# Ring-Opening of (Cyclobutylmethyl)lithium and [(3-*tert*-Butyl-1-bicyclo[1.1.1]pentyl)methyl]lithium

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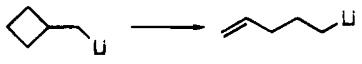
The ring-opening of (cyclobutylmethyl)lithium (**1**) to 4-pentenyllithium (**2**) has been investigated in a solvent system composed of isooctane–dibutyl ether (3:2 by volume). The isomerization of **1** to **2**, which is much more rapid than is cleavage of the corresponding Grignard reagent, is characterized by the following activation parameters: $E_a = 14.7 \pm 1.2$ kcal/mol, $\ln A = 21.6 \pm 2.5$; $\Delta H^{\ddagger} = 14.2 \pm 1.2$ kcal/mol, $\Delta S^{\ddagger} = -17.3 \pm 5$ eu. The two-step isomerization of [(3-*tert*-butyl-1-bicyclo[1.1.1]pentyl)methyl]lithium (**5**) to 4-*tert*-butyl-2-methylidene-4-pentenyllithium (**7**) via [(1-*tert*-butyl-3-methylidenecyclobutyl)methyl]lithium (**6**) in pentane–diethyl ether involves a very rapid initial ring-opening of **5** to **6** ($t_{1/2} < 15$ min at $-131$ °C) followed by a slower isomerization of **6** to **7** ($t_{1/2} \approx 24$ min at $-7.7$ °C).

Although the ring-opening of cyclobutylmethyl Grignard reagents has been well studied,[1,2] there is a dearth of information available on the rearrangement of the analogous organolithiums. In their pioneering study of the cleavage of cyclobutylmethyl organometallics, Hill, Richey, and Rees noted[3] that the isomerization of (cyclobutylmethyl)lithium (**1**) to 4-pentenyllithium (**2**) in benzene solution is more rapid than is the ring-opening of the corresponding Grignard reagents, but quantitative kinetic data for the ring-cleavage of **1** are unavailable. Herein we report the results of an investigation of the kinetics of the rearrangement of **1** to **2** as well as the results of a more limited study of the cleavage of a (1-bicyclo[1.1.1]pentylmethyl)lithium.

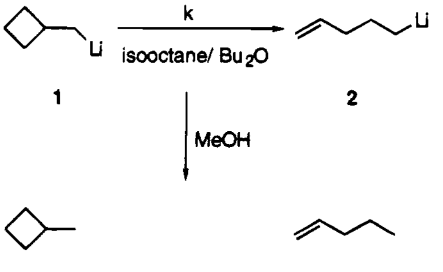


**1** **2**

## Results and Discussion

(Cyclobutylmethyl)lithium (**1**) was prepared from (iodomethyl)cyclobutane following a modification of the general protocol for low-temperature lithium–iodine exchange with *tert*-butyllithium (*t*-BuLi).[4] Thus, treatment of a 0.1 M solution of (iodomethyl)cyclobutane in dry isooctane–dibutyl ether (3:2 by volume) with 2.2 mol equiv of *t*-BuLi at $-78$ °C under argon affords **1** in essentially quantitative yield.[5] It might be noted that, although a solvent system composed of diethyl ether and *n*-pentane is normally employed for the exchange reaction,[4] it was necessary in the present case to generate **1** in a solvent mixture containing a higher boiling dialkyl ether and hydrocarbon in order to permit base line separation of the low-boiling hydrolysis products by GC analysis (vide infra) without interference from solvent.

The rearrangement of **1** to **2** is quite sluggish at temperatures well below ambient: solutions of **1** in isooctane–dibutyl ether are indefinitely stable at $-78$ °C and only 3% of 4-pentenyllithium (**2**) is formed when a solution of **1** is allowed to stand at $-50$ °C for 1 h. For this reason, the isomerization of **1** to **2** was monitored at several temperatures between $-32.1$ and $-13.2$ °C by rapid removal of aliquots, quench with dry, deoxygenated methanol to give methylcyclobutane (**3**) and 1-pentene (**4**), and quantitation of the hydrocarbons by GC analysis.



