1,3-Bridged Cyclopropenes

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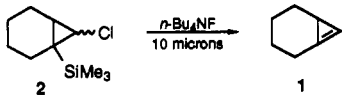
Abstract: Solid fluoride deposited on glass helices has been used to effect the gas-phase elimination of 1-(trimethylsilyl)-7-chlorobicyclo[4.1.0]heptane and 1-(trimethylsilyl)-8-chlorobicyclo[5.1.0]octane to yield bicyclo[4.1.0]hept-1(7)-ene and bicyclo[5.1.0]oct-1(8)-ene, respectively. Bicyclo[4.1.0]hept-1(7)-ene dimerizes below ca. −90 °C via an ene reaction to yield a new cyclopropene, which then couples to form tetramers. The structures of two tricyclohexane tetramers were determined by X-ray crystallography. The ene dimer was found to react with molecular oxygen to yield two carbonyl compounds identified as 2-(1-bicyclo[4.1.0]heptyl)cyclohexene-1-carboxaldehyde and 3-(1-bicyclo[4.1.0]heptyl)cyclohept-2-en-1-one. These compounds are thought to result from the reaction of molecular oxygen with carbenes that would arise from cyclopropene–vinylcarbene rearrangements. Bicyclo[5.1.0]oct-1(8)-ene is considerably more stable than its lower homologue but also dimerizes via an ene reaction. 7-Chlorobicyclo[4.1.0]hept-1(7)-ene rearranges below −90 °C to yield 2-chloro-1,3-cycloheptadiene.

Introduction

Although base-induced elimination reactions have found wide application in the synthesis of strained alkenes, the method is often complicated by a competing process in which the incipient alkene is trapped by nucleophilic addition of the base.[2] Several recent studies have shown that these bimolecular side reactions can be avoided when the base is supported on an inert surface and the reaction is carried out in vacuo.[3] This procedure, now commonly known as the vacuum gas–solid reaction (VGSR) technique,[4] has the additional advantage that very unstable species may be isolated under conditions that allow detailed studies of their physical and chemical properties. We have recently extended the scope of this procedure to include the use of solid fluoride supported on glass helices to effect the elimination of β-halosilanes.[5] This route to strained alkenes is particularly attractive since the reaction can be carried out under very mild conditions and the starting materials are readily available.[6] This paper describes our work on the gas-phase synthesis of 1,3-bridged cyclopropenes[7] and delineates some of the chemistry of these compounds. Cyclopropene **1** was chosen for our initial work since it has already been the object of considerable speculation with regard to its properties[8] but has never been synthesized.

Results and Discussion

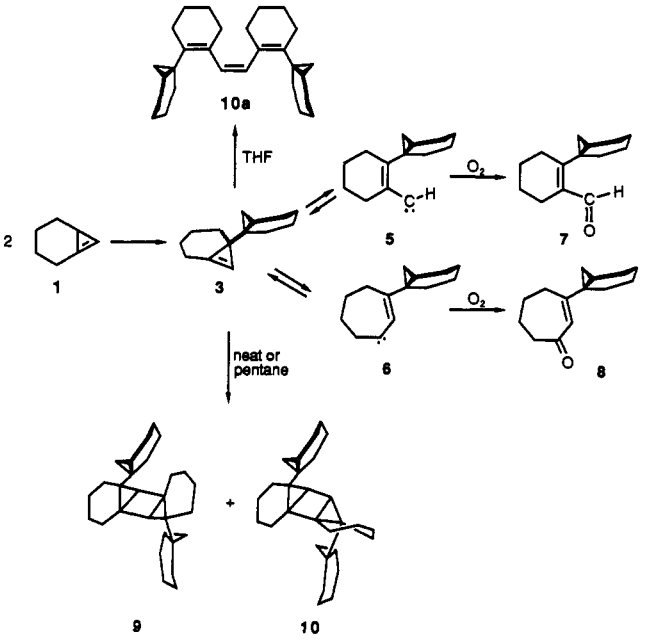
The cyclopropene can be generated at room temperature and isolated as a solid matrix at −196 °C by slowly passing **2** through a column packed with n-$Bu_4N^+F^-$ deposited on glass helices.[5]



2 **1**

The chemistry of **1** is presented in Scheme I. Dimerization was observed by NMR spectroscopy to occur readily below −90 °C. Thus, a weak NMR signal at δ 6.83 tentatively assigned to **1** (cyclopropenyl proton) disappears after a few minutes and is replaced by one at δ 6.72. This new signal is assigned to the ene dimer **3**. Cyclopropenes with hydrogen at C^{-3} often undergo an ene reaction involving the transfer of hydrogen to the double bond of a second molecule with the concurrent formation of a carbon–carbon bond between them.[9] The additional strain in **1** would probably account for this facile dimerization. Steric interactions are presumably too severe to allow transfer of hydrogen from a third molecule of **1** to yield a trimer.

Scheme I



Cyclopropene **3** is a remarkably stable compound. This is most likely due to the steric protection (corset effect) provided by the bicycloheptyl pendant. The stabilization of reactive intermediates from bimolecular reactions by use of steric protecting groups is, of course, well-documented and used frequently as a means to stabilize reactive molecules.[10]

When **3** is exposed to dioxygen, two carbonyl-containing products identified as **7** and **8** can be isolated. The formation of these products may be rationalized in terms of the cyclopropene–vinylcarbene reactions presented in the scheme. Although these rearrangements normally occur at higher temperatures,[11]

