J. Am. Chem. Soc. 1993, 115, 10653-10657 10653

Tricyclo[2.1.0.0^{1,3}]pentane

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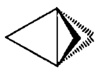
Received July 26, 1993®

Abstract: The reaction of 1-bromo-2-(chloromethyl)bicyclo[1.1.0]butane with methyllithium was examined. At –78 °C, 1-lithio-2-(chloromethyl)bicyclobutane is formed, and at –50 °C, it reacts to form cyclopentadiene. Evidence is presented that tricyclo[2.1.0.0^{1,3}]pentane, an isomer of [1.1.1]propellane, is formed as an intermediate. It could be trapped with phenylthiol to give 2-vinylcyclopropyl phenyl sulfide, and a ^{13}C NMR signal attributed to the tricyclopentane also was observed. The course of its conversion to cyclopentadiene, which must involve inversion of configuration at one carbon center, was explored theoretically. Initially, one of the central C–C bonds lengthens along with rotation of the attached hydrogen, leading to a transition state. This is followed by further rotation leading to inversion of configuration at the C–H bond and cleavage of the other central C–C bond, forming cyclopentenyl carbene. The latter would be expected to undergo a rapid hydrogen migration giving cyclopentadiene. The calculated activation energy (~23 kcal/mol) was in reasonable agreement with that estimated from the experimental data (~16 kcal/mol). The heat of formation of tricyclopentane was estimated to be 132 kcal/mol, leading to a strain energy of 143 kcal/mol. This makes it one of the most highly strained of known hydrocarbons on a per carbon basis.

[1.1.1]Propellane (**1**)[1] has proven to be a remarkably interesting hydrocarbon, and its reactions have been examined in considerable detail.[2] An isomer, tricyclo[2.1.0.0^{1,3}] pentane (**2**), again having three bridged cyclopropane rings, also appeared interesting. We have examined **2** both experimentally and theoretically.[3] It might be anticipated that **2** would have a greater strain energy than **1**, and having a bicyclobutane unit, it might be expected to undergo thermal rearrangement more easily than **1**. It is also the first member of a series of bridged spiropentanes (**3**) that has been of interest to us.[4,5]



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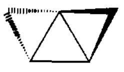

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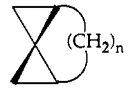

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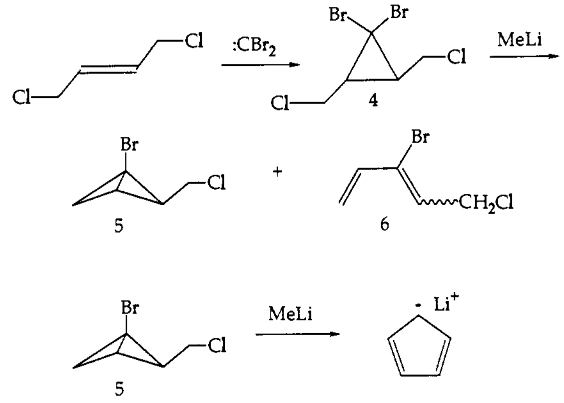
The remarkably simple synthesis of **1** developed by Szeimies et al.[6] led us to attempt the preparation of **2** by a similar method (Scheme I). The addition of dibromocarbene derived from bromoform to *trans*-1,4-dichloro-2-butene gave the tetrahalide **4** in 4% yield. A higher yield (50%) could be obtained using phenyl (tribromomethyl)mercury[7] as the source of dibromocarbene. The reaction of **4** with methyllithium in ether gave 1-bromo-2-(chloromethyl)bicyclo[1.1.0]butane (**5**) and 3-bromo-5-chloro-1,3-pentadiene (**6**). The compounds were formed in ~1:1 ratio. However, the isolation of pure **5** proved to be difficult, and it was obtained in 13% yield.

Scheme I



The reaction of **5** with methyllithium gave lithium cyclopentadienide as the product (Scheme I). In order to learn more about the course of the reaction, it was followed using ^{13}C NMR spectroscopy. This required some knowledge of the chemical shifts to be expected from each of species involved in the reaction. It is known that IGLO[8] ab initio calculations are remarkably effective in predicting ^{13}C NMR chemical shifts.[9] The initially formed product in the reaction would be 1-lithio-2-(chloromethyl)bicyclo[1.1.0]butane (**7**). Its geometry was calculated at the RHF/6-31G* theoretical level, and the ^{13}C chemical shifts were calculated using basis set II.[8] The values are shown in Table I. The geometry of **2** also was calculated, and whereas the symmetrical structure was a minimum at HF/6-31G*, it was calculated to be a transition state at MP2/6-31G* (i.e., it had one imaginary vibrational frequency). Removal of the symmetry constraint led to a somewhat unsymmetrical structure (Figure 1). Its NMR chemical shifts are also given in Table I. The difference in energy between the unsymmetrical and symmetrical structures was only 0.9 kcal/mol (Table II), and with most methods of observation, it would appear to have the average structure.