The conversion of **1** to **2** was a clean first-order process; there was no evidence of products other than **3** and **4** in any of the reaction mixtures. Rearrangements of **1** to **2** were followed through 3–4 half-lives by monitoring both the disappearance of **1** (assayed as **3**) and the appearance of **2** (assayed as **4**). The data for disappearance of **1** and appearance of **2** were independently fit by nonlinear least-squares analysis to the standard exponential form of the first-order rate expression to give the rate constants reported in Table 1. In all instances, the rate of

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[⊗] Abstract published in *Advance ACS Abstracts*, January 1, 1995.

[1] Much of the early work on the rearrangement of cyclobutylmethyl Grignard reagents has been reviewed: (a) Hill, E. A. *J. Organomet. Chem.* **1975**, *91*, 123. (b) Hill, E. A. *Adv. Organomet. Chem.* **1977**, *16*, 131.

[2] (a) Hill, E. A.; Davidson, J. A. *J. Am. Chem. Soc.* **1964**, *86*, 4663. (b) Hill, E. A.; Ni, H. R. *J. Org. Chem.* **1971**, *36*, 4133. (c) Hill, E. A.; Hallade, M. W. *J. Organomet. Chem.* **1988**, *352*, 263 and references therein.

[3] Hill, E. A.; Richey, H. G., Jr.; Rees, T. C. *J. Org. Chem.* **1963**, *28*, 2161.

[4] Bailey, W. F.; Punzalan, E. R. *J. Org. Chem.* **1990**, *55*, 5404.

[5] As noted elsewhere,[4] a small but non-negligible quantity of hydrocarbon, formally derived from reduction of the halide, is produced as a byproduct of the lithium–iodine exchange between a primary alkyl iodide and *t*-BuI. The hydrocarbon results from reaction of the organolithium product with the cogenerated *t*-BuI: $RCH_2Li + (CH_3)_3CCl \rightarrow RCH_3 + (CH_3)_2C{=}CH_2 + LiI$. Thus, solutions of **1** prepared by lithium–iodine exchange between (iodomethyl)cyclobutane and *t*-BuLi contain a small amount (2–5%) of methylcyclobutane.

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**Table 1. First-Order Rate Constants and Activation Parameters for the Ring-Opening of Cyclobutylmethyllithium (1) to 4-Pentenyllithium (2)**[a]

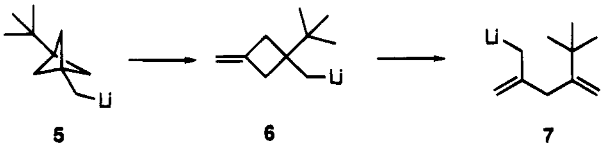
| entry | $T$, °C | $10^4k$, s$^{-1}$ | $E_a$, kcal/mol$^{-1}$ | ln $A$ | $\Delta H^{\ddagger}$, kcal/mol$^{-1}$ | $\Delta S^{\ddagger}$, eu |
|---|---|---|---|---|---|---|
| 1 | −32.1 | 1.1 ± 0.1 | 14.7 ± 1.2 | 21.6 ± 2.5 | 14.2 ± 1.2 | −17.3 ± 5 |
| 2 | −31.8 | 1.1 ± 0.1 | | | | |
| 3 | −21.7 | 4.8 ± 0.1 | | | | |
| 4 | −13.2 | 9.4 ± 0.4 | | | | |

[a] Errors are reported as propagated standard deviations.

appearance of **2** was identical, within the experimental error of the measurements, to the rate of disappearance of **1**, and the average rate constants appear in Table 1. Activation parameters for the cleavage of **1** were obtained by application of the Eyring equation: a plot of $\ln(k/T)$ versus $1/T$ was linear and gave $\Delta H^{\ddagger} = 14.2 \pm 1.2$ kcal/mol, $\Delta S^{\ddagger} = -17.3 \pm 5$ eu. The corresponding Arrhenius parameters are: $E_a = 14.7 \pm 1.2$ kcal/mol, $\ln A = 21.6 \pm 2.5$.