(1) National Science Foundation Predoctoral Fellow, 1980–1984.
(2) Shields, T. C.; Gardner, P. D. *J. Am. Chem. Soc.* **1967**, *89*, 5425. See also: Wiberg, K. B.; Barnes, R. K.; Albin, J. *J. Am. Chem. Soc.* **1957**, *79*, 4994.
(3) (a) Denis, J. M.; Niamayoua, R.; Vata, M.; Lablache-Combier, A. *Tetrahedron Lett.* **1980**, *21*, 515. (b) Billups, W. E.; Lin, L.-J.; Casserly, E. W. *J. Am. Chem. Soc.* **1984**, *106*, 3698. (c) Staley, S. W.; Norden, T. D. *J. Am. Chem. Soc.* **1984**, *106*, 3699.
(4) Lacombe, S.; Gonbeau, D.; Cabioch, J.-L.; Pellerin, B.; Denis, J. M.; Pfister-Guillouzo, G. *J. Am. Chem. Soc.* **1988**, *110*, 6964.
(5) Billups, W. E.; Lin. L.-J. *Tetrahedron* **1986**, *42*, 1575.
(6) Paquette, L. A. *Chem. Rev.* **1986**, *86*, 733.
(7) For review of this family of compounds, see: Billups, W. E.; Haley, M. M.; Lee, G.-A. *Chem. Rev.* **1989**, *89*, 1147.
(8) Köbrich, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 464.
(9) (a) Breslow, R.; Dowd, P. *J. Am. Chem. Soc.* **1963**, *85*, 2729. (b) Yoshida, Z.; Miyahara, H. *Chem. Lett.* **1972**, 335. (c) Garratt, P. J.; Tsotinis, A. *J. Org. Chem.* **1990**, *55*, 84.
(10) For some examples, see: Camp, R. L.; Greene, F. D. *J. Am. Chem. Soc.* **1968**, *90*, 7349. Crandall, J. K.; Machleder, W. H. *J. Am. Chem. Soc.* **1968**, *90*, 7347. Maier, G.; Pfriem, S.; Schäfer, U.; Matusch, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 520.

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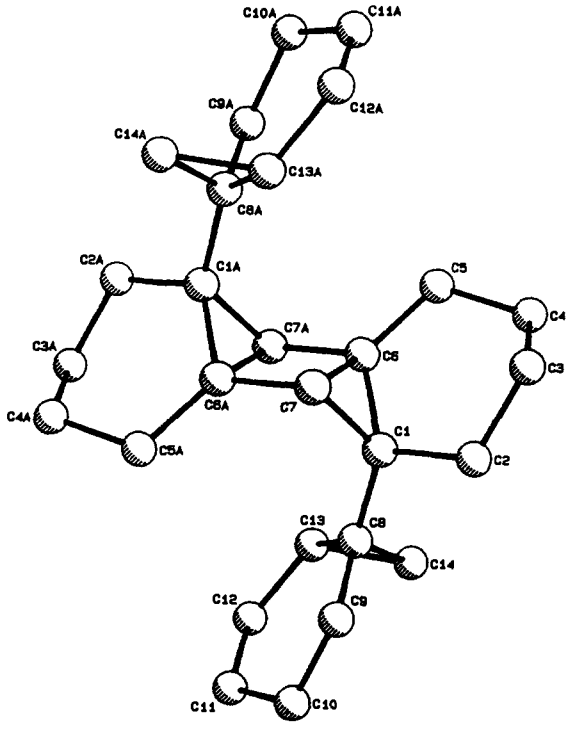


Figure 1. Structure of tetramer **9** showing atom numbering.

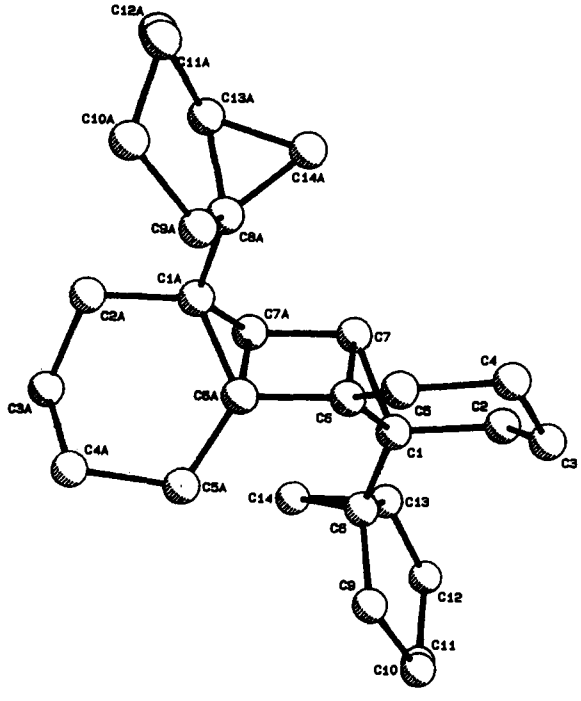
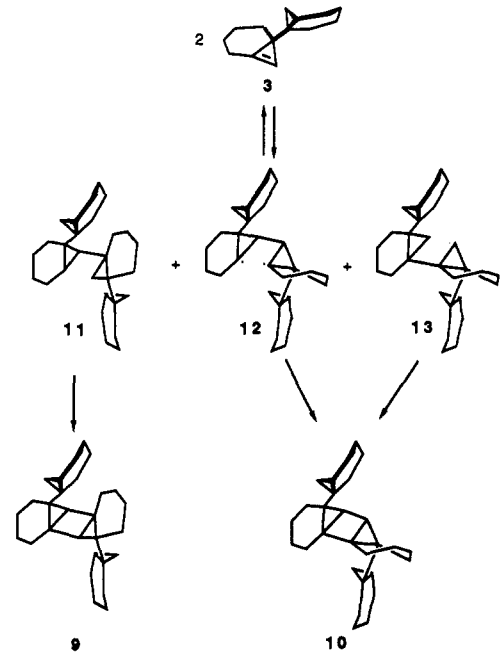


Figure 2. Structure of tetramer **10** showing atom numbering.