The reaction of **5** with methyllithium was carried out in ether/THF at –78 °C. The resonances of **5** were replaced by signals (Table I) whose shifts are in good agreement with those calculated

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® Abstract published in *Advance ACS Abstracts*, October 15, 1993.

[1] Wiberg, K. B.; Walker, F. H. *J. Am. Chem. Soc.* **1982**, *104*, 5239.

[2] For a review, see: Wiberg, K. B. *Chem. Rev.* **1989**, *89*, 975. For later studies, see: Kaszynski, P.; Friedli, A.; Michl, J. *J. Am. Chem. Soc.* **1992**, *114*, 601. Kaszynski, P.; McMurdie, N.; Michl, J. *J. Org. Chem.* **1991**, *56*, 307. Zefirov, N. S.; Sadovays, N. K.; Surmina, L. S.; Gudunov, I. A.; Kozmin, A. S.; Petekhin, K. A.; Maleev, K. A.; Struchkov, Yu. T. *Isz. Akad. Nauk. USSR, Ser. Khim.* **1988**, 2648. Bunz, U.; Szeimies, G. *Tetrahedron Lett.* **1990**, *31*, 651. Della, E. W.; Taylor, D. K.; Tsanaktsidis, J. *Tetrahedron Lett.* **1990**, *31*, 5219. Della, E. W.; Taylor, D. K. *Aust. J. Chem.* **1990**, *43*, 945. Adcock, W.; Krstic, A. R. *Tetrahedron Lett.* **1992**, *33*, 7397. Adcock, J. L.; Gakh, A. A. *J. Org. Chem.* **1992**, *57*, 6206. Scaiano, J. C.; McGarry, P. F. *Tetrahedron Lett.* **1993**, *34*, 1243.

[3] For a preliminary account of this study, see: Wiberg, K. B.; McClusky, J. V. *Tetrahedron Lett.* **1987**, *28*, 5411.

[4] Wiberg, K. B. *J. Org. Chem.* **1985**, *50*, 5285.

[5] Wiberg, K. B.; Chaves, A. *J. Am. Chem. Soc.* **1989**, *111*, 8052.

[6] Semmler, K.; Szeimies, G.; Belzner, J. *J. Am. Chem. Soc.* **1985**, *107*, 6410. Belzner, J.; Bunz, U.; Semmler, K.; Szeimies, G.; Opitz, K.; Schlüter, A. *Chem. Ber.* **1989**, *122*, 397.

[7] Seyferth, D.; Lambert, R. L., Jr. *J. Organomet. Chem.* **1969**, *16*, 21.

[8] Schindler, M.; Kutzelnigg, W. *J. Chem. Phys.* **1982**, *76*, 1919; *J. Am. Chem. Soc.* **1983**, *105*, 1360.

[9] Kutzelnigg, W. *J. Mol. Struct.* **1989**, *202*, 11.

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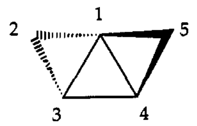
Table I. IGLO Calculations and Experimental NMR Chemical Shifts of **2** and **7**



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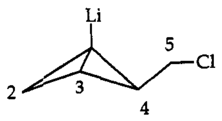


7

carbon no.	calculated shift	time-averaged shift	experimental value
trans-Tricyclo[2.1.0.0^{1,3}]pentane (**2**) MP2/6-31G* C_1 Structure[a]			
1	11.6	11.6	solvent obscured
2	62.9	44.0	38.8
3	16.9	24.5	solvent obscured
4	32.1	24.5	solvent obscured
5	25.2	44.0	38.8
1-Lithio-2-(chloromethyl)bicyclo[1.1.0]butane (**7**)			
1	-7.3		-14.0
2	38.1		43.8
3	3.1		2.1
4	23.0		27.6
5	42.6		44.5

[a] The 1,3 bond is long, and the 1,4 bond is short.

for the lithio derivative **7**. It was stable for a long time at temperatures below -70 °C. Treatment with phenylthiol at -78 °C led to the formation of 2-(chloromethyl)bicyclo[1.1.0]butane (**8**).

When the solution was warmed to -50 °C, the signals due to **7** disappeared and lithium cyclopentadienide was formed. Treatment with phenylthiol gave cyclopentadiene in good yield.

