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USES OF ADSORBED REAGENTS IN THE SYNTHESIS OF REACTIVE MOLECULES VIA ELIMINATION REACTIONS

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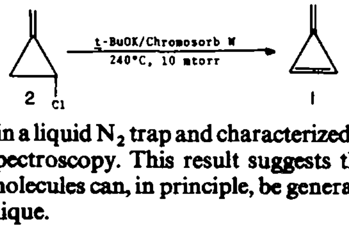
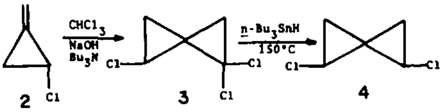
Abstract—The synthesis of reactive molecules (*in vacuo*) using reagents adsorbed on inert surfaces to effect elimination reactions has been investigated. Potassium t-butoxide adsorbed on Chromosorb W can be used to generate methylenecyclopropene from 2-chloromethylenecyclopropane and 1-vinylcyclopropene from either 1,4-dichlorospiropentane or 1-chloro-2-vinylcyclopropane. Both compounds can be characterized at low temperature using NMR and IR spectroscopy. Methyllithium on glass helices has been used in the reductive elimination of halogen from *vicinal* cyclopropyl dihalides to yield cyclopropenes. β-Halocyclopropylsilanes can be converted in high yield to the corresponding cyclopropene using tetra-n-butylammonium fluoride deposited on glass helices. The fluoride route has been used to generate bicyclo[4.1.0]hept-(1,6)-ene and bicyclo[4.1.0]hept-(1,7)-ene in the gas phase under conditions which allow either spectroscopic characterization or trapping as Diels–Alder adducts.

Small ring cycloalkenes have aroused considerable interest because their high energy content, relative to their acyclic isomers, often results in unexpected properties.[1] The high strain energy (54 kcal mol^{-1}) of the simplest small ring cycloalkenes, the cyclopropenes, results in many unusual reactions such as facile [2+2] cycloadditions and ring-opening reactions giving species normally considered to be high energy ones. As part of a program on the synthesis of reactive molecules which incorporate the cyclopropene ring, we have investigated the use of reagents adsorbed on inert surfaces to generate cyclopropenes in the gas phase via elimination reactions. This approach allows the reactive species to be isolated at low temperature for structural studies and eliminates many bimolecular side reactions that would be encountered in solution such as the addition of nucleophiles to the strained double bond.[2]

Our initial studies were carried out on the synthesis of methylenecyclopropene (**1**).[3] This highly reactive compound (stable only below ~ −70°) was synthesized using potassium t-butoxide adsorbed on Chromosorb W[4] to effect the elimination of hydrogen chloride from **2**. Methylenecyclopropene prepared in this way can be collected in a liquid N_2 trap and characterized by NMR and IR spectroscopy. This result suggests that other reactive molecules can, in principle, be generated using this technique.



The dehydrochlorination of **4**, which can be prepared from **2** via **3** as illustrated in Scheme 1, provides an interesting test of the method, since the double elimination of hydrogen chloride would yield spiropentadiene (**5**).† Although the high strain energy (calculated to be 145 kcal mol^{-1})[5] and resulting instability would probably preclude **5** as an isolable product, it seems reasonable that products derived from **5** or other equally interesting compounds might be isolated.



Scheme 1.

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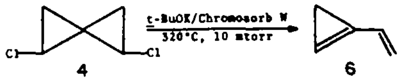
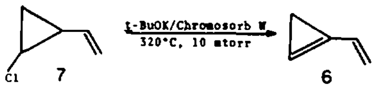
The slow introduction of **4** into the column (Fig. 1) packed with the potassium t-butoxide/Chromosorb W reagent at 320° and 5–10 MTorr yielded a major product, 1-vinylcyclopropene (**6**). The identity of **6** was based on its ^1H-NMR spectrum. Singlets at δ 0.99 (2H) and 7.14 (1H) are assigned to the cyclopropenyl ring protons. The signals at 5.62 (d, 1H, J = 15.8 Hz), 5.77 (d, 1H, J = 10.1 Hz) and 6.77 (dd, 1H, J = 15.8, 10.1 Hz) are characteristic vinylic resonances. Additional proof of this assignment was provided by comparison (NMR) with an "authentic sample" of **6** prepared by dehydrochlorination of **7** using the potassium t-butoxide/Chromosorb W reagent.