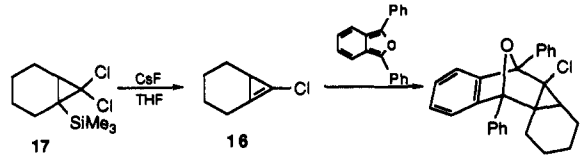
the high strain energy of **3** might be expected to lead to an unusually facile rearrangement for this compound.

Since the reaction of carbenes with dioxygen to yield oxygenated products is well-established,[12] it seems reasonable to implicate the carbenes as the precursors to **7** and **8**; however, the reaction of the cyclopropene itself with molecular oxygen to yield the carbonyl derivatives is a viable alternative.

Scheme II



Scheme III



When an oxygen-free matrix of **3** was allowed to warm slowly to room temperature, a white crystalline compound, mp 210–210.5 °C, shown by mass spectrometry to be a tetramer of **1**, could be isolated in 84% yield. The structure of this compound was shown by single-crystal X-ray analysis to be the tricyclohexane **9**, with trans,anti stereochemistry about the tricyclohexane framework. The X-ray structure of **9** is presented in Figure 1. The carbon connectivities shown in this structure firmly establish the stereochemistry of the precursor cyclopropene as that shown for **3** in Scheme I. Indeed, the transition state leading to **3** would appear to be lower in energy than the one leading to the remaining diastereomer of **3**.[13]

A second tetramer, mp 181–182 °C, identified as **10** by X-ray crystallography (Figure 2), could be isolated when **3** was diluted with pentane and allowed to stand at room temperature for several days. The carbon connectivities in **10** show that it is also a dimer of **3**, with trans,syn stereochemistry with respect to the tricyclohexane framework.

An attractive rationalization for the formation of the tricyclohexane tetramers is illustrated in Scheme II.[14] Initial bond formation would occur to generate biradicals **11**, **12**, and **13**. Simple collapse of **11** with carbon–carbon bond formation would yield **9**. Formation of **10** would require either biradical **12** or **13**, with subsequent formation of the four-membered ring. Biradical **12** with both radical centers tertiary is presumably more stable than **13**. The factors controlling the regiochemistry of these dimerization reactions are obviously delicately balanced and remain to be explained.

A solution of **3** in tetrahydrofuran was observed by NMR spectroscopy to give a new compound with a sharp singlet in the

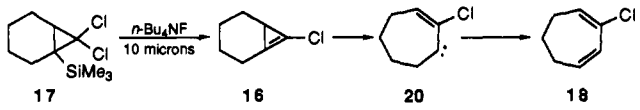
(11) York, E. J.; Dittmar, W.; Stevenson, J. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1973**, *95*, 5680.

(12) (a) Bartlett, P. D.; Traylor, T. G. *J. Am. Chem. Soc.* **1962**, *84*, 3408. (b) Kirmse, W. *Carbene Chemistry*; Academic Press: New York, 1964; p 58. (c) Werstiuk, N. H.; Casal, H. L.; Scaiano, J. C. *Can. J. Chem.* **1984**, *62*, 2391. (d) Girard, M.; Griller, D. *J. Phys. Chem.* **1986**, *90*, 6801. (e) Scaiano, J. C.; McGimpsey, W. G.; Casal, H. L. *J. Org. Chem.* **1989**, *54*, 1612.

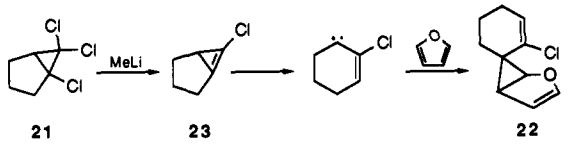
(13) Although no evidence for the formation of a diastereomer of **3** was found, diastereomeric isomerization could occur by epimerization at C-3 via the carbenes shown in Scheme I.

(14) 1,4-Diyls have been implicated previously to explain the products formed from the cycloaddition reactions of cyclopropenes. For an example, see: Padwa, A.; Kennedy, G. D.; Newkome, G. R.; Fronczek, F. R. *J. Am. Chem. Soc.* **1983**, *105*, 137.

Scheme IV



Scheme V



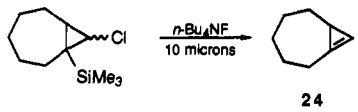
proton NMR spectrum at δ 6.94, suggesting that **3** had rearranged to a new cyclopropene; however, the absence of a C=C stretching frequency for the cyclopropene eliminated this as a viable process. A more careful inspection of both the ^1H and ^{13}C spectra revealed that the spectral properties of this compound are indistinguishable from those exhibited by the triene **10a** (Scheme I), isolated by Wiberg and Artis[15] from the reaction of 1,6-diiodobicyclo-[4.1.0]heptane with methyllithium in ether. These results are consistent with the formation of a long-lived carbene ylide that could dimerize to yield the triene. In the absence of basic solvents, **3** dimerizes to yield the tricyclohexanes illustrated in Scheme II.

Halogenated derivatives of **1** can also be synthesized by using fluoride ion to induce the elimination of β-halocyclopropylsilanes. Chan and Massuda[16] found that **16** can be generated in solution by treating **17** with cesium fluoride in tetrahydrofuran. The cyclopropene was trapped as the Diels–Alder adduct of 1,3-diphenylisobenzofuran. These results are summarized in Scheme III.

