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Competing 1,n-Elimination Reactions of 1-Bromo-5-bromomethyl-6,6-dichlorobicyclo[3.1.0]hexane: A Strained 1,3-Bridged Cyclopropene and a Vinylcarbene as Reactive Intermediates.†

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Abstract: 1-Bromo-5-bromomethyl-6,6-dichlorobicyclo[3.1.0]hexane (**9**) was treated with alkyllithium at different temperatures. After halogen metal exchange in **9**, two competing 1,n-elimination reactions take place. A 1,2-elimination of organolithium compound **12** leads to strained 1,3-bridged cyclopropene **10** which undergoes a cyclopropene-vinylcarbene rearrangement to **17**. Insertion of **17** into the ether solvent affords isomers **18a** and **18b**. In contrast, 1,4-eliminations of organolithium compound **13** generate butadienes **14** and **16**, respectively. The formation of the products is temperature dependent. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

The dehydrohalogenation and the dehalosilylation of monohalocyclopropanes are the most common type of reactions used to produce strained cyclopropenes.[1] But when dihalo- and polyhalocyclopropyl compounds are reacted with alkyllithium, two halogens can be eliminated. The relative positions of the halogens thus determine the structure of the resulting elimination products. A 1,2-elimination of two halogens in di- and tetrahalocyclopropanes provides a good synthetic pathway to cyclopropenes and 1,2-dihalocyclopropenes **2** (Figure 1).[2,3]

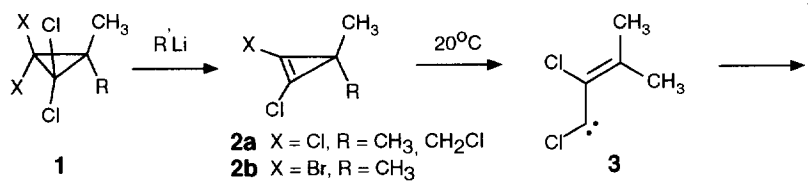


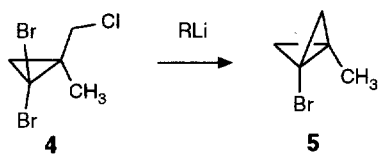
Figure 1. 1,2-Dehalogenation of polyhalocyclopropanes

Many of these compounds readily undergo, even at room temperature, the cyclopropene-vinylcarbene rearrangement.[4] Thus, for example, carbene **3** dimerizes to form a conjugated hexatriene or inserts into ether C-H bonds.[5] When a double bond is offered, an addition proceeds with formation of vinylcyclopropanes. In the case where two different halogens remain on the cyclopropene, the ring opening can lead to two vinylcarbenes.

† Carbene Rearrangements, 46; for part 45, see: Rosenberg, M. G.; Kam, S. M.; Brinker, U. H., *Tetrahedron Lett.* **1996**, *37*, 3235-3238.

A very important dehalogenation reaction is the 1,1- or α-elimination of geminal dihalocyclopropanes which generates the carbenoid cyclopropylidenes.[6,7] The cyclopropylidene-allene rearrangement has been studied in much detail.[7] Other significant intramolecular reactions of cyclopropylidenes are additions to double bonds[8] or insertions into different sigma bonds to hydrogen *i.e.* C-H,[9] O-H, and N-H.[10]

Aside from 1,1- and 1,2-eliminations, a few examples of 1,3-eliminations have been reported.[11] All types of 1,n-elimination reactions involve the same mechanistic sequence. In the first step, a halogen-metal exchange takes place followed by a 1,n-elimination (n=1,2,3 etc.) step. One instance of a 1,3-elimination is the reaction of trihalocyclopropane **4** with methyllithium and formation of bromobicyclobutane **5** (Figure 2).[11]



4 **5**

Figure 2: 1,3-Elimination to bicyclobutanes

The 1,1-elimination and carbene generation is not a competing reaction under the conditions applied. This approach is extended in the synthesis of [1.1.1]-propellane, where two consecutive 1,3-eliminations are performed.[12] The original propellane synthesis, likewise, involves a 1,3-elimination starting from dihalobicyclo[1.1.1]pentane.[13]

We have been interested in the synthesis of geminal dihalobicyclo[1.1.0]butanes and their rearrangements.[14] In this paper we report the preparation of 1-bromo-5-bromomethyl-6,6-dichloro-bicyclo[3.1.0]hexane (**9**) (Figure 3) and its competing 1,n-elimination reactions upon treatment with different alkyllithium reagents. Among other possibilities, the construction of 6,6-dichloro[3.1.1]-propellane (**15**) (Figure 4) from **9** is plausible. Bromine-lithium exchange followed by a 1,3-elimination of lithium bromide could provide access to **15**.