The data summarized in Table 1 demonstrate that the rearrangement of **1** to **2** is, as previously noted,[3] much more rapid than is cleavage of the corresponding Grignard reagents. While detailed comparison of kinetic data for lithium and magnesium halide organometallics may be inappropriate due, inter alia, to differences in the solvent used for the studies, the greater kinetic stability of (cyclobutylmethyl)magnesium halides vis-à-vis **1** is evident from the fact that the half-time for cleavage of **1** in isooctane−dibutyl ether at 0 °C (i.e., $t_{1/2} \approx 3$ min) is much shorter than that of (cyclobutylmethyl)magnesium bromide in THF at +90 °C (i.e., $t_{1/2} \approx 6.5$ h).[2]

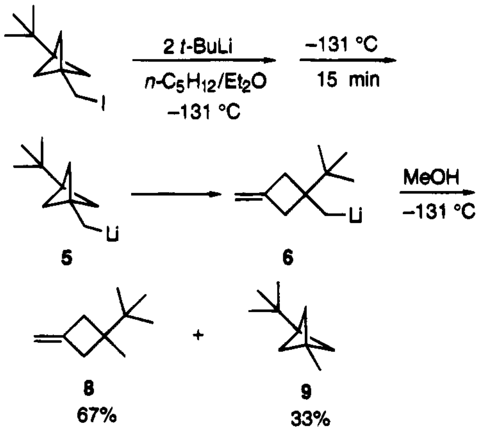
The effect of ring-strain on the rate of cleavage of a (cyclobutylmethyl)lithium was investigated in a less extensive analysis of the two-step isomerization of [(3-*tert*-butyl-1-bicyclo[1.1.1]pentyl)methyl)lithium (**5**) to (4-*tert*-butyl-2-methylidene-4-pentenyl)lithium (**7**) via [(1-*tert*-butyl-3-methylidenecyclobutyl)methyl]lithium (**6**).



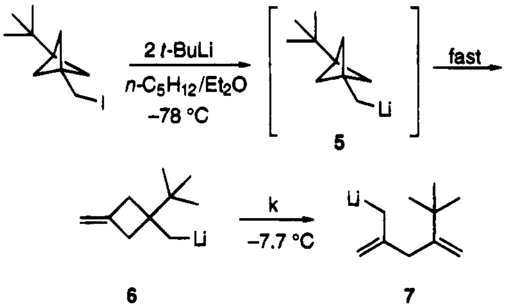
Bicyclic organolithium **5** was generated as an approximately 0.1 M solution in dry *n*-pentane−diethyl ether (3:2 by vol) by treatment of 3-*tert*-butyl-1-(iodomethyl)bicyclo[1.1.1]pentane with 2 mol equiv of *t*-BuLi at −131 °C. In light of the considerable strain that is relieved by cleavage of **5** to give **6**, it is perhaps not surprising that the initial ring-opening of **5** was found, as illustrated in Scheme 1, to be a remarkably rapid process. Quench of a reaction mixture that had been allowed to stand at −131 °C for 15 min prior to quench with deoxygenated MeOH afforded a 2:1 mixture of 1-*tert*-butyl-1-methyl-3-methylidenecyclobutane (**8**) and 1-*tert*-butyl-3-methylbicyclo[1.1.1]pentane (**9**), respectively. Thus, the half-time for isomerization of **5** to **6** at −131 °C is less than 15 min ($k >$ ca. $8 \times 10^{-4}$ s$^{-1}$). The subsequent ring-opening of **6** is a much less facile process.

A solution of **6** in dry *n*-pentane−diethyl ether (3:2 by vol) was generated, as shown in Scheme 2, by allowing the rapid ring-opening of **5** to proceed to completion at −78 °C. The rather sluggish rearrangement of **6** to **7** was monitored through two half-lives at −7.7 °C by observation of the $CH_2Li$ singlets of **6** and **7** in the $^1H$ NMR spectrum: the $CH_2Li$ protons of **6** absorb at $\delta = +0.021$ while those of **7** resonate at $\delta = -0.069$. Integration of the singlets as a function of time gave a data set for the appearance of **7** and the disappearance of **6**, and the rate of both processes were well fit by the standard exponential form of the first-order rate expression. The rate constants for both the appearance of **7** and the disappearance of **6**, which were identical within experimental error, give a first-order rate constant for the ring-opening of **6** to **7** of $4.9 \pm 0.2 \times 10^{-4}$ s$^{-1}$ ($t_{1/2} \approx 24$ min) at −7.7 °C. This rate constant is comparable in magnitude to that for the isomerization of the parent (cyclobutylmethyl)lithium (**1**) at −22 °C (cf. Table 1, entry 3). Thus, the more highly substituted derivative **6** appears to open more slowly than does the parent **1**. While solvent effects may be responsible for a portion of this rate difference, since different solvent systems were employed for the two kinetic studies, it is perhaps somewhat surprising that the cleavage of **6** is slower than that of **1**. Indeed, relief of the additional strain engendered by the C(3)-methylene moiety upon cleavage of **6** might be expected to facilitate the ring-opening of **6** vis-à-vis **1**. Apparently, the presence of the bulky *tert*-butyl substituent at C(1) in **6** slows the ring-opening via steric destabilization of the transition state: similar steric congestion in the vicinity of C(1) is known to retard the cleavage of cyclobutylmethyl Grignard reagents.[1,2,6]