In contrast, we have found that elimination of **17** in the gas phase by solid fluoride yields 2-chloro-1,3-cycloheptadiene (**18**) as the only isolable product. This observation can be rationalized in terms of cyclopropene–vinylcarbene rearrangement with subsequent intramolecular insertion of the carbene **20** into a C–H bond, as illustrated in Scheme IV. The cyclopropene–vinylcarbene rearrangement is an unusually facile process in this case, as only **18** could be detected by NMR spectroscopy even at −90 °C. The manner in which the chlorine accelerates this process is not clear. Overlap of the nonbonding orbitals of the halogen with the vacant orbital at the reactive site may be the most important factor.[17b]

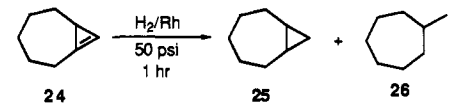
Evidence for cleavage of the central bond of a 1-halocyclopropene has also been observed when **21** is reacted with methyllithium in ether at 25 °C in the presence of furan.[17] The isolation of **22** would require the intermediacy of **23**, opening to the carbene, with subsequent addition to the furan as illustrated in Scheme V.

Other 1,3-bridged cyclopropenes, including the parent hydrocarbon **24**, have also been synthesized as described above for **1**. The fate of this surprisingly stable compound was monitored by observing the cyclopropenyl resonance at δ 6.46. This signal

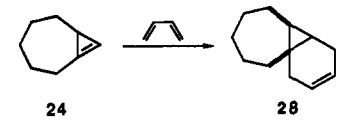


persisted at room temperature for several hours, but was replaced gradually by one at δ 6.38 arising from the ene dimer. Under more controlled conditions, a trimer could also be detected.

Compound **24** is sufficiently long-lived for studies of its chemistry to be carried out. Hydrogenation (50 psi, 1 h) over 5% Rh/C at room temperature yielded a mixture of **25** (53.4%) and **26** (28.6%). A control experiment showed that **25** is not converted to **26** under the reaction conditions, suggesting that **26** arises either by hydrogenolysis of the trans isomer of **25** or via a rhodium complex of the cyclopropene.



The interesting compound **28**, a member of the group of compounds of possible interest with regard to twist-bent bonds,[18] could be prepared by trapping **24** with 1,3-butadiene.



In conclusion, this work demonstrates that the VGSR technique using solid fluoride to eliminate β-halocyclopropylsilanes is widely applicable to the generation and isolation, at low temperature, of very unstable compounds. Since these species can be isolated in the absence of solvents or nucleophiles, studies of their chemical properties can be investigated readily.

Experimental Section

General. Nuclear magnetic resonance spectra were recorded on a JEOL FX90Q (^1H, 90 MHz; ^{13}C, 22.63 MHz) or an IBM AF 300 (^1H, 300.13 MHz; ^{13}C, 75.5 MHz) spectrometer. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane. Coupling constants are expressed in hertz. Unless otherwise noted, NMR spectral data were obtained in $CDCl_3$. Mass spectra were recorded on either a Finnigan Model 3300 GC/MS spectrometer (low resolution, 30 eV) or a double-focussing CEC 21-110 spectrometer (high resolution). Infrared spectra were recorded on a Perkin-Elmer Model 1320 spectrophotometer. A Hewlett-Packard Model 700 gas chromatograph with a thermal conductivity detector and an outlet flow rate of 60 cc of helium per minute was used for all analytical and preparative gas chromatography. X-ray structures were recorded on a Rigaku AFC5S diffractometer with a Texsan Data Reduction and Intensity Analysis program. All boiling and melting points are uncorrected.

Materials. Tetrahydrofuran was distilled from calcium hydride just prior to use. *n*-Pentane and methylene chloride were distilled from calcium hydride under an atmosphere of nitrogen. Redistilled chlorotrimethylsilane was used when this reagent was required. Column chromatography was performed on Baker reagent grade silica gel (60–200 mesh). Merck precoated silica gel plates were used for analytical (100 × 50 × 0.2 mm) and preparative (200 × 200 × 2 mm) thin-layer chromatography. All other chemicals were of reagent quality and used as obtained from the manufacturers. All reactions were carried out in an atmosphere of dry nitrogen.

Vacuum Gas–Solid Reaction (VGSR) Apparatus. The apparatus described previously[5] was used. The apparatus was prepared by charging a column (21 × 3.5 cm with a 34/45 ground-glass joint at the top and a high-vacuum stopcock with a #9 O-ring joint at the bottom) with the adsorbed fluoride reagent described below. The glass helices were supported by a glass-wool plug (3 cm) at the bottom of the column. The entire apparatus was evacuated to 10 mTorr, and that portion of the tube containing the fluoride reagent was either heated by a heating tape or cooled by passing ice water through Tygon tubing wrapped around the column. A series of two to four traps was used to collect and/or fractionate the products. Once the system had reached equilibrium, the rate of addition of starting material could be controlled by adjusting the temperature of the introduction flask.

Preparation of Tetra-*n*-butylammonium Fluoride on Glass Helices. Tetra-*n*-butylammonium fluoride trihydrate (5 g, 15.8 mmol), methylene chloride (30 mL), and glass helices (50 g) were added to a 1-L round-bottomed flask. The solvent was removed under vacuum at room temperature with shaking to prevent formation of a solid mass. The coated glass helices were then transferred to the reaction column described above and dried under vacuum at 25 °C until the final pressure was 10 mTorr.

1-Bromocyclohexene. A solution of sodium amide (50 g, 1.28 mol) in THF (500 mL) was cooled to −40 °C. *tert*-Butyl alcohol (52 g, 0.70

(15) Wiberg, K. E. Personal communication.
(16) Chan, T. H.; Massuda, D. *Tetrahedron Lett.* **1975**, 3383.
(17) (a) Baird, M. S.; Hussain, H. H.; Nethercott, W. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1845. (b) Baird, M. S.; Nethercott, W. *Tetrahedron Lett.* **1983**, *24*, 605. See also: Baird, M. S. *Functionalized Cyclopropenes as Synthetic Intermediates*; In *Top. Curr. Chem.*; de Meijere, A., Ed.; Springer-Verlag: Berlin, 1988; Vol. 144.
(18) Gassman, P. G. *Chem. Commun.* **1967**, 793. Gassman, P. G.; Williams, F. J. *J. Am. Chem. Soc.* **1971**, *93*, 2704.
(19) Sheldrick, G. M. *Acta Crystallogr.*, in press.
(20) Scattering factors were taken from *The International Tables for X-Ray Crystallography*; D. Reidel Publishing Company: Dordrecht, The Netherlands, 1987; Vol. 4, pp 55, 99, and 149.

mol) was then added dropwise and the mixture was stirred for 0.5 h followed by the dropwise addition of 1,2-dibromocyclohexane (42 g, 0.17 mol) in THF (150 mL). This mixture was stirred for 1 h at −40 °C and then for 1 h at room temperature. The precipitated salts were filtered and the THF removed in vacuo. The residue was extracted into ether (200 mL), washed with water and brine, and then dried over anhydrous magnesium sulfate. Distillation provided 18 g (63% yield) of 1-bromocyclohexene.

