR spectrum of this sample gave three signals appearing at 11.1, 95.6, and 127.4 ppm. It seems likely that these signals arise from a small amount of 3, although confirmation of these assignments was not possible.

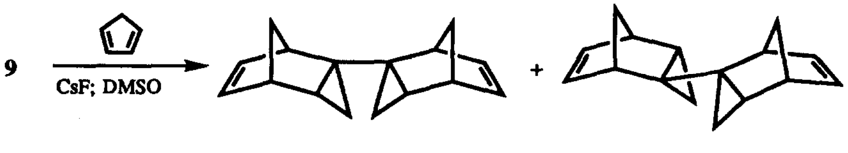


Compound 9 was envisoned as a more promising starting material for 3. The formation of 3 from 9 would be expected to involve a facile 1,4-elimination. The synthesis of 9 is outlined in Scheme 2. Thus addition of dibromocarbene to 10[11] provided 11 in 65% yield. Treatment of 11 with methyllithium at -40 °C gave the allene 12 in 29% yield. Exposure of 12 to a two-fold excess of chlorocarbene yielded a 3:1 mixture of 9 and 13. The desired isomer 9 could be purified by preparative gas chromatography in ca. 20% yield.

Scheme 2



The gas phase elimination of **9** over solid fluoride yielded the same copious polymeric material obtained from **4d**. However, when the elimination was carried using CsF in dimethyl sulfoxide containing cyclopentadiene, a mixture of the Diels-Alder adducts, provisionally identified as **14** and **15**, could be isolated in 61% yield. The ^{13}C NMR spectrum of the mixture of isomers exhibits sixteen signals, eight for each diastereomer. The four olefinic carbon atoms were observed at 132.1, 132.2, 133.1, and 133.2 ppm.



14 **15**

Since the conversion **9** → **3** requires that both double bonds form simultaneously, this result demonstrates conclusively that the cyclopropene can be generated as a discrete intermediate. In view of the yield of the Diels-Alder adducts, it seems reasonable to assume that **3** is produced in high yield. These observations support the assumption that the polymer produced from the gas phase elimination originates from **3**, probably via an ene reaction. Use of **3** as a synthon remains to be explored.

EXPERIMENTAL SECTION

General. Proton and carbon-13 NMR spectra were recorded in deuteriochloroform using an IBM AF 300 (^{1}H: 300.13 MHz, ^{13}C: 75.5 MHz) or a JEOL FX90Q (^{1}H: 90 MHz, ^{13}C: 22.63 MH) spectrometer. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane using the residual chloroform as internal standard (^{1}H: 7.26, ^{13}C: 77.0). Coupling constants are expressed in Hertz. Infrared spectra of new compounds were recorded using a Perkin-Elmer Model 1320 spectrophotometer on NaCl plates. High resolution mass spectra were recorded using a double-focusing CEC 21-110 spectrometer. A Hewlett Packard Model 700 gas chromatograph with a thermal conductivity detector using a quarter-inch column (5% SE-30 on Chrom W-AW DMCS) with an outlet flow rate of 60cc of helium per minute was used for all analytical and preparative gas chromatography. All boiling and melting points are uncorrected. The alkenylsilanes were prepared according to the literature. Methylene chloride was distilled from calcium hydride under an atmosphere of nitrogen prior to use. All other chemicals were of reagent quality and used as obtained from the manufacturers. Column chromatography was performed using Baker reagent grade silica gel (230-400 mesh) with petroleum ether (40-65°C) as eluent. Merck precoated silica gel plates were used for analytical (100 x 50 x 0.255 mm) thin layer chromatography. Reactions were carried out in an inert atmosphere of dry nitrogen when necessary.

General Procedure for the Addition of chlorocarbene to Alkenylsilanes. Methyllithium (230 mL, 1.4 M, 0.32 mol) and CH_2Cl_2 (32 mL, 0.50 mol) were added simultaneously at a ratio of five drops to one, respectively, to a stirred solution of the bis(trimethylsilyl)buta-1,3-diene[9] (0.04 mol) in dry CH_2Cl_2 (1 mL) under an atmosphere of N_2. This rate of addition requires about one hour and was sufficient to maintain a gentle reflux. A Dean-Stark trap was used to remove the ether. Additional CH_2Cl_2 (5 mL) was then added to the pale yellow solution and the mixture was stirred for 15 min to ensure complete reaction of the methyllithium. The reaction mixture was filtered and the solids were washed with ether (3 x 50 mL). The combined organics were then washed with water (100 mL), brine (100 mL), and dried over $MgSO_4$. The solution was concentrated by distillation through a 30cm column of glass helices and the residue distilled through a 10 cm Vigreaux column. Further purification by distillation afforded **6a-d** as colorless liquids.