**Scheme 1**



**Scheme 2**



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[6] Hill, E. A.; Li, B. *J. Organomet. Chem.* **1993**, *448*, 9 and references therein.

## Experimental Section

**General.** General spectroscopic and chromatographic procedures, methods used for the purification of reagents and solvents, and precautions regarding the manipulation of organolithiums have been previously described.[7] Temperature control during kinetic studies was accomplished using a Frigomix 1495 constant temperature bath equipped with a Thermomix 1460 controller and an Omega HH22 type J-K digital thermometer and are considered to be accurate to ±1 °C. Probe temperature during kinetic studies monitored by $^1$H NMR spectroscopy was measured as described by Van Geet[8] and are considered to be accurate to ±0.5 °C. Solutions of *t*-BuLi in isooctane were prepared by addition of scrupulously dry isooctane to commercial *t*-BuLi in *n*-pentane while continuously removing volatile components by distillation. The concentration of solutions of *t*-BuLi was determined immediately prior to use by the method of Watson and Eastham.[9]

**(Iodomethyl)cyclobutane.** Following the general procedure of Crossland and Servis,[10] 1.62 g (18.8 mmol) of cyclobutanemethanol was converted to its mesylate. The crude mesylate was added to a solution of 6.20 g (41.4 mmol) of dry sodium iodide in 60 mL of anhydrous acetone, and the mixture was stirred at room temperature under an atmosphere of nitrogen for 10 h followed by heating at gentle reflux for an additional 2 h. The reaction mixture was then cooled to room temperature, inorganic salts were removed by filtration, and the filtrate was concentrated by rotary evaporation. The residue was taken up in pentane, washed successively with 10% aqueous sodium thiosulfate, water, and brine, dried ($MgSO_4$), and concentrated. The residue was purified by flash chromatography over silica gel using hexanes as eluent to afford 1.88 g (51%) of the known iodide:[11] $R_f = 0.77$ (hexanes); $^1$H NMR ($CDCl_3$) $\delta$ 1.58–1.82 (m, 4 H), 2.01–2.11 (m, 2 H), 2.57–2.70 (m, 1 H), 3.22 (d, $J$ = 7.70 Hz, 2 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 14.32, 15.90, 29.15, 38.49.

**Kinetics of the Ring-Opening of (Cyclobutylmethyl)lithium (1).** A septum-capped, 100-mL, three-necked, round-bottomed flask, equipped with a Teflon-clad thermometer probe and a magnetic stirring bar, was charged with an accurately weighed quantity of (iodomethyl)cyclobutane (2–3 mmol). Enough dry dibutyl ether and anhydrous isooctane (3:2 by volume) were added to make an approximately 0.1 M solution. The flask was then lowered into a dry ice–acetone bath (−78 °C), and the solution was stirred. After 5 min, 2.2 mol equiv of *t*-BuLi in isooctane was slowly added via syringe and stirring was continued for an additional 5 min. The flask was then transferred to a constant temperature bath that was preequilibrated to the temperature of the kinetic study. Aliquots were withdrawn at regular intervals via a 4-in. Teflon cannula that was directly connected to a 5-mL test tube containing approximately 3 mL of oxygen-free methanol. The resulting solutions were washed with equal volumes of water and brine, dried ($MgSO_4$), and analyzed by GC on a 19-m × 0.20-mm 20% methyl phenyl silicone (0.33-$\mu$m film thickness) fused-silica capillary column using temperature programming (0 °C for 5 min, 20 °C/min to 200 °C, 200 °C for 5 min) to effect base line separation of methylcyclobutane (**3**) and 1-pentene (**4**). The normalized peak areas of **3** and **4** were fit by nonlinear least-squares analysis to the exponential form of the first-order rate law: $A = A_o\ e^{-k1t}$ for the disappearance of **1**, where $A$ is the relative area of **3** at time $t$, $A_o$ is the initial area of **3**, and $k_1$ is the rate constant for the disappearance of **1**; $B = B_\omega\ (1 - e^{-k2t})$ for the appearance of 4-pentenyllithium (**2**), where $B$ is the relative area of **4** at time $t$, $B_\omega$ is the final area of **4**, and $k_2$ is the rate constant for the appearance of **2**. In all instances, $k_1 = k_2$ within the error of the determinations and the first-order rate constants summarized in Table 1 are the average of these values.