RESULTS AND DISCUSSION

The preparation of bicyclohexane **9** was accomplished through a four step synthesis starting from cyclopentanone (Figure 3). A formylation reaction of cyclopentanone with dimethylformamide in the presence of phosphorous tribromide led to 2-bromocyclopent-1-ene-1-carboxaldehyde (**6**)[15,16] in an isolated yield of 62%. Reduction of the aldehyde function with lithium aluminum hydride to the corresponding alcohol **7**,[16] followed by replacement of the hydroxyl group by bromine using phosphorous tribromide,[16,17] was achieved in an overall yield of 74%. Dichlorocarbene addition to cyclopentene **8**, following the general ultrasonication procedure of Xu *et al.*,[18] gave waxy, white, menthol-scented crystals of previously unreported 1-bromo-5-bromomethyl-6,6-dichlorobicyclo[3.1.0]hexane (**9**) in 71%.

The reactions of tetrahalobicyclohexane **9** with alkyllithium can follow a varity of reaction pathways. Within the same molecule, four different types of 1,n-eliminations (n=1,2,3,4) can take place. The first step of each elimination is a halogen-metal-exchange reaction. The reaction conditions and the choice of the reagent determines which of the halogens is primarily exchanged. Figure 4 outlines possible pathways that would

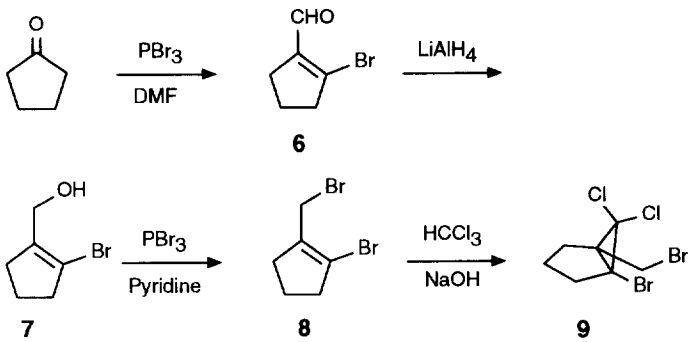


Figure 3. Synthesis of 1-bromo-5-bromomethyl-6,6-dichlorobicyclo[3.1.0]hexane (**9**)

result from an exchange of a bromine atom in **9** by a lithium atom. The intermediate lithio-derivative **12** could undergo a 1,2-elimination of lithium chloride and produce the highly strained bicyclic cyclopropene **10**. On the other hand, an exchange of the side chain bromine atom would lead to the lithium compound **13**. Two different 1,3-eliminations are possible from either **12** or **13** leading to 1) 6,6-dichloro[3.1.1]propellane (**15**) and producing 2) 5-bromo-6-chlorotricyclo[3.2.0.$0^{1,6}$]heptane (**11**). There are also two conceivable pathways of 1,4-elimination which both involve rupture of the cyclopropane ring. The cleavage of the central bond in **13** and loss of lithium chloride should give methylenecyclohexene **14**, whereas the opening of side bond C5-C6 should result in the formation of diene **16** and lithium bromide. Products resulting from a chlorine-lithium