1-(2-Trimethylsilylethenyl)-2-chloro-3-trimethylsilylcylopropane (6a). **6a** was prepared from **5a** in 68% yield; bp 48-60°C/0.1 torr; two isomers were resolved by column chromatography; ^1H NMR (300 MHz): *cis* 5.88 (d, 1H, *J*=18.1), 5.83 (dd, 1H, *J*=18.1, 6.9), 3.16 (dd, 1H, *J*=6.4, 5.8), 1.62 (AB, 1H, *J*=8.0, 6.9), 0.30 (dd, 1H, *J* =8.0, 5.8), 0.07 (s, 9H), 0.01 (s, 9H); *trans* 5.73 (d, 1H, *J*=18.4), 5.55 (dd, 1H, *J*=18.4, 7.9), 3.28 (dd, 1H, *J*=8.4, 2.9), 1.78 (td, 1H, *J*=7.9), 0.31 (dd, 1H, *J*=8.4, 7.9), 0.14 (s, 9H), 0.04 (s, 9H); ^{13}C NMR (75.5 MHz): *cis* 144.6, 131.7, 38.4, 27.5, 18.4, -1.2, -2.5; *trans* 146.4, 129.4, 41.1, 31.5, 16.7, -0.7, -1.3; IR (neat): 3140, 2960, 2900, 1605, 1405, 1360, 1285, 1250, 1010, 980, 850, 765, 700 cm^{-1}; HRMS for $C_{11}H_{23}ClSi_2$: calcd 246.1027; found 246.1031.

1-(2-Trimethylsilylethenyl)-2-chloro-1-trimethylsilylcyclopropane (6b) and 1-(1-trimethylsilylethenyl)-2-chloro-3-trimethylsilylcyclopropane (6c). A mixture of **6b** and **6c** were prepared in 65% yield from **5b**; bp 44-52°C/0.1 torr; isomers were resolved partially by column chromatography; ^1H NMR (300 MHz): 6.13-5.48 (m, 2H), 3.19-3.05 (m, 1H), 1.28-0.21 (m, 2H), 0.16 to -0.04 (8 s, 18H); ^{13}C NMR (75.5 MHz): 146.9, 144.3, 134.0, 130.6, 129.6, 128.7, 41.4, 40.5, 37.2, 36.5, 22.4, 21.3, 19.7, 18.7, 18.1, 0.3, -0.2, -1.1, -1.2, -1.4, -2.6, -3.4; IR (neat): 3170, 3150, 2960, 2900, 1595, 1430, 1405, 1285, 1250, 985, 925, 875, 840, 755, 725, 690, 670 cm^{-1}; HRMS for $C_{11}H_{23}ClSi_2$: calcd 246.1027; found 246.1024.

1-(1-Trimethylsilylethenyl)-2-chloro-1-trimethylsilylcyclopropane (6d). **6d** was prepared from **5d** in 60% yield; bp 46-51°C/0.1 torr; isomers were resolved partially by column chromatography; ^1H NMR (300 MHz): *cis* 5.66 (AB, 2H, *J*=2.2), 3.17 (dd, 1H, *J*=6.6, 3.5), 1.23 (dd, 1H, *J*=6.6, 5.3), 0.88 (dd, 1H, *J*=5.3, 3.5, 0.14 (s, 9H), -0.03 (s, 9H); *trans* 5.54 (AB, 1H, *J*=2.2), 3.09 (dd, 1H, *J*=7.1, 4.2), 1.18 (dd, 1H, *J*=7.1, 5.4), 1.16 (dd, 1H, *J*=5.4, 4.2), 0.14 (s, 9H), 0.12 (s, 9H); ^{13}C NMR (75.5 MHz): *cis* 155.5, 128.7, 41.4, 25.6, 21.3, 0.2, -0.2; *trans* 150.2, 130.6, 41.1, 37.2, 19.7, 0.3, -2.2; IR (neat): 3150, 2960, 2900, 1575, 1435, 1405, 1285, 1250, 1080, 940, 925, 840, 760, 690, 670 cm^{-1}; HRMS for $C_{11}H_{23}ClSi_2$: calcd 246.1027; found 246.1025.