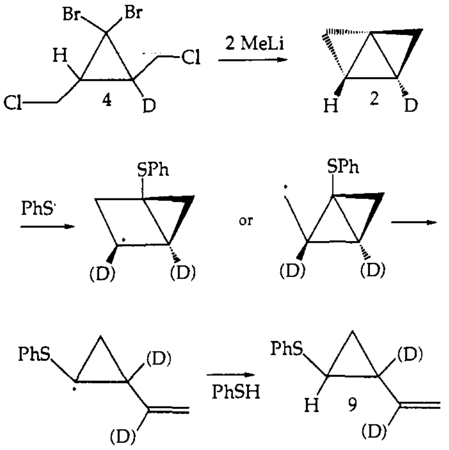
A solution of **7** was then warmed to -55 °C, and after 45 min, phenylthiol was added. If tricyclopentane **2** were present, phenylthiol would be expected to react readily, in accord with observations on other bicyclobutane derivatives.[10] The products were 2-(chloromethyl)bicyclo[1.1.0]butane (**8**), 2-vinyl-1-cyclopropyl phenyl sulfide (**9**), and cyclopentadiene in a 2:1:1 ratio. Sulfide **9** could be purified by preparative TLC. Decoupling of the protons at C_3 in the NMR spectrum showed a 3.7-Hz coupling between the protons at C_1 and C_2 which is consistent with a trans configuration.

An examination of the ^{13}C NMR spectrum of the solution of **7** at -55 °C showed the formation of a new signal at δ 39, which then decreased as the cyclopentadienide ion was formed. Thus, there was an intermediate between the lithio compound **7** and cyclopentadiene. The calculated NMR spectrum of **2** had a band at δ 44 (for the time-averaged spectrum) plus other bands that would be obscured by the solvent. Therefore, **2** is the most likely intermediate.

These data provide good evidence that **2** is formed as an intermediate in the reaction. The addition of phenylthiol is presumably a free-radical process and probably proceeds as shown in Scheme II. Further evidence for this course of reaction was obtained by preparing **4** with one deuterium. The deuterium-labeled 1,4-dichloro-2-butene was prepared by the procedure of Corey et al.[11] The reaction with methyllithium followed by phenylthiol gave **9** containing deuterium only at the positions indicated in the scheme. This is in accord with the proposed mode of formation.

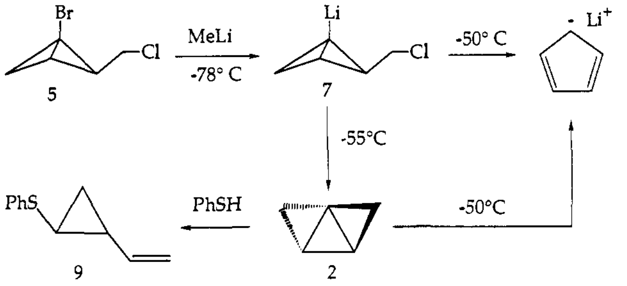
The entire course of the reactions is summarized in Scheme III. It seems quite clear that **2** is formed, but its high reactivity makes it impractical to try to isolate it as a pure substance. The facile rearrangement forming cyclopentadiene is of special interest because of the change in the stereochemistry of the hydrogens during the reaction. In **2**, the hydrogens attached to the center cyclopropane ring must be trans, but in cyclopentadiene, the corresponding hydrogens are cis. Therefore, inversion of configuration is required at one of the carbons. If it were not for this problem, the reaction could easily be formulated as a retrocarbene addition giving **10**, which would be expected to undergo a facile hydrogen migration leading to cyclopentadiene.

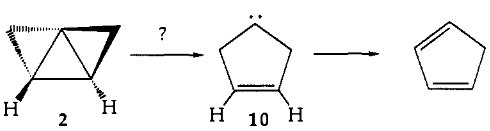
Scheme II[a]



[a] The addition of PhS· to **2** may break either of the indicated C–C bonds, thus leading to products having the deuterium distributed between the indicated positions.