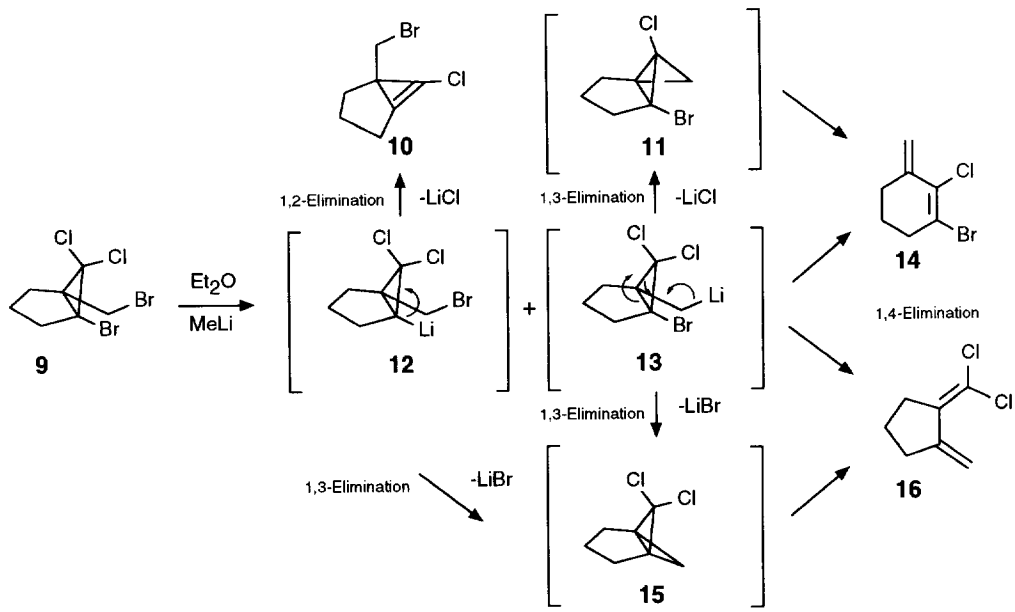


Figure 4. 1,n-Elimination reactions of tetrahalobicyclohexane **15**

exchange in **9** should primarily be the same as those depicted in Figure 4. An additional process in **9** is that of a 1,1-elimination generating the corresponding cyclopropylidene.

When the reaction was performed with methyllithium as the lithiating reagent at -40°C, three major products were detected by analytical gas chromatography. Indeed, one of the products was, as predicted, the 1,4-elimination product **14**, along with an isomeric mixture of the ether products **18a** and **18b** (Figure 5). The overall yield after purification (preparative GC separation of **14** and HPLC separation of **18a** and **18b**) was 40%.

The formation of **14** is thought to be the result of the ring-opening of intermediate lithium derivative **13**. A similar reaction has been observed by Schlosser *et al.*[19] Thus, 1-chloro-1-fluoro-2-iodo-2-methylcyclopropane undergoes a 1,4-elimination to 2-fluoro-3-methyl-1,3-butadiene.

The incorporation of an ether molecule into products **18a** and **18b** suggests the involvement of a carbene (Figure 5). It has been previously reported that some cyclopropenes rearrange to vinylcarbenes.[1,3,20] Indeed, a 1,2-elimination reaction in **9** leads to the highly strained cyclopropene **10**. The cyclopropene-vinylcarbene rearrangement **10** → **17** proceeds through the opening of the central bond of bicyclic compound **10**. The resulting cyclohexenylidene **17** stabilizes itself through an intermolecular C-H bond insertion into the ether solvent. A product of an intramolecular 1,2-hydrogen shift of the carbene **17** was not detected.

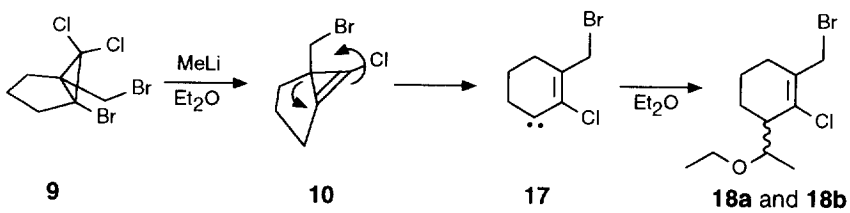


Figure 5. Formation of cyclohexenylidene **17** from cyclopropene **10**

When the reaction was performed at a lower temperature (-78°C), the ratio of 1,4-elimination versus 1,2-elimination changed in favor of carbene products **18a** and **18b** resulting from the preceeding 1,2-elimination (s. Table 1). A similar insertion reaction of a cyclohexenylidene into THF has been previously reported.[3a,21] Again, as in **17**, no 1,2-hydrogen shift and formation of a 1,3-cyclohexadiene was observed.