1-(2-Chloro-3-trimethylsilyl-1-cyclopropyl)-2-chloro-3-trimethylsilylcyclopropane (4a). 45% yield from **6a**; bp 70-120°C (bath temperature)/0.03 torr; ^1H NMR (300 MHz): 3.29-3.01 (m, 2H), 1.44-0.87 (m, 2H), 0.54 to -0.21 (2H, m), 0.12 to -0.06 (8 s, 18H); ^{13}C NMR (75.5 MHz): 39.3, 39.2, 38.5, 38.0, 37.3, 37.1, 36.9, 27.1, 26.4, 25.3, 24.8, 23.8, 22.6, 21.7, 17.1, 16.1, 14.9, 13.7, 13.4, 11.5, -0.7, -0.8, -2.3, -2.4, -2.5, -2.6; IR (neat): 3140, 2960, 2900, 1405, 1325, 1285, 1250, 1005, 950, 895, 850, 760, 700 cm^{-1}; HRMS for $C_{12}H_{24}Cl_2Si_2$: calcd 294.0794; found 294.0790. A solid formed after microdistillation; isolation and recrystallization from pentane provided one pure isomer; mp 108-110°C; ^1H NMR (300 MHz): 3.12 (t, 2H, *J*=5.5), 0.88 (t, 2H, *J*=5.0), 0.08 (dd, 2H, *J*=5.5, 5.0), 0.01 (s, 18H); ^{13}C NMR (75.5 MHz): 37.1, 22.6, 17.1, -2.4.

1-(2-Chloro-1-trimethylsilyl-1-cyclopropyl)-2-chloro-3-trimethylsilycyclopropane (4b). 42% yield from the mixture **6b** and **6c**; bp 70-120°C (bath temperature)/0.03 torr; ^1H NMR (300 MHz): 3.35-2.65 (m, 2H), 1.55-0.55 (m, 3H), 0.45 to -0.45 (1H, m), 0.25 to -0.08 (12 s, 18H); ^{13}C NMR (75.5 MHz): 39.1, 38.4, 38.0, 37.9, 37.5, 37.3, 37.0, 36.4, 36.1, 29.6, 24.7, 22.5, 22.2, 19.0, 17.0, 16.2, 16.1, 14.5, 14.1, 13.4, 1.9, -0.2, -0.3, -0.5, -0.8, -1.1, -1.2, -1.9, -2.2, -2.3, -2.6, -3.0; IR (neat): 2960, 2900, 1435, 1405, 1375, 1290, 1250, 955, 850, 755, 690 cm^{-1}; HRMS for $C_{12}H_{24}Cl_2Si_2$: calcd 294.0794; found 294.0791.

1-(2-Chloro-1-trimethylsilyl-1-cyclopropyl)-2-chloro-1-trimethylsilylcyclopropane (4c). 12% yield from **6d**; bp 70-120°C (bath temperature)/0.03 torr; ^{1}H NMR (300 MHz): 3.30-2.85 (m, 2H), 1.45-0.65 (m, 4H), 0.30 to -0.05 (6 s, 18H); ^{13}C MNR (75.5 MHz): 41.7, 37.2, 21.2, 19.7, 19.4, 2.1, 1.5, 1.1, -0.3, -0.7, -2.6; IR (neat): 2960, 2900, 1445, 1405, 1375, 1285, 1250, 1080, 1035, 930, 840, 755, 685, 670 cm^{-1}; HRMS for $C_{12}H_{24}Cl_2Si_2$: calcd 294.0794; found 294.0791.

1,1-Dibromo-3-trimethylsilylspiropentane (11). A solution of sodium hydroxide (15 mL, 50 wt %) was added to a solution of alkenylsilane **10**[11] (7.58g, 60 mmol), cetrimide (0.3g), and bromoform (25 mL) under an atmosphere of nitrogen. The resulting solution was stirred vigorously at 50 °C for 12 h. The reaction mixture was then diluted with water (75 mL) and extracted with CH_2Cl_2 (3 x 100 mL). The organic layer was washed with water (75 mL) and dried over $MgSO_4$. Distillation through a 10 cm Vigreaux column afforded 11.63g of **11**. 65% yield; bp 59-62°C/2 torr; ^{1}H NMR (300 MHz): 1.96 (d, 2H, J=1.3), 1.44 (dd, 1H, J=10.5, 3.9), 1.15 (dd, 1H, J=7.7, 3.9), 0.65 (dd, 1H, J=10.5, 7.7), -0.01 (s, 9H); ^{13}C NMR (75.5 MHz): 31.6, 30.8, 28.6, 15.2, 11.4, -2.4; IR (neat): 3150, 2980, 2950, 2890, 1395, 1255, 1245, 1085, 045, 1030, 1000, 940, 860, 835, 750, 685 cm^{-1}; HRMS for $C_8H_{14}Br_2Si$: calcd 295.9231; found 295.9223.