The NMR signals of **6** were persistent at −100° in THF-d_8 but began to diminish as the solution was warmed above ~ −70°. At room temperature, a dimer of **6**, compound **8** was observed. On standing at room temperature **8** isomerized slowly to **9**. An attractive rationalization of these results is illustrated in Scheme 2.

Elimination of hydrogen chloride from **4** would yield spiropentene **10**. Cleavage of **10** to the biradical **11**, a process that would be facilitated by the high temperature required to effect the elimination, followed by scission of the C—Cl bond would yield radical **12**.

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† Although several small ring, spiro-connected cycloalkenes have been reported, and their spectroscopic properties investigated in line with theoretical predictions of spiroconjugation, spiropentadiene itself is unknown. For a discussion of this area, see Ref. 1.

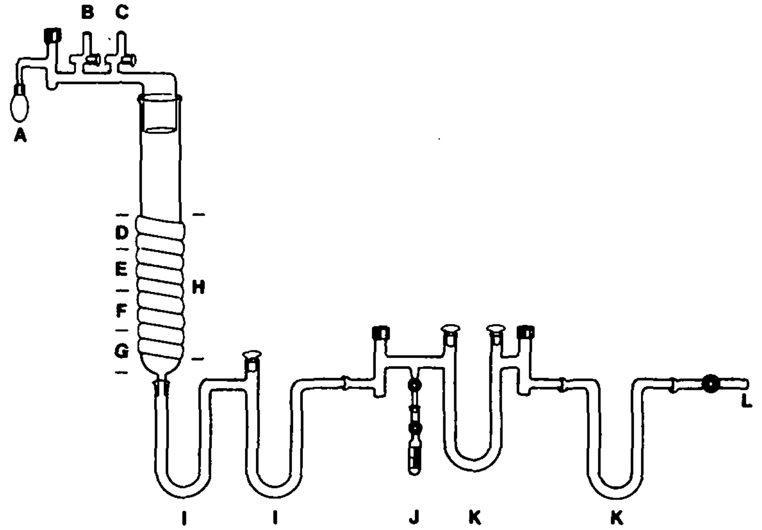
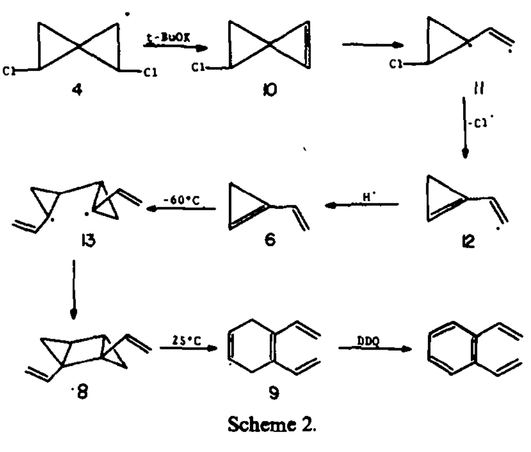


Fig. 1. Gas phase reaction apparatus: A, starting material; B, to N_2 bubbler; C, to vacuum gauge; D, Chromosorb W, 2 cm; E, t-BuOK/Chromosorb W, 4 cm; F, Chromosorb W, 3 cm; G, glass wool, 3 cm; H, heating tape; I, dry ice/acetone bath; J, NMR solvent or trapping reagent; K, liquid N_2 bath; L, to vacuum line (5–10 mTorr).

Abstraction of a H atom from t-butanol (or other H atom donors) would furnish **6**. Support for the hypothesis that t-butanol serves, at least in part, as the source of H atoms is found in the observation that acetone is collected in the liquid N_2 trap along with **6**. The isolation of **8** suggests that **6** dimerizes via biradical **13**. Simple collapse of **13** with C—C bond formation furnishes **8** which undergoes a subsequent cycloreversion to yield **9**. *ortho*-Divinylbenzene was isolated when **9** was treated with DDQ.