Scheme III





We have carried out some calculations dealing with the process. The potential energy surface was explored at the UMP2/6-31G* theoretical level. The length of one of the internal C–C bonds ($r(C_1C_3)$) might be appropriate as a description of the reaction coordinate. However, a set of geometry optimizations for different values of $r(C_1C_3)$ led only to an increase in energy without much change in the other bond lengths or in the orientation of the hydrogen at C_3. The geometry for $r(C_1C_3)$ = 1.8 Å was then taken as a starting point, and the hydrogen at C_3 was set to give an approximately planar radical center. A UMP2/6-31G* optimization of the other coordinates led to a geometry with $r(C_1C_3)$ = 2.06 Å with an energy (PMP2) 10 kcal/mol above that of **2**. A UMP2/6-31G* geometry optimization to a transition state led to structure **11** (Figure 1), and an activation energy of 24 kcal/mol (Table II). The calculation led to considerable spin contamination (s^2 = 1.01), and so there was concern about the accuracy of projecting out the spin contamination. For a structure of this type, one might expect the singlet and triplet energies to be close, with the latter somewhat higher because of the little residual bonding in the activated complex. Spin contamination is usually considerably smaller for triplets. Therefore, a geometry optimization for the corresponding triplet also was carried out giving essentially the same geometry (rC_1C_3) = 2.075 vs 2.095 Å for the singlet transition state). It had about the same energy (Table II), corresponding to an activation energy of 23 kcal/mol. This would be an upper limit to the activation energy.

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(10) Skattebol, L. *Tetrahedron Lett.* **1970**, 2361.

(11) Corey, E. J.; Kim, C. U.; Takeda, M. *Tetrahedron Lett.* **1972**, 4339.

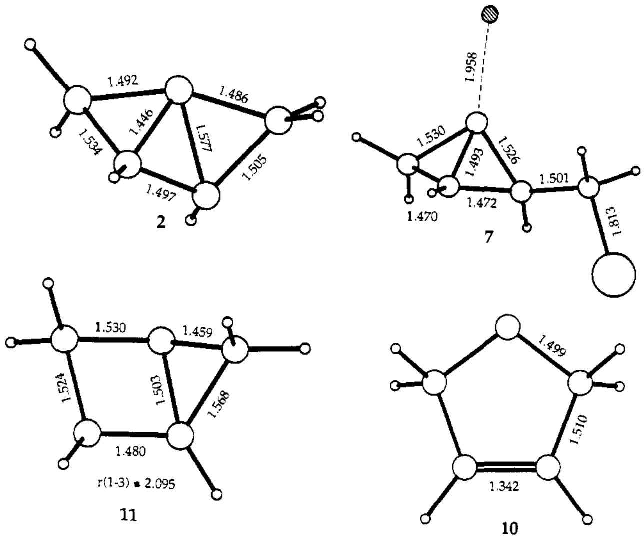


Figure 1. Calculated structures for tricyclopentane **2**, 1-lithio-2-(chloromethyl)bicyclobutane **7**, the transition state **11**, and cyclopentenylcarbene **10**.

Table II. Calculated MP2/6-31G* Energies[a]

compound	*E*, H	ZPE, kcal/mol	rel *E*, kcal/mol	
tricyclopentane **2**, C_1	–193.31131	56.0	86.2	0.0
tricyclopentane **2**, C_2	–193.31035	56.3	87.1	0.9
transition state **11**, singlet	–193.27128[b]	54.7		23.8
transition state **11**, triplet	–193.27177[c]	54.7		23.5
cyclopentadiene	–193.44967	56.6	0.0	–86.2
cyclopentenylcarbene **10**, RMP2	–193.32320	55.5	78.3	–8.0
cyclopentenylcarbene **10**, UMP2	–193.32385[d]	55.5	77.9	–8.4
[1.1.1]propellane	–193.37471	57.7	38.1	–48.1

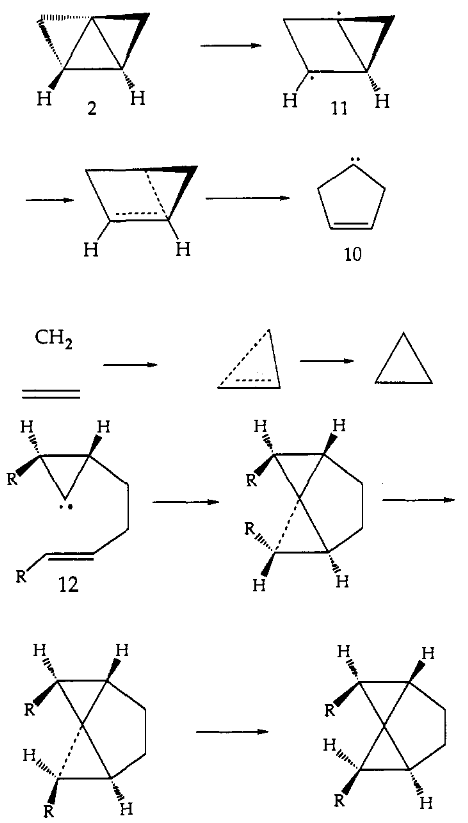
[a] All electrons were correlated (MP2 = full). The energies for the diradical species were obtained via UMP2/6-31G* calculations and have the first component of the spin contamination projected out. The ZPE energies are based on the MP2/6-31G* vibrational frequency calculations and were scaled by 0.96. The relative energies include the zero-point energies. [b] UMP2/6-31G* = –193.26648, s^2 = 1.01; after correction for spin contamination, s^2 = 0.00. [c] UMP2/6-31G* = –193.26895, s^2 = 2.025; after correction for spin contamination, s^2 = 2.00. [d] UMP2/6-31G* = –193.32026, s^2 = 0.589; after correction for spin contamination, s^2 = 0.00.