When the reaction of **9** with one equivalent of methyllithium was performed at -5°C, a new product with spectra similar to methylenecyclohexene **14** was detected. Mass spectrometric data indicated the presence of two chlorine atoms in the molecule. This seems, along with a short retention time on the analytical GC, good evidence for the existence of the second 1,4-elimination product **16**. The product, however, was rather unstable and could not be fully characterized to confirm the suggested structure **16**. Upon treatment of **9** with excess methyllithium, instead of **14**, 2-chloro-1-methyl-3-methylenecyclohexene was observed as a major product.

When, instead of methyllithium, *tert*-butyllithium was used in the reaction with **9**, one major product was found. An aliquot drawn from the reaction in progress indicated, however, through GC analysis, the presence of more than 50% of unreacted starting material. A second equivalent of *tert*-butyllithium was

Temperature Dependency of the Reaction of **9** with Alkyllithium					
COMPOUND	**14**	**16**	**18a**	**18b**	**9**
RETENTION TIME [min] [a]	6.98	4.98	15.15	16.34	14.22
Experiment A CH_3Li, -40 °C	50.3	6.5	9.6	32.5	1.1
Experiment B CH_3Li, -78 °C	20.3	0.8	4.7	38.2	36.0
Experiment C CH_3Li, -5 °C	24.6 [b]	4.1	10.5	25.8	35.0
Experiment D *t*-BuLi, -40 °C	68 [c]	--	--	--	32

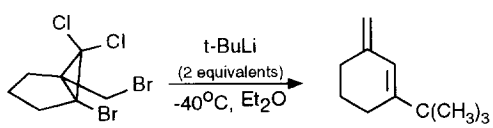
a) Analytical Gaschromatograph

b) Includes 18% of 2-chloro-1-methyl-3-methylenecyclohex-1-ene

c) Isolated as 3-methylene-1-*tert*-butylcyclohex-1-ene (**19**)

Table 1. Temperature dependency of the reaction of **9** with alkyllithium

introduced for completion of the reaction. The product isolated turned out to be **19** (Figure 6), a reduced derivative of the 1,4-elimination product **14**. It appears that **14** is more reactive towards *tert*-butyllithium than the starting compound **9**, thus explaining the need for a second equivalent of lithium reagent.



9 **19**

Figure 6. Reaction of bicyclohexane **9** with *t*-butyllithium

In all the reactions of tetrahalobicyclohexane **9** with alkyllithiums, no conclusive evidence for a competing 1,3-elimination has been found. Products **18a** and **18b**, deriving from a 1,2-elimination, were formed together with the products from the competing 1,4-elimination. A more detailed look into the different halogen-metal-exchange reactions which are possible in **9**, reveals interesting results. Bromine-lithium-exchange of the primary bromine in **9** affords **13** (Figure 4). Two 1,4-eliminations in **13**, as indicated by the curved arrows lead directly to the butadienes **14** and **16**.[22] These compounds, however, can also be formed through 1,3-eliminations of LiCl to 5-chloro-6-bromotricyclo[3.2.0.0^{1,6}]heptane (**11**) or of LiBr to propellane **15**, respectively. By releasing substantial ring strain, **11** and **15** could rearrange to the butadienes **14** and **16**. A 1,2-elimination to generate bicyclic cyclopropene **10** is not possible from **13** but from **12** (Figure 4) in which the tertiary bromine atom has been exchanged by lithium. The cyclopropene-vinylcarbene rearrangement

transforms **10** into **17** which undergoes C-H insertions into the solvent ether. A competing 1,3-elimination reaction in **12** could lead to propellane **15** which could rearrange to butadiene **16**.[22] It is interesting to note, that bromo-chlorobutadiene **14** cannot be obtained from organolithium compound **12**. Therefore, obviously *both* bromine atoms have to be exchanged in **9** by lithium in order to explain all four products obtained. Thus, **16** can derive from either **12** or **13**. In contrast, **14** can only be formed from **13** while the ether insertion products **18a** and **18b** derive from **12** *via* **10** and **17**.