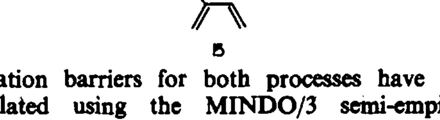
Although the formation of a biradical would normally be an endothermic process, the facile dimerization of **6** can be understood from a thermodynamic standpoint. Benson's and O'Neal's additivity rules[6] can be used to estimate the heats of formation of **6** and **13** as 26.2 and 65.6 kcal mol^{-1}, respectively. These values and the known strain energies of cyclopropene (53.7 kcal mol^{-1}) and cyclopropane (27.6 kcal mol^{-1}) can then be used to show that the dimerization $6 \rightarrow 13$ is exothermic by 39.0 kcal mol^{-1}. The driving force for the dimerization is, of course, mostly due to loss of strain in **6**.



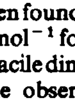
Scheme 2.

When the reaction was carried out using potassium t-butoxide-d_9 and the dimer **9** analyzed by mass spectroscopy, no species incorporating more than two deuterium atoms could be detected. This observation, which is consistent with Scheme 2, would seem to eliminate spiropentadiene **5** as a viable intermediate, since any vinylcyclopropene arising from **5** would incorporate two deuterium atoms and thus yield a d_4 dimer.

Vinylcyclopropene is also of interest with regard to its interconversion with divinylcarbene (**14**). This process could lead to the degenerate rearrangement illustrated in Scheme 3. Alternatively, cleavage of the C_2—C_3 bond in **6** would yield carbene **15**. The activation barriers for both processes have been calculated using the MINDO/3 semi-empirical method.[7] Allowing complete geometric minimization, these barriers have been found to be 41.2 kcal mol^{-1} for $6 \rightarrow 14$ and 52.3 kcal mol^{-1} for $6 \rightarrow 15$. These relatively high barriers and the facile dimerization of **6** would then seem to preclude the observation of thermal ring-opening reactions; however, photolysis of an argon matrix of **6** led to the rapid appearance of new bands which could be assigned to vinylallene.[8] This transformation can be rationalized in terms of the carbene **14** which would yield the allene by insertion into one of the adjacent C—H bonds at C_2 or C_4.



Scheme 3.



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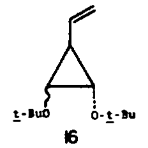
The results from a study of the dehydrochlorination of **4** in solution stand in contrast to those from the gas phase elimination. Experiments which might elucidate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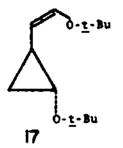
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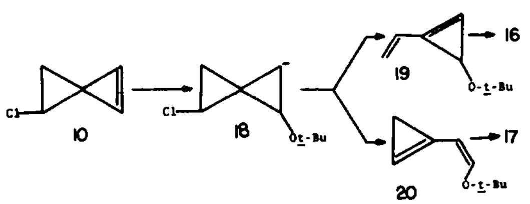
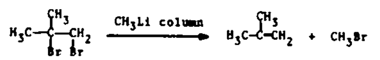
the origin of these products have not been carried out; however, both products could, in principle, arise from spiropentene **10** (Scheme 4). The double bond in **10** would be expected to experience addition of t-butoxide yielding the anion **18**.[2] Collapse of the anion to **19** followed by addition of t-butoxide[2] and protonation would yield **16**. Alternatively, ring opening of the cyclopropyl anion with loss of chloride would yield **17** (via **20**). The NMR spectrum of the crude reaction product shows that a single isomer of **17** is produced, consistent with a concerted ring-opening reaction. The small coupling of the olefinic protons (J = 6.3 Hz) suggests that the double bond in **17** has a *cis* configuration.



Scheme 4.

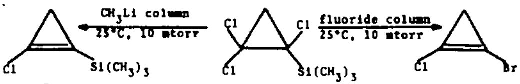
The synthesis of both methylenecyclopropene and vinylcyclopropene under conditions which allow complete spectral characterization encouraged us to investigate the generation of additional reactive species via gas phase elimination reactions using other adsorbed reagents. The use of alkyllithium reagents in the reductive elimination of halogen from *vicinal* cyclopropyl dihalides[9] and the conversion of β-halosilanes into alkenes using fluoride[10] have both been reported. The feasibility of carrying out the dehalogenation reaction in the gas phase was demonstrated by passing isobutylene dibromide through a "methyllithium column" (methyllithium adsorbed on glass helices).[11] Isobutylene was produced



$$H_3C{-}\underset{Br}{\overset{CH_3}{C}}{-}\underset{Br}{CH_2} \xrightarrow{CH_3Li\ column} H_3C{-}\overset{CH_3}{C}{=}CH_2 + CH_3Br$$

in nearly quantitative yield along with the co-product methyl bromide.