1-(Trimethylsilyl)cyclohexene. A dry two-necked 250-mL flask was charged with magnesium turnings (3.25 g, 0.134 mol) and fitted with a 150-mL equilibrating addition funnel and a reflux condenser. To the magnesium were added THF (50 mL), trimethylsilyl chloride (15 g, 0.15 mol), and a small crystal of iodine. The mixture was stirred for 0.25 h. 1-Bromocyclohexene (12 g, 74.5 mmol) in THF (75 mL) was then added dropwise so as to maintain a gentle reflux. After the addition was completed, the mixture was heated to maintain reflux for 1 h and then cooled to room temperature. The precipitated salts and excess magnesium were filtered, and the THF was removed in vacuo. The residue was dissolved in ether (200 mL), washed exhaustively with water/brine, and then dried over anhydrous magnesium sulfate. Distillation provided 9.03 g (78.5% yield) of 1-(trimethylsilyl)cyclohexene.

Synthesis of 1-(Trimethylsilyl)-7-chlorobicyclo[4.1.0]heptane (2). 1-(Trimethylsilyl)cyclohexene (5.0 g, 32.4 mmol) in methylene chloride (5 mL) was placed in a 250-mL three-necked flask fitted with two equilibrating addition funnels, a Barrett distilling receiver with condenser, a magnetic stirrer, and a bubbler to maintain a positive nitrogen pressure. The addition funnels were charged with methyllithium (250 mL, 1.4 M) in ether and methylene chloride (20 mL). With vigorous stirring, the methyllithium was added at a rate of 2 drops per second as the methylene chloride was added at about one-fifth this rate. When the addition was completed, methylene chloride was added carefully to quench the methyllithium. The mixture was filtered and the solid was dissolved in ether (200 mL). The combined organic phases were washed with water and brine and dried over anhydrous magnesium sulfate. The solvent was removed under vacuum to give an oil. Distillation of the oil provided 3.61 g of **2** (55% yield) as a mixture of cis and trans isomers. This mixture was purified by preparative gas chromatography (5% SE-30 on Chromosorb WAW, 145 °C).

Elimination of 1-(Trimethylsilyl)-7-chlorobicyclo[4.1.0]heptane (2) over Solid Tetra-*n*-butylammonium Fluoride. Compound **2** (50 mg, 0.25 mmol) was passed through the column containing the solid fluoride at 25 °C. After the product had been collected onto the walls of a cold trap at −196 °C, the liquid nitrogen was replaced by a pentane–liquid nitrogen slush, which allowed the product to flow into a 5-mm NMR tube that had been affixed to the bottom of the cold trap. Solvent (CD_2Cl_2) was distilled into the NMR tube as the product was collected. A torch was then used to seal the NMR tube under vacuum. The ^1H NMR spectrum was taken at −90 °C.

Characterization of Dimer 3. Compound **2** (50 mg, 0.25 mmol) was passed through a fluoride column at 25 °C. Trimethylsilyl fluoride and a small amount of butene were removed in vacuo at −50 °C, and the product was then collected in a tube that had been attached to the cold trap as described above. Spectral properties are as follows: ^1H NMR (90 MHz) δ 6.83 (t, 1 H, J = 1.3 Hz), 2.70–2.30 (m, 2 H), 2.1–0.9 (m, 14 H), 0.7–0.3 (m, 2 H), 0.1 (dd, 1 H, J = 1.8 and 3.1 Hz); ^{13}C NMR δ 111.5, 30.9, 28.1, 24.3, 24.2, 24.0, 23.0, 21.9, 21.7, 17.3, 16.6; IR (CS_2, CCl_4) ν 3055, 2990, 2920, 2850, 2660, 1740, 1660, 1448 cm^{-1}; MS m/e calcd for $C_{14}H_{20}$ 188.1565, found 188.1560; calcd for $^{13}CC_{13}H_{20}$ 189.1599, found 189.1595.

Dimerization of 3 in THF. Compound **2** (201.0 mg, 0.99 mmol) was passed through a fluoride column at 25 °C as described above. After the product was collected, THF (5 mL) was distilled into the cold trap with the exclusion of dioxygen. After 7 days, the mixture was transferred to a small flask and the solvent removed under vacuum. The residue was purified by column chromatography (hexane) to give 78.7 mg of **10a** (yield 84%): ^1H NMR (250 MHz) δ 6.94 (s), 2.3–2.15 (m), 2.14–2.05 (m), 2.07–1.95 (m), 1.90–1.75 (m), 1.71–1.52 (m), 1.40–1.10 (m), 1.05–0.90 (m), 0.64 (dd), 0.42 (dd); ^{13}C NMR δ 143.1 (C), 129.5 (C), 124.9 (CH), 30.2, 29.0, 26.0, 25.6, 23.9, 23.6, 23.0, 22.0, 21.2; IR (CS_2, CCl_4) ν 3055, 2990, 2920, 2850, 2660, 1610, 1445 cm^{-1}.