Vinylidenetrimethylsilylcyclopropane (12). A solution of dibromide **11** (8.94g, 30.0 mmol) in dry ether (10 mL) was added dropwise over 45 min to a stirred solution of MeLi (23 mL, 1.4 M, 32.2 mmol). The temperature was -40 °C initially and was maintained between -35 and -45 °C. The orange-brown mixture was then refluxed for 30 min. After cooling to -10 °C, ice water (20 mL) was added carefully. The aqueous layer was extracted with ether (2 x 25 mL) and the combined extracts were dried over $MgSO_4$. The solution was then concentrated by distillation through a 10 cm Vigreaux column and the residue distilled to afford 1.22g of **12**. 29% yield; bp 57-59°C/20 torr; ^{1}H NMR (300 MHz): 4.84-4.80 (m, 2H), 1.73-1.65 (m, 1H), 1.39-1.31 (m, 1H), 1.13-1.04 (m, 1H), 0.02 (s, 9H); ^{13}C NMR (75.5 MHz): 193.6, 78.7, 10.9, 10.0, -2.7; IR (neat) 3140, 2970, 2950, 2890, 2010, 1650, 1475, 1420, 1400, 1330, 1245, 1205, 1030, 985, 970, 920, 905, 840, 755, 695, 660 cm^{-1}; HRMS for $C_8H_{14}Si$: calcd 138.0865; found 138.0865.

2-Chlorocyclopropylidenetrimethylsilylcyclopropane (9). The general procedure for chlorocarbene addition was used except that only a twofold excess of methyllithium was used; 27% yield as a 3:1 mixture of regioisomers **9**:**13**; bp 58-62°C/4 torr. Spectral data for **9**: ^{1}H NMR (300 MHz): 3.76-3.64 (m, 1H), 1.90-0.75 (m, 5H), 0.06 to -0.03 (4 s, 9H); ^{13}C NMR (75.5 MHz): 121.6, 107.6, 28.8, 28.7, 28.6, 19.0, 17.3, 15.4, 15.2, 15.1, 6.2, 6.0, 5.6, 5.4, 4.6, -2.4, -2.5; IR (neat): 3130, 2940, 2880, 1820, 1400, 1280, 1235, 1215, 1180, 1020, 1000, 985, 955, 900, 820, 740, 685, 640 cm^{-1}; HRMS for $C_9H_{15}ClSi$: calcd 186.0632; found 186.0626. Spectral data for **13**: ^{1}H NMMR (300 MHz): 5.70-5.28 (m, 2H), 3.75-2.75 (m, 1H), 1.72-0.80 (m, 3H), 0.06-0.00 (2 s, 9H); ^{13}C NMR (75.5 MHz): 147.5, 136.8, 136.6, 104.0, 38.0, 34.4, 23.5, 23.4, 17.2, 15.3, 14.8, 11.8, -2.4, -2.5; IR (neat): 3170, 3150, 2980, 2940, 2880, 1725, 1415, 1395, 1345, 1235, 1205, 1040, 970, 935, 925, 905, 875, 825, 775, 740, 685, 645 cm^{-1}; HRMS for $C_9H_{15}ClSi$: calcd 186.0632; found 186.0634.

Generation of Bicyclopropenyls. The bicyclopropyls **4a-c** (0.5 mmol) were vaporized at 40 °C and passed over tetra-*n*-butylammonium fluoride at 25 °C and 20 mtorr as described by Lin and Billups.[10] The coproduct fluorotrimethylsilane was separated from the bicyclopropenyls by low temperature (-100 °C) distillation.

Trapping by Cyclopentadiene. Trapping experiments were carried out by introducing about 0.2 mL of cyclopentadiene into the cold trap used to collect the bicyclopropenyls. The elimination reaction was carried out and more cyclopentadiene (1.0 mL) was then added. The mixture was allowed to melt slowly and then stirred for three hours at -50 °C. The trap was cooled to -78 °C and the excess cyclopentadiene removed *in vacuo*. The residue was dissolved in pentane and purified by preparative gas chromatography or thin layer chromatography.