Baird *et al.*[1d,23] reported on the reaction of **1** with methyllithium. In the case of compound **1a** (X = Cl, R = CH_2Cl), a 1,2-elimination occured exclusively (Figure 1), while **1b** (X = Br, R = CH_2Cl) gave only a product that derives from a 1,3-elimination, i.e. ring closure.[23]

Overall, the scope of 1,n-elimination reactions in synthesis seems widespread and useful for the preparation of different ring and also open-chain compounds.

EXPERIMENTAL SECTION

General Methods. Melting points are uncorrected. IR spectra were recorded on a FT-IR spectrophotometer. ^1H and ^{13}C NMR spectra were acquired at 360 (90) MHz, respectively. For the ^1H NMR spectra TMS served as an internal chemical shift reference. ^{13}C spectra were referenced to the center line of $CDCl_3$ at 77.0 ppm. Coupling constants are reported in Hertz. Low resolution mass spectra were obtained by GC-MS. Analytical gas chromatography was performed using a Methylsilicone 20 m x 0.2 mm glass capillary column (Temperature program, Inj. 150 °C; Oven, initial: 100 °C for 2 min; rate 5 °C/min; final: 200 °C). Flash chromatography was done on a 35 cm column (i.d. = 2.4 cm) using silica gel (230–400 mesh). Preparative HPLC was performed using a Si60 Polygosil 60-5 (Macherey & Nagel) column (25 cm x 3 cm). Combustion analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

1-Bromo-2-hydroxymethylcyclopent-1-ene (7).[16] The reduction of 15.5 g (88.6 mmol) of **6** was performed with 3.8 g (100 mmol) of lithium aluminum hydride in dry diethyl ether. The mixture was stirred for two hours, after the addition of **6** was completed. Hydrolysis was accomplished with dilute hydrochloric acid. This also dissolved the main part of the hydroxides. Extractions with ether, drying over magnesium sulfate and evaporation of the solvents completed the work-up procedure; Analytical GC (1) retention time: 6.30 minutes, (2) purity: 93.5%; ^1H NMR ($CDCl_3$), δ 4.22("t", 2H), 2.60-2.67 ("t", 2H), 2.41-2.48 ("t", 2H), 1.90-1.99 (m, 2H), 1.65 (s, broad, 1H, OH) ppm; ^{13}C NMR($CDCl_3$), δ 139.7(s), 118.0(s), 60.4 (t, J_{C-H}=143.1 Hz), 40.3 (t, J_{C-H}=133.8 Hz), 32.4 (t, J_{C-H}=129.6Hz), 21.7 (t, J_{C-H}=131.4Hz)ppm.

1-Bromo-2-bromomethylcyclopent-1-ene (8).[16] 11.4 g (42 mmol) of phosphorous tribromide in dichloromethane were placed into a three-necked flask equipped with a dropping funnel, a gas inlet and an outlet. Under stirring, 3.3 g (42 mmol) of pyridine in 50 mL of methylene chloride were slowly added. The flask was then cooled to -5°C. A solution containing (1) 14.0 g (80 mmol) of alcohol (7) and (2) 3.3 g (42 mmol) of pyridine in 25 mL of methylene chloride was added dropwise. Stirring was continued at room temperature for 48 hours. For the work-up, hydrolysis with ice water was followed by extraction with chloroform. This was followed by sodium bicarbonate and water washings of the combined organic layers. Finally, the solvent was evaporated and the crude product was chromatographed with pentane as a solvent; Yield: 15.75 g (74% starting from aldehyde **6**); Analytical GC; (1) retention time: 6.22 minutes, (2) purity: 99%; ^1H NMR ($CDCl_3$), δ 4.08 (s, 2H), 2.65-2.71 (t, 2H), 2.47-2.53 ("t", 2H), 1.95-2.05 ("t", 2H)ppm; ^{13}C

NMR ($CDCl_3$), δ 136.7(s), 122.0(s), 40.4 (t, J_{C-H}=134.7Hz), 32.8(t, J_{C-H}=130.9Hz), 28.7(t, J_{C-H}=154.1Hz), 21.4(t, J_{C-H}=133.5Hz)ppm.