Cyclopropane **21**[12] can be used as a starting material in both processes. Thus dehalogenation, using the "methyllithium column", yielded cyclopropene **22** (85%), whereas cyclopropene **23** was isolated in comparable yield, using a "fluoride column". These observations imply that other suitably elaborated cyclopropanes can be converted to cyclopropenes of either synthetic or theoretical interest using these reagents.



22 21 23

In this regard, the small ring bicyclic alkenes **24**–**27** seemed a worthy challenge.[13] These compounds have been the object of both theoretical and experimental studies. Wagner *et al.*[14] calculated the geometries and found all four to have a bent structure. Experimentally, evidence has been presented for the formation of derivatives of **24**,[15] **25**,[15] and **27**.[16,17] More recently Wiberg and Bonneville have generated and trapped both **26** and **27** as Diels–Alder adducts.[9] Compound **27** was found to dimerize rapidly even at −120°. The nonplanar structure is probably responsible for this high reactivity.

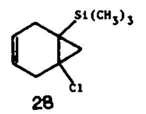

24


25


26


27

We chose **27** as a target since the required precursor for the fluoride route, compound **29**, can be prepared readily from the Diels–Alder adduct **28** of cyclopropene **22** and butadiene. The elimination to **27** proceeded smoothly when **29** was passed through the "fluoride column". Although the predominate fate of **27** seems to be dimerization, it was possible to isolate the adduct **30** when the surface of the cold trap was coated with cyclopentadiene. *This observation shows conclusively that* **27** *can be generated and transferred in the gas phase.*



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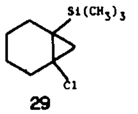

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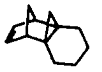
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31

An isomer of **27**, cyclopropene **31**, can also be generated using the "fluoride column". This compound is, as expected, much more stable than **27**, and it is possible to isolate the Diels–Alder adduct of cyclopentadiene in 85% yield. The NMR spectrum of **31**, recorded at −90° in CD_2Cl_2, exhibited a signal that can be assigned to the cyclopropenyl proton at δ 6.8. Studies on the dimerization of both **27** and **31** are underway as well as studies of their spectroscopic properties (and thus structure).

In conclusion, we believe that the use of these and other adsorbed reagents offers convenient routes to many additional reactive intermediates or new functional groups. These studies are in progress.

EXPERIMENTAL

^1H- and ^{13}C-NMR spectra were recorded using a JEOL FX90Q spectrometer at 90 and 22.63 MHz, respectively. Unless otherwise noted, NMR spectra were recorded in chloroform-d_1. High resolution mass spectra were recorded on a double-focusing CEC 21-110 mass spectrometer. Low resolution spectra were recorded on a Finnigan Model 3300 GC/MS spectrometer operated at 30 eV. A Hewlett Packard Model 700 gas chromatograph equipped with a thermal conductivity detector and operated at a flow rate of 60 cm^3 of helium per minute was used for all analytical and preparative gas chromatography. All b.ps are uncorrected.

Tetrahydrofuran (THF) was distilled from sodium-benzophenone ketyl prior to use. All other chemicals were reagent grade and used as received from the manufacturers. Column chromatography was carried out using Baker reagent grade silica gel (60–200 mesh).

Preparation of potassium t-*butoxide/Chromosorb W*. Chromosorb W non-acid washed (45–60 mesh) was dried at 300° and 10 mTorr for 3 h. A slurry of t-BuOK (15 g) and Chromosorb W (31 g) in THF (250 ml) was heated to reflux for 1 h. Most of the solvent was then removed by distillation and the solid was dried *in vacuo* overnight at room temp.