Attempts to locate an intermediate between the initial transition state and the product carbene at this theoretical level proved to be unsuccessful.[12] The structure and energy of cyclopentenylcarbene **10** also were calculated. The UMP2 structure had considerable spin contamination (s^2 = 0.59), but here, the energy after projecting out the spin contamination was essentially the same as that obtained using RMP2/6-31G*. Both energies are given in Table II. The structures of the compounds and the transition state are shown in Figure 1.

The reaction appears to take the following course (Scheme IV). Stretching one of the internal C–C bonds in tricyclopentane **2** leads to the transition state **11** which lies about 23 kcal/mol above **2**. Here, the hydrogen at the CH center has moved about halfway toward inversion of configuration. It is now possible to open the other central C–C bond giving cyclopentenylcarbene. It is likely that there are no intermediates between the first transition state and the carbene product.

It is possible to make an estimate of the activation enthalpy for the ring opening of **2**. At –55 °C, the product ratio found in the phenylthiol trapping experiment suggests that the half-life of **2** must be on the order of 30 min, leading to a first-order rate constant of about 4×10^{-4} s^{-1}. In view of the close similarity between the structures of **2** and the transition state, the entropy change must be close to zero. With these assumptions, $\Delta H^{\ddagger} \simeq$ 16 kcal/mol. Thus, the theoretical estimate of the activation enthalpy is in reasonable agreement with the experimental data, especially considering the modest theoretical level that was used.

Scheme IV



This course of reaction bears an interesting resemblance to the mechanism of the addition of methylene to a C=C double bond[13] and to the anomalous intramolecular carbene closure observed with a substituted 2-(3-buten-1-yl)cyclopropylidene (**12**, R = $CH_3OCH_2CH_2$-) which occurs with inversion of configuration at one center.[5] The addition of methylene to ethylene is believed to involve an unsymmetrical approach in which one C–C bond is initially formed to a considerable extent and the other is formed only weakly (Scheme IV). The reverse of the ring opening of **2** corresponds to an extreme of this process. On going from the carbene to the transition state, one C–C bond is formed essentially completely and the second is best described as a diradical. Similarly, in the closure of **12**, if the second C–C bond is formed weakly, the steric interaction of the substituent groups could allow inversion of configuration at the substituted center before the second ring is formed. The details of these transformations continue to be studied.

The calculated energies also allow an estimate of the heat of formation and the strain energy of **2**. The difference in energy compared to [1.1.1]propellane is 48 kcal/mol, and the latter has a heat of formation of 84 ± 1 kcal/mol.[14] This leads to a heat of formation of **2** of 132 kcal/mol and a strain energy of 143 kcal/mol, making it one of the most highly strained of organic compounds on a per carbon basis (29 kcal/mol/carbon).

Experimental Section

General Information. Compounds obtained commercially were purchased from Aldrich Chemical Co. and used without further purification unless otherwise noted. The NMR spectra were taken in $CDCl_3$ (δ 7.24 for ^{1}H NMR and δ 77.0 for ^{13}C NMR) unless otherwise noted. Gas

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[12] A bicyclo[2.1.0]pentane-1,3-diyl intermediate was found at the UHF/6-31G* level, but it is probably an artifact of this lower level of theory.

[13] Zurawski, B.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1978**, *100*, 2654.