Reaction of Dimer 3 with Dioxygen. Compound **3** (130.7 mg, 0.64 mmol) was generated as described above and exposed to air. After 7 days the mixture was purified by preparative thin-layer chromatography (methylene chloride) to give three compounds. The first compound (R_f = 0.91) is **10a**. The second compound (R_f = 0.46) is 2-(1-bicyclo[4.1.0]heptyl)cyclohexene-1-carboxaldehyde (**7**), and the third (R_f = 0.19) is 3-(1-bicyclo[4.1.0]heptyl)cyclohept-2-en-1-one (**8**). Spectral data of **8** are as follows: ^1H NMR (300 MHz) δ 5.91 (s, 1 H), 2.54 (t, 2 H, J = 6.1 Hz), 2.48 (t, 2 H, J = 5.9 Hz), 0.80 (dd, 1 H, J = 4.5 and 9.7 Hz), 0.47 (dd, 1 H, J = 4.5 and 5.0 Hz); ^{13}C NMR δ 205.2, 167.4, 128.0, 41.7, 30.6, 29.7, 28.3, 25.5, 23.5, 21.7, 21.0, 20.6, 18.3, 17.3; IR (neat) ν 3058, 2980, 2905, 2842, 2660, 1650 cm^{-1}; MS m/e calcd for $C_{14}H_{20}O$ 204.1514, found 204.1513; calcd for $^{13}CC_{13}H_{20}O$ 205.1548, found 205.1548. Spectral data for **7**: ^1H NMR δ 10.39 (s, 1 H), 2.31 (m, 2 H), 2.14 (m, 2 H), 2.00–1.85 (m, 2 H), 1.80–1.50 (m, 6 H), 1.40–1.20 (m, 4 H), 1.07 (m, 1 H), 0.80 (dd, 1 H, J = 4.7 and 9.3 Hz), 0.63 (dd, 1 H, J = 4.7 and 5.4 Hz); ^{13}C NMR δ 193.2 (CH), 166.4 (C), 134.0 (C), 31.3 (CH_2), 29.7 (CH_2), 23.0 (CH_2), 22.7 (C), 22.4 (CH_2), 22.0 (CH), 22.0 (CH_2), 21.6 (CH_2), 21.5 (CH_2), 20.5 (CH_2), 18.4 (CH_2); IR (neat) ν 1655 cm^{-1}; MS m/e calcd for $C_{14}H_{20}O$ 204.1514, found 204.1514; calcd for $^{13}CC_{13}H_{20}O$ 205.1548, found 205.1548. Spectral data for **7**: ^1H NMR δ 10.39 (s 1 H), 2.31 (m, 2 H), 2.14 (m, 2 H), 2.00–1.85 (m, 2 H), 1.80–1.50 (m, 6 H), 1.40–1.20 (m, 4 H), 1.07 (m, 1 H), 0.80 (dd, 1 H, J = 4.7 and 9.3 Hz), 0.63 (dd, 1 H, J = 4.7 and 5.4 Hz); ^{13}C NMR δ 193.2 (CH), 166.4 (C), 134.0 (C), 31.3 (CH_2), 29.7 (CH_2), 23.0 (CH_2), 22.7 (C), 22.4 (CH_2), 22.0 (CH), 22.0 (CH_2), 21.6 (CH_2), 21.5 (CH_2), 20.5 (CH_2), 18.4 (CH_2); IR (neat) ν 1655 cm^{-1}; MS m/e calcd for $C_{14}H_{20}O$ 204.1514, found 204.1514; calcd for $^{13}CC_{13}H_{20}O$ 205.1548, found 205.1548.

Preparation of Tetramer 9. Compound **2** (130.7 mg, 0.64 mmol) was passed through the fluoride column at 25 °C as described above. The product was transferred under vacuum to a second cold trap and then warmed to room temperature. A white solid appeared on the wall of the trap after 1 day. The product was purified by preparative thin-layer chromatography (hexane) to give 51.0 mg of tetramer **9** (84% yield). The tetramer was then crystallized from pentane as colorless crystals, mp 210.0–210.5 °C. The X-ray structure of **9** showed that it is *anti*-1,8-bis(bicyclo[4.1.0]hept-1-yl)pentacyclo[8.4.0.0^{2,10}.0^{3,8}.0^{3,9}]tetradecane: ^1H NMR (300 MHz) δ 2.12–2.04 (m, 2 H), 1.88–1.70 (m, 18 H), 1.40 (s, 2 H), 1.38–1.10 (m, 12 H), 1.10–1.00 (m, 2 H), 0.40 (dd, 1 H, J = 9.1 and 3.6 Hz), 0.20 (dd, 1 H, J = 4.8 and 3.6 Hz); ^{13}C NMR δ 50.8 (C), 37.4 (CH), 34.4 (C), 33.6 (CH_2), 27.9 (CH_2), 25.6 (CH_2), 24.00 (C), 23.7 (CH), 23.6 (CH_2), 22.4 (CH_2), 21.6 (CH), 21.1 (CH), 19.9 (CH_2), 14.4 (CH); IR (CS_2, CCl_4) ν 3055, 3005, 2980, 2910, 2845, 2660, 1445 cm^{-1}; MS m/e calcd for $C_{28}H_{40}$ 376.3130, found 376.3120; calcd for $^{13}CC_{27}H_{40}$ 377.3164, found 377.3164.