General procedure for gas phase dehydrohalogenations over potassium t-*butoxide/Chromosorb W*. The reaction column (a 21 × 3.5 cm tube equipped with a 34/45 ground glass joint at the top and a 14/20 joint at the bottom) illustrated in Fig. 1 was loaded with 3 cm of glass wool, 3 cm of Chromosorb W, 4 cm of t-BuOK/Chromosorb W and 2 cm of Chromosorb W. The entire apparatus was evacuated to 10 mTorr and the portion of the tube containing the Chromosorb W was heated by a heating tape. The temp was measured by a thermocouple inserted into a small tube placed between the column and the heating tape. A series of four traps, the first two cooled by dry ice, acetone baths and the latter two by liquid N_2 baths, were used to collect products. An NMR tube was attached to the bottom of the third U-trap. Once the system had equilibrated, the rate of addition of the starting material (50 μl h^{-1}) was controlled by a high vacuum Teflon stopcock (0–3 mm) and measured by a vacuum gauge. NMR samples were prepared by introducing 0.2 ml of THF-d_8 or CH_2Cl_2-d_2 into the first liquid N_2 cooled trap before the reaction was started so that the solvent froze near the top of the trap. After the reaction was completed, an additional 0.2 ml of THF-d_8 or CH_2Cl_2-d_2 was introduced into the trap which was then isolated from the vacuum pump. The liquid N_2 bath was replaced with a pentane/liquid N_2 slush bath cooled to about −100°. After the soln was collected in the NMR tube, the tube was sealed. NMR spectra were recorded at −100° (THF-d_8) or −90° (CD_2Cl_2). Mass spectral studies were carried out with the product that was collected in the first liquid N_2 cooled U-trap. The trap was then removed and the product was introduced into the mass spectrometer via the direct inlet. IR spectra were taken by slowly introducing the reactive species and argon onto a polished Cu surface cooled to 15 K with a closed-cycle helium refrigerator. The spectra were recorded on an IBM Model 98 FTIR spectrometer.

Preparation of 1,1,4-*trichlorospiropentane* (3). A mixture of 2-chloromethylenecyclopropane (1.9 g, 21.5 mmol), $CHCl_3$ (15 ml, 0.187 mol), tributylamine (0.3 ml), CH_2Cl_2 (20 ml), and 50% NaOH aq (30 g) was stirred vigorously at 50° for 6 h. The mixture was then diluted with water (50 ml) and CH_2Cl_2 (50 ml). The layers were separated and the aqueous phase extracted twice with CH_2Cl_2. The combined organic layers were washed with water, brine, dried over Na_2SO_4, and concentrated *in vacuo*. Purification by distillation through a short path column followed by column chromatography (silica gel, pentane) afforded 3.1 g (84% yield) of product, b.p. 83–85°/65 Torr. ^{1}H-NMR δ 1.52 (dd, 1H, J = 7.0, 4.1 Hz), 1.86 (t, 1H, J = 7.0 Hz), 1.97 (s, 2H), and 3.61 (dd, 1H, J = 7.0, 4.1 Hz); mass spectrum calc for $C_5H_5Cl_3$ 169.9456, found 169.9453.

Preparation of 1,4-*dichlorospiropentane* (4). A soln of 3 (2.91 g, 16.9 mmol), tri-n-butyltin hydride (5.93 g, 20.4 mmol), and AIBN (~10 mg) in THF was stirred at 150° for 24 h. The product was separated from the tin by-products by bulb-to-bulb distillation at 25°/10 mTorr. Preparative gas chromatography (10% FFAP on Chromosorb W AW/DMCS) afforded 1.73 g (75% yield) of 4 as a mixture of two geometric isomers. ^{1}H-NMR δ 1.15–1.75 (m, 4H) and 3.38–3.58 (m, 2H); mass spectrum calc for $C_5H_6Cl_2$ 135.9847, found 135.9848.