[14] Wiberg, K. B.; Dailey, W. P.; Waddell, S. T.; Crocker, L. S.; Newton, M. *J. Am. Chem. Soc.* **1985**, *107*, 7247.

chromatographic analysis was performed on a Hewlett-Packard 5890 gas chromatograph using a 30-m bonded MeSi capillary column with a 2-mm i.d. Preparative GC was performed using a Varian Aerograph Model 950 gas chromatograph using columns described below. Electronic impact ionization mass spectra were recorded at 70 eV. CIMS spectra were taken using isobutane as the reactant gas. High-resolution mass spectra were obtained using a Kratos MS-80 RFA high-resolution mass spectrometer. Boiling points and melting points are uncorrected. Vacuum-transfer distillations reported below were performed at pressures of less than 10^{-3} Torr on a system equipped with a mercury diffusion pump. Ab initio structures and energies were calculated using the GAUSSIAN 92 and GAUSSIAN 93 packages.[15] Chemical shift calculations were performed using the IGLO program.[8]

1,1-Dibromo-2,3-*trans*-bis(chloromethyl)cyclopropane (4). To a rapidly stirred, ice-bath-cooled solution of 185 mL of bromoform (2.15 mol), 110 mL (130 g, 1.05 mol) of 1,4-dichloro-2-butene (85% trans, freshly distilled), 5.0 g of benzyltriethylammonium chloride, 5 mL of ethanol, and 120 mL of methylene chloride was added 500 mL of 50% (w/w) aqueous sodium hydroxide. Addition occurred over 15–20 min so that the reaction temperature remained below 30 °C. After the addition of base, the reaction mixture was allowed to stir overnight. Then, 500 mL of water and 500 mL of hexanes were added, and the reaction mixture was allowed to partially separate. The top aqueous layer was then suctioned off. The remaining black suspension was filtered through Celite. The filtrate was separated and the aqueous layer discarded. The organic layer was first dried with $MgSO_4$ and then concentrated on a rotary evaporator to remove the hexanes and methylene chloride. The concentrate was then fractionally distilled (≤60 °C, 18 mmHg) to remove the bromoform and unreacted olefin. The remaining dark liquid was distilled via Kugelrohr (≤90 °C, 1 mmHg) to give 43 g of crude product. During distillation and isolation, an isomer of the desired product was formed which made isolation of the compound difficult because of nearly identical retention times, weights, and rates of chromatographic elution. Triple recrystallization from pentane at −78 °C gave 12.75 g (0.43 mol, 4.3% yield based upon starting olefin) of pure 1,1-dibromo-2,3-*trans*-bis(chloromethyl)cyclopropane, white crystals with a melting point of 43.5 °C. ^{1}H NMR: δ 3.64 (d, J = 7.9 Hz, 4H, CH_2Cl), 1.79 (t, J = 7.9 Hz, 2H, cyclopropyl). ^{13}C NMR (ether-d_{10}): δ 45.98, 37.87, 31.98. EI mass spectrum (70 eV): 296 (1.1), 247 (73), 234 (62), 199 (100), 155 (70), 100 (58). GCCI: 297 (9), 261 (100), 181 (59). Elemental analysis calcd for $C_5H_6Br_2Cl_2$: C, 20.23; H. 2.04; Cl, 23.89; Br, 53.68. Found: C, 20.34; H, 2.05; Cl, 23.89; Br, 52.84.

The tetrahalide may also be prepared as follows. A mixture of 6.9 g (48 mmol) of *trans*-1,4-dichloro-2-butene and 5.6 g (11 mmol) of phenyl (tribromomethyl)mercury was heated with stirring at 95 °C for 2 h. Most of the unreacted starting material was removed under aspirator pressure. The product was extracted from the resulting paste with pentane, and the pentane solution was concentrated. The product was chromatographed using Kieselgel 60 with pentane as the eluent. The purified material was recrystallized from pentane giving 1.64 g (52%) of the tetrahalide.

1-Bromo-2-(chloromethyl)bicyclo[1.1.0]butane (5). To a magnetically stirred solution of 2.96 g (10.0 mmol) of 1,1-dibromo-2,3-*trans*-bis-(chloromethyl)cyclopropane in 10 mL of diethyl ether at −78 °C under an argon atmosphere was added 14.3 mL of a solution of 1.4 M MeLi in diethyl ether (low salt). This mixture was allowed to stir at −78 °C for 50 min. Then, 1.60 g (10.0 mmol) of 2-naphthalenethiol, which had been dissolved in 30 mL of dry ether, was added. After the addition was complete, the flask was allowed to warm to 0 °C in an ice bath. Stirring at 0 °C was continued for 30 min. After the additional stirring time, the ether was concentrated to approximately one-fourth of the original volume by careful use of a rotary evaporator equipped with an ice bath. The remaining ether solution was then purified by vacuum transfer to remove all the salts and higher boiling products. The rest of the ether was carefully removed by rotary evaporation to yield 225 mg (1.24 mmol, 12.4% based upon starting tetrahalide) of material shown to be 94% pure 1-bromo-2-(chloromethyl)bicyclo[1.1.0]butane by GC analysis. The compound is a liquid which is acid sensitive and polymerizes quickly at room temperature in air. ^{1}H NMR: δ 1.12 (br s, 1H), 1.53 (br t, J = 6.4 Hz, 1H), 1.95 (d, 3.1 Hz, 1H), 2.09 (d, 3.1 Hz, 1H), 3.53 (dd, J = 6.4 Hz, $\Delta\nu$ = 3.1 Hz, 2H). ^{13}C NMR (in ether d_{10}): δ 48.86 (CH_2Cl), 42.65 (CH wing methine), 35.37 (CH_2), 21.92 (C–Br), 12.01 (CH bridgehead). EIMS: 184 (1), 182 (5), 180 (4), 145 (3), 119 (2), 103 (4), 101 (13), 65 (100). CIMS: 183 (70), 147 (40), 145 (40), 103 (42), 101 (100). HRMS: calcd 181.9322, found 181.9313.