1-Bromo-5-bromomethyl-6,6-dichlorobicyclo[3.1.0]hexane (9). A 100 mL flask was charged with 20 g (0.5 mol) of sodium hydroxide powder, a solution of 2.4 g (10 mmol) of olefin **8** in 50 mL of dry chloroform and catalytical amounts of TEBA. The flask was swirled and quickly connected to an extra long condenser (40 cm). The reaction started instantly and was so vigorous that the mixture extended up into the condenser. The mixture was ultrasonicated for 35 minutes, after the reaction had calmed down. The cooled mixture was then filtered through filter aid (Celite® 454) and the filter cake was washed with several portions of methylene chloride. The solvents were evaporated and the dark brown residue was taken up in petroleum ether and chromatographed through silica gel. Further purification was accomplished through recrystallization from hexanes; Yield: 2.3 g (71.2%); Analytical GC; (1) retention time: 14.2 minutes, (2) purity: 99.2%; ^1H NMR ($CDCl_3$), δ 3.65 ("d," 1H, J_{gem}=-12.7 Hz), 3.62(d, 1H, J_{gem}=-12.7 Hz), 2.68-2.79 (m, 2H), 2.43-2.53(m, 1H), 2.26-2.35 (m, 1H), 1.83-1.95 (m, 1H), 1.66-1.80 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$), δ 72.9(s, C6), 54.3(s, C1), 46.6 (s, C5), 40.8 (t, J_{C-H}=134.6 Hz, C2), 34.6 (t, J_{C-H}=155.0 Hz,C7), 32.8 (t, J_{C-H}=132.6 Hz, C3 or C4), 23.8(t, J_{C-H}=132.7 Hz, C3 or C4) ppm; IR(KBr): 2987, 2964, 2932, 2923, 2857, 1468, 1438, 1313, 1289, 1274, 1231, 1216, 1186, 1091, 1047, 996, 937, 898, 886, 870, 849, 840, 774, 681, 656, 625 cm^{-1}; MS(70eV), m/z(%): M+ not found, 290, 288, 286, 284([M-Cl]$^+$, 15, 20, 9), 289, 287, 285([M-HCl]$^+$, 9, 15, 5), 247, 245, 243, 241([M-Br]$^+$, 4, 31, 73, 42), 209(12), 207(55), 205(41), 171(10), 169(10), 164(10), 163(39), 162(10), 161(58), 129(11), 128(23), 127(58), 126(66), 125(100), 99(15), 91(80), 89(19), 77(12), 75(13), 73(21), 65(17), 63(34), 62(23), 51(17); $C_7H_8Br_2Cl_2$(322.85): calcd: C 26.04%, H 2.50%; found: C 26.17%, H 2.56%.

Reactions of 1-Bromo-5-bromomethyl-6,6-dichlorobicyclo[3.1.0]hexane (9) with Alkyllithium.

General Procedure: A moisture-free flask with an argon inlet and a rubber septum was charged with 500 mg (1.55 mmol) of tetrahalobicyclohexane **9** in 10 mL of anhydrous diethyl ether. The flask was cooled to one of the temperatures stated below. 1.2 Equivalents (1.86 mmol) of an alkyllithium solution were slowly added with a syringe. The mixture was stirred for 45 minutes and then allowed to warm up to room temperature. Hyrolysis with water was followed by extraction with diethyl ether. The combined organic layers were then washed with water and dried over potassium carbonate. The sample was analyzed on the analytical gas chromatograph.

Experiment A:

The alkyllithium reagent used was methyllithium and the temperature of addition was -40°C. The crude mixture contained three major components- **14, 18a,b** and **16** (s. Table 1).

Experiment B:

The alkyllithium reagent used was methyllithium and the temperature of addition was -78°C. The crude mixture contained three major products as well as unreacted starting material **9**. The ratio of products to **9** was 61 : 39.

Experiment C:

The reaction was performed with methyllithium and the temperature of addition was -5°C. The crude mixture contained besides **14, 16, 18**, also 2-chloro-1-methyl-3-methylenecyclohex-1-ene.