Dehydrochlorination of 1,4-*dichlorospiropentane* (4) *over potassium* t-*butoxide/Chromosorb W*. The spiropentane (60 mg, 0.44 mmol) was passed through the t-BuOK/Chromosorb W column at 320° and 10 mTorr as described under the general procedure. The ^{1}H- (see text) and ^{13}C-NMR spectra of 6 were recorded at −100° in THF-d_8. The ^{13}C spectrum exhibits signals at 5.08, 104.4, 125.6 and 126.2 ppm. The quaternary carbon was not observed. The mass spectrum gave a parent molecular ion at *m/e* 66. Prominent IR bands were observed at 1844.1, 1758.0, 1607.9, 1400.3, 1035.8, 1028.1, 920.8 and 722.7 cm^{-1}. Other spectral data: dimer 8: ^{1}H-NMR δ 1.16–1.30 (m, 4H), 1.51–1.64 (m, 2H), and 4.89–5.64 (m, 6H); dimer 9: ^{1}H-NMR δ 2.93 (s, 4H), 5.10 (dd, 2H, J = 11.0, 1.3 Hz), 5.21 (dd, 2H, J = 17.4, 1.3 Hz), 5.79 (s, 2H), and 7.15 (dd, 2H, J = 17.4, 11.0 Hz); ^{13}C-NMR δ 28.17, 114.07, 124.70, and 134.89; mass spectrum calc for $C_{10}H_{12}$ 132.0939, found 132.0936. Photolysis of 6 in an argon matrix through a quartz window using a mercury lamp for 30 min converted all of 6 to vinylallene which displayed characteristic terminal allenes absorptions at 1953.3, 1945.3, and 849.0 cm^{-1}.

Aromatization of dimer 9. A mixture of 9 (5 mg, 0.038 mmol), purified by preparative gas chromatography, DDQ (10 mg, 0.044 mmol) and $CDCl_3$ (2 ml) was stirred at room temp for 40 min and then filtered through silica gel. The product was shown to be *ortho*-divinylbenzene by comparison (NMR and GC/MS) with an authentic sample.

Preparation of 1-*chloro*-2-*vinylcyclopropane* (7). A mixture of 1,1-dichloro-2-vinylcyclopropane[18] (2.3 g, 16.7 mmol), tributyltin hydride (6.2 g, 20.6 mmol), and AIBN (10 mg) were heated to 200° for 48 h as the mixture was irradiated with a sunlamp. Bulb-to-bulb distillation of the product at 25°/10 mTorr followed by preparative gas chromatography (10% SE-30 on Chromosorb W AW/DMCS) afforded 0.41 g (23.9% yield) of 7 as a mixture of *cis* and *trans* isomers. ^{1}H-NMR δ 0.76–1.60 (m, 2H), 1.68–1.98 (m, 1H), 2.92–3.24 (m, 1H), and 4.94–5.90 (m, 3H); mass spectrum calc for C_5H_7Cl 102.0236, found 102.0235.

Reaction of 1-*chloro*-2-*vinylcyclopropane* (7) *with potassium* t-*butoxide/Chromosorb W*. Compound 7 (60 mg, 0.58 mmol) was passed through the t-BuOK/Chromosorb W column at 320° and 10 mTorr. The major product was shown by NMR spectroscopy to be 6.

Reaction of 1,4-*dichlorospiropentane* (4) *with potassium* t-*butoxide in tetrahydrofuran*. A mixture of t-BuOK (1.4 g, 12.5 mmol) and 1,4-dichlorospiropentane (200 mg, 1.46 mmol) in THF (6 ml) was stirred at room temp for 30 h. Bulb-to-bulb distillation at 10 mTorr followed by concentration *in vacuo* afforded a mixture of 16 and 17. Preparative gas chromatography (10% FFAP on Chromosorb W AW/DMCS) gave 67 mg (21.7% yield) of 16 as approximately a 1:1 mixture of *cis* and *trans* isomers and 102 mg (32.8% yield) of 17. Compound 16 has NMR signals at 1.22 (s, 9H), 1.26 (s, 9H), 1.25–1.70 (m, 2H), 3.03 (d, 2H, J = 3.5 Hz), 3.16 (dd, 1H, J = 4.5, 2.2 Hz), 3.45 (dd, 1H, J = 7.4, 2.2 Hz), and 4.78–5.78 (m, 6H). Compound 17 exhibits signals at 0.59 (m, 1H), 0.98 (m, 1H), 1.26 (s, 18H), 1.60–1.98 (m, 1H), 3.09 (m, 1H), 3.90 (dd, 1H, J = 9.3, 6.3 Hz), and 6.18 (d, 1H, J = 6.3 Hz); mass spectrum calc for $C_{13}H_{24}O_2$ 212.1776, found 212.1777.