The other product, 3-bromo-1-chloro-2,4-pentadiene was formed in about equal amount and could be isolated by preparative GC (5% OV-101) if the reaction was quenched with methanol. ^{1}H NMR: δ 4.17 (d, 1H), 5.48 (d, 1H), 5.76 (d, 1H), 6.26 (t, 1H), 6.57 (dd, 1H). EIMS: 180 (20), 145 (37), 101 (19), 66 (39), 65 (100), 39 (31). HRMS: calcd 181.9322, found 181.9312.

1-Lithio-2-(chloromethyl)bicyclo[1.1.0]butane (7). A. Low-temperature ^{13}C NMR Studies. MeLi (0.420 mmol, 0.3 mL, 1.4 M) in diethyl ether was placed into an NMR tube and cooled to −78 °C. To the tube was added 8 μL of THF-d_8. To this mixture was then added 38 mg (0.21 mmol) of 1-bromo-2-(chloromethyl)bicyclo[1.1.0]butane in 300 μL of diethyl ether-d_{10}. The NMR tube was placed into the probe of the spectrometer which had been precooled to −78 °C. The probe temperature was held constant during the acquisition. A series of spectra were taken over time which showed the disappearance of starting material and the appearance of six new signals. Five of these peaks are assignable to the lithio species with the sixth peak being the signal for the MeBr which is produced during the halogen–metal exchange. After approximately 1.5 h, the starting material was completely consumed to yield the stable lithio compound. ^{13}C NMR: δ 44.45 (CH_2Cl), 43.79 (CH wing methine), 27.57 (CH_2 wing methylene), 2.11 (CH bridgehead methine), −14.04 (CLi). The ^{1}H NMR spectrum of the compound was not obtainable because of overlap with the extremely large solvent signals.

The spectrum is closely matched by the predictions from IGLO calculations performed on the gas-phase MP2/6-31G*-optimized structure which has the lithium and chlorine atoms arranged in the anti configuration (Table I).

B. Trapping Studies. Formation of 2-(Chloromethyl)bicyclo[1.1.0]-butane (8). Into a dry round-bottom flask equipped with a magnetic stirrer and an argon atmosphere and cooled to −78 °C was placed 40 mg (0.22 mmol) of 1-bromo-2-(chloromethyl)bicyclo[1.1.0]butane in 2 mL of diethyl ether. To this was added 10 μL of dry THF. Next, 0.5 mL of a solution of 1.4 M MeLi (0.7 mmol) in ether was added over 2 min. The reaction mixture was then allowed to stir for 1 h at −78 °C. Then, an excess of thiophenol was added via syringe to quench all the lithio compounds. The flask was then allowed to warm to 0 °C. Analysis by GC and GCMS against the internal THF standard showed that there was 90% conversion to 2-(chloromethyl)bicyclo[1.1.0]butane. ^{13}C NMR (1:1 ether-d_{10} and -h_{10}): δ 49.71 (CH_2Cl), 44.53 (CH wing methine), 27.36 (CH_2 wing methylene), 9.02 (CH bridgehead). ^{1}H NMR: δ 3.54 (d, J = 6.8 Hz, 2H), (the other bands were obscured by the solvent). EIMS: 104 (M^+, 1.2), 102 (M^+, 3.7), 67 (M − Cl, 100), 65 (29), 51 (10), 41 (46), 39 (58).