Bicycloprop-2-enyl (1). ^{1}H NMR (300 MHz): 7.11 (d, 4H, *J*=1.3), 1.50 (t, 2H, *J*=1.3); ^{13}C NMR (75.5 MHz): 113.2, 20.8. Spectral data for **7**: ^{1}H NMR (300 MHz): 5.67 (t, 4H, *J*=2.0), 2.76 (br s, 4H), 1.67 (dt, 2H, *J*=6.6, 1.5), 1.65 (d, 2H, *J*=6.6), 1.46 (d, 4H, *J*=1.5), 1.26 (t, 2H, *J*=1.5); ^{13}C NMR (75.5 MHz): 131.2, 63.0, 42.8, 31.2, 19.3; IR (CS_2): 3120, 3050, 3020, 2950, 2920, 2850, 1325, 1250, 1240, 1085, 1040, 1015, 970, 890, 800, 760, 725 cm^{-1}; HRMS for $C_{16}H_{18}$: calcd 210.1409; found 210.1407.

Bicycloprop-1,2'-enyl (2). ^{1}H NMR (90 MHz): 7.29 (d, 2H, *J*=1.3), 6.38 (t, 1H, *J*=1.8), 2.59 (t, 1H, *J*=1.3), 0.83 (d, 2H, *J*=1.8); ^{13}C NMR (22.6 MHz): 123.6, 109.4, 95.5, 11.2, 3.5. Spectral data for **8**: ^{1}H NMR (300 MHz): 5.85 (dd, 1H, *J*=5.1, 3.3), 5.76 (t, 2H, *J*=2.0), 5.70 (dd, 1H, *J*=5.1, 3.3), 2.80 (br s, 2H), 2.77 (br s, 1H), 2.49 (br s, 1H), 1.88 (dt, 1H, *J*=6.7, 1.5), 1.69 (dt, 1H, *J*=6.6, 1.6), 1.63 (d, 2H, *J*=6.7), 1.26 (d, 2H, *J*=1.5), 1.11 (t, 1H, *J*=1.5), 0.97 (t, 1H, *J*=1.6), 0.44 (d, 2H, *J*=1.6); ^{13}C NMR (75.5 MHz): 132.7, 131.7, 131.4, 131.3, 63.1, 61.9, 47.7, 43.1, 42.8, 32.9, 29.7, 21.6, 18.6, 18.4, 17.9; IR (CS_2): 3130, 3050, 3020, 2960, 2920, 2850, 1550, 1440, 1325, 1240, 1045, 855, 845, 830, 820, 745, 730, 705 cm^{-1}; HRMS for $C_{16}H_{18}$: calcd 210.1409; found 210.1405.

Bicycloprop-1-enyl (3). ^{1}H NMR (90 MHz, CD_2Cl_2): 7.36 (t, 2H, *J*=1.8), 0.71 (d, 4H, *J*=1.8); ^{13}C NMR (22.6 MHz, CD_2Cl_2): 127.4, 95.6, 11.1.

Generation and Trapping of Bicycloprop-1-enyl (3) in Solution. Cyclopropylidenecyclopropane **9** (75 mg, 0.4 mmol) was added dropwise to a solution of cesium fluoride (365 mg, 2.4 mmol) and cyclopentadiene (1.0g, 15.1 mmol) in DMSO (5 mL). The mixture was stirred at room temperature for 12 hr, diluted with water (25 mL), and then extracted with pentane (4 x 25 mL). The combined extracts were washed with water (2 x 25 mL), dried over $MgSO_4$, and concentrated. Chromatography of the residue over silica gel (pentane) gave 51 mg of **14** and **15** (61% yield) as a colorless oil. Spectral data: ^{1}H NMR (300 MHz): 5.97-5.90 (m, 2H), 5.79-5.74 (m, 2H), 2.82 (br s, 2H), 2.74 (br s, 1H), 2.66 (br s, 1H), 1.93-1.88 (m, 2H), 1.69-1.58 (m, 2H), 1.27-1.20 (m, 1H), 0.98-0.93 (m, 1H), 0.78-0.67 (m, 2H), 0.61-0.57 (m, 1H), 0.51-0.45 (m, 1H); ^{13}C NMR (75.5 MHz): 133.2, 133.1, 132.2, 132.1, 62.0, 61.2, 47.7, 47.1, 43.1, 43.0, 26.7, 26.5, 23.4, 23.0, 19.3, 19.0; IR (neat): 3130, 3065, 2970, 2860, 1450, 1330, 1240, 1220, 1085, 1045, 845, 805, 745, 715 cm^{-1}; HRMS for $C_{16}H_{18}$: calcd 210.1409; found 210.140.

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