Preparation of Tetramer 10. Cyclopropane **2** (150 mg, 0.74 mmol) was passed through a fluoride column at 25 °C. Pentane (5 mL) was introduced into the cold trap already containing the collected product, and this solution was warmed to room temperature. The system was kept under vacuum at all times. After 7 days, the mixture was passed through a small silica gel column, and the solvent was removed in vacuo. The residue was kept at room temperature for 1 week and then purified by preparative thin-layer chromatography to give 20.9 mg of **10** (30% yield). Crystallization from acetone yielded colorless crystals, mp 181–182 °C: ^1H NMR (300 MHz) δ 2.15–2.0 (m, 2 H), 2.0–1.85 (m, 4 H), 1.83–1.54 (m, 6 H), 1.40–1.05 (m, 18 H), 1.12 (s, 2 H), 1.05–0.85 (m, 4 H), 0.8–0.7 (m, 2 H), 0.13 (dd, 1 H, J = 4.4 and 6.2 Hz); ^{13}C NMR δ 50.14, 38.15, 32.93, 31.60, 31.59, 23.66, 23.73, 23.35, 22.96. 22.03, 20.63, 18.66, 15.06; IR (CS_2, CCl_4) ν 3090, 3055, 3005, 2985, 2910, 2845, 2660, 1445 cm^{-1}; MS m/e calcd for $C_{28}H_{40}$ 376.3130, found 376.3136; calcd for $^{13}CC_{27}H_{40}$ 377.3164, found 377.3164.

Elimination of 1-(Trimethylsilyl)-7,7-dichlorobicyclo[4.1.0]heptane over Solid Tetra-*n*-butylammonium Fluoride. The silane (100 mg) was passed through the fluoride column at 25 °C. The product was then transferred to an NMR tube and monitored by NMR spectroscopy from −90 °C to 0 °C at 10-deg intervals. Diene **18** was the only detectable product.

Addition of Monochlorocarbene to 1-(Trimethylsilyl)cycloheptene. 1-(Trimethylsilyl)cycloheptene (5.0 g, 29.7 mmol) and methylene chloride (5 mL) were placed into a 250-mL three-necked flask fitted with two equilibrating addition funnels, a Barrett distilling receiver with condenser, a magnetic stirrer, and a bubbler to maintain a positive nitrogen pressure. The addition funnels were charged with 250 mL of 1.4 M methyllithium in ether and 20 mL of methylene chloride. While the solution was stirring vigorously, the methyllithium was added at the rate of 2 drops per second as the methylene chloride was introduced at the rate of one-fifth of the rate of addition of methyllithium. When the addition was completed, methylene chloride (5 mL) was added carefully to quench the unreacted methyllithium. The mixture was filtered and the solid was washed with ether (200 mL). The combined organic solutions were washed with water and brine and dried over anhydrous magnesium sulfate. The solvent was removed under vacuum. Bulb-to-bulb distillation of the residue yielded 3.21 g of 1-(trimethylsilyl)-8-chlorobicyclo-[5.1.0]octane (50% yield) as a mixture of cis and trans isomers: MS m/e calcd for $C_{11}H_{21}ClSi$ 216.1101, found 216.1105; calcd for $^{13}CC_{10}H_{21}ClSi$ 217.1135, found 217.1129; $C_{11}H_{21}{}^{37}ClSi$ 218.1072, found 218.1071.

Elimination of 1-(Trimethylsilyl)-8-chlorobicyclo[5.1.0]octane over Solid Tetra-*n*-butylammonium Fluoride. 1-(Trimethylsilyl)-8-chlorobicyclo[5.1.0]octane (50 mg, 0.23 mmol) was passed through a fluoride column at 25 °C. The product **24** was collected in a trap that was cooled

with liquid N_2. Replacement of the liquid N_2 by an acetone/dry ice bath afforded removal of the volatile side products. Before sealing the sample tube, NMR solvent was added by distillation: ^1H NMR (CD_2Cl_2, 90 MHz) δ 6.5 (bs, 1 H), 2.8–2.1 (m, 2 H), 2.1–0.9 (m, 9 H); ^{13}C NMR δ 125.8, 101.1, 34.8, 29.4, 28.8, 26.8, 25.4, 15.2; IR (CS_2, CCl_4) ν 2660, 1768 cm^{-1}. The signal for the cyclopropenyl proton disappeared with the concomitant appearance of another signal at δ 6.4. The second compound, examined by GC/MS, is a dimer: MS *m/e* calcd for $C_{16}H_{24}$ 216.1878, found 216.1873; calcd for $^{13}CC_{15}H_{24}$ 217.1912, found 217.1908. Another compound with a parent molecular ion at *m/e* 324 was a trimer of **24**.

Trapping of Bicyclo[5.1.0]oct-1(8)-ene (24) with Butadiene. 1-(Trimethylsilyl)-8-chlorobicyclo[5.1.0]octane (627.7 mg, 2.89 mmol) was allowed to pass through a column of fluoride at 25 °C as described previously. The product **24** was isolated in a cold trap, and butadiene (5 mL) was then distilled onto the cyclopropene. The mixture was then transferred to a 25-mL flask by a double-ended needle, stirred at −30 °C for 2 h, and refluxed for an additional 2 h. Excess butadiene was then removed, and the residue was purified by column chromatography to give 458 mg (96% yield) of tricyclo[5.5.0.$0^{1,6}$]dec-3-ene (**28**): ^1H NMR (300 MHz) δ 6.67 (t, 2 H, J = 1.8 Hz), 2.55–2.45 (m, 1 H), 2.45–2.20 (m, 2 H), 2.2–2.08 (m, 1 H), 2.08–1.9 (m, 2 H), 1.9–1.4 (m, 5 H), 1.35–1.08 (m, 3 H), 1.08–0.85 (m, 1 H), 0.8–0.65 (m, 1 H); ^{13}C NMR δ 124.2 (CH), 124.0 (CH), 39.2 (CH_2), 32.7 (CH_2), 31.4 (CH_2), 29.9 (CH_2), 28.4 (CH), 26.5 (CH_2), 24.8 (CH_2), 24.6 (CH), 22.8 (C); MS *m/e* calcd for $C_{12}H_{18}$ 162.1409, found 162.1410; calcd for $^{13}CC_{12}H_{18}$ 163.1442, found 163.1438.