Tricyclo[2.1.0.0^{1,3}]pentane. A. Trapping Study. *trans*-(2-Vinyl-1-cyclopropyl) Phenyl Sulfide. To a flame-dried flask equipped with magnetic stirring and purged with argon was added 20 mg (0.11 mmol) of 1-bromo-2-(chloromethyl)bicyclo[1.1.0]butane in 3 mL of dry ether. To this was added 10 μL of dry tetrahydrofuran. The mixture was cooled to −78 °C in a dry ice-acetone bath, and 0.25 mL of a 1.4 M solution of MeLi (low salt) in ether was added. The reaction mixture was allowed to stir for 2 h at −78 °C and then carefully warmed to −55 °C for 45 min. Thiophenol (0.075 mL) was then carefully added to the reaction flask. GCMS analysis showed three major products from the reaction: 2-(chloromethyl)bicyclo[1.1.0]butane identical to the product described above, *trans*-(2-vinyl-1-cyclopropyl) phenyl sulfide, and cyclopentadiene in a 2:1:1 ratio (approximately a 20% yield of trapping product, based upon calculations from internal standards). Cyclopentadiene was identified by comparison with an authentic sample. The sulfide could be purified by preparative TLC using 2:1 ethyl acetate/hexanes. Using decoupled ^{1}H NMR spectra, it was possible to show that there was a 3.7-Hz coupling between the protons located at the 1 and 2 positions of the cyclopropyl ring, which is consistent with a trans configuration. ^{1}H NMR: δ 1.15 (m, 2H, ring methylene), 1.69 (m, 1H, allyl), 2.16 (m, 1H, thiol carbon methine), 5.15 (dd, 2H, terminal vinyl), 5.5 (m, 1H, vinyl), 7.05–7.20 (m, 5H, phenyl). GCEI: 176 (M^+, 7), 110 (40), 99 (4), 67 (100), 65 (19), 40 (5). HRMS: calcd for $C_{11}H_{12}S$ 176.0660, found 176.0666.

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(15) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. GAUSSIAN92, Revision A; Gaussian, Inc.: Pittsburgh, PA, 1992. Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. GAUSSIAN93, developmental version, Revision C3; Gaussian, Inc.: Pittsburgh, PA, 1993.

B. Low-Temperature ^{13}C NMR Studies. MeLi (0.30 mL, 1.4 M, 0.42 mmol) in diethyl ether-h_{10} was placed into a dry argon-purged NMR tube which had been sealed with a rubber septum. To this was then added 8 μL of THF-d_8. An NMR spinner was placed on the tube, and then the tube was cooled to −78 °C in a flask of powdered dry ice. 1-Bromo-2-(chloromethyl)bicyclo[1.1.0]butane (38 mg, 0.21 mmol) in 0.25 mL of diethyl ether-d_{10} was then carefully added to the MeLi solution. After a quick shaking of the entire dry ice container to mix the layers, the NMR tube was inserted into the probe of the NMR which had been precooled to −78 °C. ^{13}C NMR spectra of 1200 scans each were then taken for 2 h which showed the decrease in signals from the starting material and the development of peaks assigned to 1-lithio-2-(chloromethyl)bicyclo[1.1.0]butane and methyl bromide as described above. At the end of the 2 h most of the starting material had been consumed and the dominant spectrum was that of the lithio compound. The probe was then warmed to −55 °C. The same procedure for acquiring spectra was followed as described above. The signals for the lithio compound decreased, and peaks assignable to cyclopentadiene and the lithium-stabilized cyclopentadienyl anion appeared at δ 41.81, 132.72, 133.29 and δ 76.24, 94.35, 115.49, 133.15 respectively. After the formation of the bridgehead lithio compound, an additional signal grew into the spectrum at δ 38.8 which was present while there was a detectable concentration of the lithio species and before only cyclopentadiene-derived products remained in the spectrum. This signal is in good agreement with the time-averaged signal predicted by the IGLO calculations of δ 44.0 for the methylene carbons on the wings of the tricycle. Other peaks appeared to be obscured by the broad solvent and THF signals.

Reaction of 2,3-Bis(chloromethyl)-1,1-dibromocyclopropane-*2-d*$_1$ with Methyllithium and Phenylthiol. The deuterium-labeled tetrahalide was prepared from *trans*-1,4-dichloro-2-butene-*2-d*$_1$ by the procedure described above. The reaction with methyllithium followed by phenylthiol as described above gave 2-vinyl-1-cyclopropyl phenyl sulfide. ^{1}H and ^{2}H NMR analysis showed the deuterium to be located at the 1-vinyl and 2-cyclopropyl carbons. ^{2}H NMR (CH_2Cl_2 referenced to a trace of $CDCl_3$ at δ 7.24): δ 5.53 (br s), 1.63 (br s). The two bands were of equal size.

Acknowledgment. This investigation was supported by a grant from the National Science Foundation. We thank the Pittsburgh Supercomputing Center for a generous allocation of computer time.