Purification of the products formed in experiments A and B was accomplished through flash column chromatography (hexanes/ether 98 : 2). The first fractions eluted contained mainly product **14**, whereas the subsequent fractions gave **18a** and **18b**. Further purification of **14** involved preparative gas chromatography (Column: 20% QF1 on Chromosorb W (AW) 45-60 mesh, 15′, aluminum tubing, 0.19″ i.d., 120 ml He/min; oven: 90°C, injector 120°C, detector: 130°C). The separation of the products of experiment A gave 67 mg (21%) of **14**. The later fractions of the column chromatography contained the higher boiling compounds **18a** and **18b**. These fractions were separated using HPLC (hexanes); Yield: 15 mg (4.6%) **18a** and 45 mg (13.9%) **18b**, from experiment A. Purification of 2-chloro-1-methyl-3-methylenecyclohex-1-ene, a major product from experiment C, was accomplished through short-path distillation. An analytical sample was separated through preparative gas chromatography (Column, s. above, oven: 85°C, injector 100°C, detector 110°C).

Experiment D:

The alkyllithium reagent used was *tert*-butyllithium and the temperature of addition was -40°C. A sample drawn from the reaction in progress indicated one major product along with more than 50% of unreacted starting material **9** (with a retention time of 14.22 minutes). A second equivalent of *tert*-butyllithium was added and the reaction time doubled. After work-up, the GC analysis indicated more formation of product **19**.

Product **19** was separated through short-path distillation. Preparative gas chromatography (Column, s. above; oven: 70°C, injector 90°C, detector 90°C) gave 61 mg (26%) of **19** (92.6% purity).

1-Bromo-2-chloro-3-methylenecyclohex-1-ene (14). ^{1}H NMR ($CDCl_3$), δ 5.45 (d, 1H, J=0.8 Hz), 5.00-5.02 (m, 1H), 2.74 (tt, 2H, J=6.4Hz, J=0.8 Hz), 2.46-2.52 (m, 2H), 1.77-1.86 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$), δ 139.8(s), 131.2(s), 126.0(s), 113.6 (t, J_{C-H}=159.2 Hz, C7), 37.9 (t, J_{C-H}=133.6 Hz), 31.7 (t, J_{C-H}=131.3 Hz), 23.8 (t, J_{C-H}=130.3 Hz) ppm; MS(70eV), m/z(%): 210, 208, 206(M^+, 9, 36, 27), 129, 127([M-Br]$^+$, 18, 55), 92($C_7H_8^+$, 16), 91($C_7H_7^+$, 100), 65(17), 63(17).

1,1-Dichloromethyliden-2-methylencyclopentane (16). ^{1}H NMR ($CDCl_3$), δ 5.51 (s, 1H), 4.74 (s, 1H), 2.23 (t, 2H), 1.94-1.89 (m, 2H), 1.11 (quint., 2H); MS (70 eV), m/z (%): 166, 164, 162 (M^+, 5, 27, 41) 129, 127 ([M-Cl]$^+$, 26,85), 125 (10), 99 (13), 92 (11), 91 (100), 73 (11), 65 (13), 63 (18).

2-Chloro-1-methyl-3-3-methylenecyclohex-1-ene. ^{1}H NMR ($CDCl_3$), δ 5.29 (s, 1H), 4.82 (s, 1H), 2.43 (t, 2H), 2.24 (t, 2H), 1.92 (s, 3H), 1.70 (quint. 2H); ^{13}C NMR ($CDCl_3$), δ 141.1 (s), 135.6 (s), 110.1 (t), 33.5 (t), 32.7 (t), 22.6 (t), 21.5 (q); MS (70 eV), m/z (%): 144, 142 (M^+, 10, 28), 129, 127 ([M-CH_3]$^+$, 10, 30), 107 ([M-Cl]$^+$, 47), 105 (24), 92 (19), 91 (100), 79 (23), 77 (22), 65 (17), 63 (12), 51 (20).