Hydrogenation of Bicyclo[5.1.0]oct-1(8)-ene (24). 1-(Trimethylsilyl)-8-chlorobicyclo[5.1.0]octane (771.8 mg, 3.56 mmol) was passed through a fluoride column at 25 °C. The product was collected in a trap that was cooled with liquid N_2. Replacement of the liquid N_2 by an acetone/dry ice bath afforded removal of the volatile side products. The residue was dissolved in a mixture of pentane (10 mL) and methanol (5 mL) and reduced over 5% Rh/C at 50 psi for 0.5 h. The solution was filtered through silica gel, and the solvents were removed in vacuo. Purification by column chromatography (pentane) gave *cis*-bicyclo[5.1.0]-octane (**25**) and methylcycloheptane (**26**). The yields of **25** and **26** were determined to be 53.4% and 28.6%, respectively, by gas chromatography with toluene as an internal standard. The ^1H NMR spectrum (300 MHz) of **25** displayed resonances at δ 2.2–2.15 (m, 2 H), 1.85–1.75 (m, 1 H), 1.75–1.6 (m, 2 H), 1.4–1.3 (m, 2 H), 1.2–1.05 (ddt, 1 H), 1.0–0.7 (m, 4 H), 0.7–0.6 (m, 1 H), 0.1–0.0 (m, 1 H); ^{13}C NMR δ 32.7, 31.1, 29.8, 16.4, 14.8. The ^1H NMR spectrum (90 MHz) of **26** displayed resonances at δ 0.84 (d, 3 H) and 1.0–1.8 (m, 13 H).

Hydrogenation of *cis*-Bicyclo[5.1.0]octane over Rh/C. A solution of *cis*-bicyclo[5.1.0]octane (389 mg, 3.56 mmol) in pentane (10 mL) and methanol (5 mL) was reduced over 5% Rh/C at 50 psi for 0.5 h. After filtration, the solvents were removed in vacuo and the residue was purified by column chromatography (pentane) to give 370.4 mg of recovered *cis*-bicyclo[5.1.0]octane (95.2%). GC/MS showed no methylcycloheptane.

X-ray Analyses. Colorless crystals of compounds **9** and **10** were mounted at the tips of glass fibers and data were collected as per the parameters listed in Table 1 (supplementary material) with the TEXSAN (v. 2.0, Molecular Structure Corp.) data collection software. Both compounds tended to twin and a number of specimens had to be examined before ones that suitably diffracted were found. The structures were solved with use of the SHELXS86[1] program, which located all of the carbon atoms for both structures. The structures were refined to convergence with the TEXSAN program package.[2] The molecular structures and atom labeling schemes are shown in Figures 1 and 2. Atomic coordinates for the carbon atoms and selected bond metricals are given in Tables 2–5 (supplementary material). The molecules are very similar in the arrangement of the fused-ring system made up of one cyclobutane, two cyclopropane, and two cyclohexane rings. The major difference is that in **9** the cyclohexane rings lie on opposite sides of the cyclobutane moiety while in **10** they occur on the same side. For **9**, the molecule sits about a crystallographic inversion center and only half of the molecule is unique. All C–C bond distances are within the range of normal single bonds. Because of the limited data the carbon atom positions of **10** were only refined isotropically while those of **9** were refined anisotropically. Hydrogen atoms were included in calculated positions that were not refined.

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Registry No. 1, 107396-10-1; *trans*-**2**, 135759-60-3; *cis*-**2**, 135663-43-3; **3**, 135663-38-6; **7**, 135663-40-0; **8**, 135695-40-8; **9**, 135720-61-5; **10**, 135663-41-1; **10a**, 135663-39-7; **17**, 58660-83-6; **18**, 90084-82-5; **24**, 135695-42-0; **25**, 286-43-1; **26**, 4126-78-7; **28**, 135663-42-2; tetrabutylammonium fluoride, 429-41-4; 1-bromocyclohexene, 2044-08-8; 1-(trimethylsilyl)cyclohexene, 17874-17-8; 1-(trimethylsilyl)cycloheptene, 61892-24-8; *cis*-1-(trimethylsilyl)-8-chlorobicyclo[5.1.0]octane, 135695-41-9; *trans*-1-(trimethylsilyl)-8-chlorobicyclo[5.1.0]octane, 135759-61-4; 1,3-butadiene, 106-99-0; 1,2-dibromocyclohexane, 5401-62-7.

Supplementary Material Available: Tables of anisotropic displacement parameters for **9** and tables of hydrogen atom positional parameters for **9** and **10** (14 pages); tables of structure factors for **9** and **10** (14 pages). Ordering information is given on any current masthead page.

Is Halogen–Lithium Exchange Intramolecularly Competitive with Removal of an Acidic Hydrogen? Reinvestigation of a Recent Claim

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Abstract: A careful reinvestigation of a recent report in which the iodine–lithium exchanges of 2-iodo-3-(deuterioxymethyl)quinoline (**1**) and 2-iodo-3-(hydroxymethyl)quinoline (**4**) are interpreted to have occurred prior to abstraction of the alcoholic hydrogen has been carried out. Accurate analyses of the reaction products by FI mass spectrometry give results that are different from those recently reported and are consistent with a mechanism in which removal of the acidic hydrogen takes place prior to iodine–lithium exchange on a molecular scale. The interpretation that suggested the opposite sequence was based on deuterium incorporation values that appear to be inaccurate due to the limitations of the ^1H NMR methods used.

In previous work we investigated the lithiations of molecules that contain both an acidic deuterium and an exchangeable bromine or iodine. We suggested that the formation of products in which the deuterium replaces the halogen does not require the interpretation that halogen–lithium exchange is followed by intramolecular deuterium transfer.[1,2] Our results, as well as earlier

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