Preparation of methyllithium adsorbed on glass helices ("*methyllithium column*"). The reaction column (Fig. 1) was connected to a 500 ml 3-neck flask containing 60 g of glass helices. The system was evacuated for about 30 min and then filled with N_2. MeLi (1.6 M) in ether (30 ml) was then added to the flask through a rubber septum and mixed with the glass helices. The solvent was removed *in vacuo* leaving the glass helices coated with MeLi. The coated helices were then transferred to the column. After the column was reconnected to the apparatus, the system was pumped for ~6 h to give a final pressure of 10 mTorr.

Dehalogenation of 1-*bromo*-1-*trimethylsilyl*-2,2-*dichlorocyclopropane* (21) *using the "methyllithium column"*. Cyclopropane 21 (40 mg, 0.15 mmol) was passed through the "methyllithium tube" at 25° and 10 mTorr yielding 22 in ~85% yield. The ^{1}H-NMR spectrum (CD_2Cl_2) was recorded at −90° and showed two singlets at 0.11 (9H) and 1.38 (2H). This compound slowly decomposes in CD_2Cl_2 at room temp.

Preparation of tetra-n-*butylammonium fluoride on glass helices* ("*fluoride column*"). Tetra-n-butylammonium fluoride trihydrate (5 g, 15.85 mmol), CH_2Cl_2 (30 ml) and glass helices (50 g) were added to a 250 ml 1-neck flask. The solvent was removed under vacuum at room temp. The coated glass helices were then transferred to the column and dried *in vacuo* overnight at 10 mTorr.

Reaction of 1 - *bromo* - 1 - *trimethylsilyl* - 2,2 - *dichloro* - *cyclopropane* (**21**) *with tetra*-n-*butylammonium fluoride adsorbed on glass helices.* Cyclopropane **21** (45 mg, 0.17 mmol) was passed through the "fluoride column" at 25° and 10 mTorr. The yield of **23**[13] was 80–90%.

Preparation of 1 - *chloro* - 6 - *trimethylsilylbicyclo* - [4.1.0]*heptane* (**29**). Cyclopropane **21** (1.40 g, 5.34 mmol) was passed through the "CH_3Li column" (prepared from 60 ml of 1.6 M MeLi and 90 g of glass helices) at 25° and 10 mTorr. 1,3-Butadiene (6 ml) was then introduced into the cold trap containing **22**. The mixture was transferred with a double-ended needle into a pressure bottle and cooled to $-25°$ for one week, 5° for a second week and then stirred at 25° for one day. The excess butadiene was then removed and the crude product was reduced in MeOH using 5% Rh/C at 50 psi. Column chromatography (silica gel, pentane) afforded 0.72 g (66.7% yield) of **29**. ^{1}H-NMR signals were observed at δ 0.82 (d, 1H, J = 5.7 Hz), 1.12 (d, 1H, J = 5.7 Hz), 1.08–1.64 (m, 6H), and 1.92–2.40 (m, 2H).

Generation and trapping of bicyclo[4.1.0]*hept* - (1,6) - *ene* (**27**). Compound **29** (50 mg, 0.25 mmol) was passed through the "fluoride column" at 25° and 10 mTorr and the products collected in a liquid N_2 trap containing cyclopentadiene. The Diels–Alder adduct **30** was isolated in ~10% yield by preparative gas chromatography (10% SE-30 on Chromosorb W AW/DMCS) and showed ^{1}H-NMR ($CDCl_3$) signals at δ 0.39 (dd, 1H, J = 5.2, 2.6 Hz), 0.63 (d, 1H, J = 5.2 Hz), 1.25–2.0 (m, 10H), 2.50 (m, 2H), and 5.83 (t, 2H, J = 2.2 Hz). The ^{13}C-NMR spectrum displayed signals at 22.58, 26.86, 28.65, 50.60, 60.30, and 132.60 ppm. The mass spectrum gave a parent molecular ion at *m/e* 160.

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