1-Bromomethyl-2-chloro-3-(1-ethoxy-ethyl)cyclohex-1-ene (18a) and (18b). HPLC first fraction: **18a**; ^{1}H NMR ($CDCl_3$), δ 4.14 (q, 2H, J=9.4Hz), 4.08 (dq, 1H, J=6.5Hz, J=2.5Hz), 3.49-3.58 (m, 1H), 3.37-3.46 (m, 1H), 2.20-2.31 (m, 3H), 1.83-1.97 (m, 2H), 1.67-1.80 (m, 1H), 1.48-1.60 (m, 1H), 1.18 (d, 3H, J=6.4Hz), 1.12 (t, 3H, J=7.0Hz) ppm; ^{13}C NMR ($CDCl_3$), δ 135.1(s), 132.2(s), 74.2 (d, J_{C-H}=138.3Hz), 64.9 (t, J_{C-H}=140.8Hz), 47.8 (d, J_{C-H}=126.4Hz), 34.2 (t, J_{C-H}=154.6Hz), 29.2 (t, J_{C-H}=123.0Hz), 23.5 (t, J_{C-H}=128.0Hz), 20.7 (t J_{C-H}=128.9Hz), 18.3 (q, J_{C-H}=125.4Hz), 15.7 (q, J_{C-H}=124.1Hz) ppm; MS(70eV), m/z(%): no M^+ found, 201([M-Br]$^+$, 0.1), 128(3), 73([C_4H_9O]$^+$, 100), 93(6), 91(6), 65(3); IR(film): 2972, 2932, 2865, 1639, 1596, 1459, 1442, 1383, 1370, 1342, 1299, 1259, 1209, 1165, 1096, 1019, 983, 943, 900, 805, 696 cm^{-1}; HPLC second fraction: **18b**; ^{1}H NMR ($CDCl_3$), δ 4.11 (q, 2H, J=9.5Hz), 4.03-4.10 (m, 1H), 3.44-3.56 (m, 2H), 2.75-2.85 (m, 1H), 2.25-2.31 (m, 2H), 1.74-1.86 (m, 2H), 1.64-1.73 (m, 1H), 1.49-1.62 (m, 1H), 1.20 (t, 3H, J=7.0 Hz), 1.04 (d, 3H, J=6.4 Hz). ppm; ^{13}C NMR (CDCl), δ 133.8(s), 132.7(s), 75.4

(d, J_{C-H}=142.5 Hz), 64.0 (t, J_{C-H}=139.8z), 44.4 (d, J_{C-H}=128.4 Hz), 33.6 (t, J_{C-H}=154.3 Hz), 29.4 (t, J_{C-H}=126.6 Hz), 23.1 (t, J_{C-H}=130.2 Hz), 21.0 (t J_{C-H}=127.7 Hz), 15.6 (q, J_{C-H}=126.7 Hz), 15.1 (q, J_{C-H}=126.0 Hz) ppm; IR (film): 2973, 2934, 2865, 2836, 2359, 1642, 1481, 1451, 1439, 1380, 1344, 1308, 1265, 1210, 1160, 1106, 1066, 1049, 1021, 984, 970, 941, 892, 807, 735, 694, 668, 647, cm^{-1}; MS(70eV), m/z(%): no M^+ found, 200([M-HBr]$^+$, 0.4), 73([C_4H_9O]$^+$, 100), 93(5), 91(6).

3-Methylene-1-*tert*-butylcyclohex-1-ene (19). ^1H NMR ($CDCl_3$), δ 6.01 (s, 1H), 4.73 (br. s, 1H), 4.70 (br. s, 1H), 2.30 (tt, 2H), 2.12 ("t", 2H), 1.65-1.73 (m, 2H), 1.05 (s, 9H)ppm; ^{13}C NMR ($CDCl_3$), δ 150.7(s), 144.5(s), 121.2 (d, J_{C-H}=151.5 Hz, C2), 108.8 (t, J_{C-H}=155.0Hz, C7), 35.6(s), 30.7 (t, J_{C-H}=125.1Hz), 28.7 (q, J_{C-H}=127.9Hz), 25.1 (t, J_{C-H}=126.7Hz), 23.7 (t, J_{C-H}=129.0Hz) ppm.

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