**3-*tert*-Butylbicyclo[1.1.1]pentanol.** A solution of 2.75 g (6.37 mmol) of 3-*tert*-butylbicyclo[1.1.1]pentane-1-carboxylic acid[12] in 70 mL of dry ether was added dropwise over 10 min to a solution of 1.5 g of lithium aluminum hydride in 70 mL of dry ether. The solution was heated under reflux for 1 h and then cooled to room temperature before being treated with 5 mL of a saturated, aqueous solution of $Na_2SO_4$. After 15 min the mixture was filtered, the solids were washed with fresh ether, and the combined ether extracts were dried ($MgSO_4$) and concentrated. Distillation (Kugelrohr, 70 °C (2 mm)) of the residue gave 2.5 g (98%) of the title alcohol which crystallized rapidly: mp 46–47 °C; IR (Nujol) 3345 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 0.84 (s, 9H), 1.48 (s, 6H), 1.65 (s, 1H), 3.58 (s, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 25.86, 29.52, 37.04, 44.94, 48.25, 63.64. Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.50: H, 11.90.

**3-*tert*-Butyl-1-[(tosyloxy)methyl]bicyclo[1.1.1]pentane.** A solution of 2.30 g (14.9 mmol) of 3-*tert*-butylbicyclo[1.1.1]pentanol in 20 mL of methylene chloride containing 2 mL of pyridine was treated with tosyl chloride (1.1 equiv) under the usual conditions. Normal workup gave the crude product which, upon recrystallization from hexane, afforded 4.0 g (87%) of the title ester: mp 96–97 °C; $^1$H NMR ($CDCl_3$) $\delta$ 0.82 (s, 9H), 1.47 (s, 6H), 2.47 (s, 3H), 3.98 (s, 2H), 7.37, 7.76 (d, $J$ = 8.6 Hz, 4H); $^{13}$C NMR ($CDCl_3$) $\delta$ 21.66, 25.79, 29.50, 34.19, 45.84, 49.03, 70.64, 127.90, 129.79, 133.35, 144.61. Anal. Calcd for $C_{17}H_{24}O_3S$: C, 66.20; H, 7.84. Found: C, 66.20; H, 8.00.

**3-*tert*-Butyl-1-(iodomethyl)bicyclo[1.1.1]pentane.** A solution of 1.2 g (3.9 mmol) of 3-*tert*-butyl-1-[(tosyloxy)methyl]bicyclo[1.1.1]pentane in 25 mL of 1,2-dimethoxyethane was treated with 3.0 g of sodium iodide and the mixture was stirred at 65 °C for 24 h under a nitrogen atmosphere. After addition of 100 mL of hexane, the mixture was washed with three 25-mL portions of water and then dried ($MgSO_4$) and concentrated. The residue was distilled (Kugelrohr, 90 °C (2 mm)) giving 0.94 g (91%) of the pure iodide: $^1$H NMR ($CDCl_3$) $\delta$ 0.83 (s, 9H), 1.48 (s, 6H), 3.32 (s, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 10.46, 25.89, 29.07, 37.49, 46.07, 46.57. Anal. Calcd for $C_{10}H_{17}I$: C, 45.47; H, 6.49. Found: C, 45.8; H, 6.5.

**3-*tert*-Butyl-1-(bromomethyl)bicyclo[1.1.1]pentane.** A solution of 2.0 g (6.5 mmol) of 3-*tert*-butyl-1-[(tosyloxy)methyl]bicyclo[1.1.1]pentane in 35 mL of dry THF was treated with 2.26 g of lithium bromide and the mixture stirred at 24 °C for 24 h under a nitrogen atmosphere. The solvent was evaporated and ether was added to the residue which was then washed with three 20-mL portions of water, dried ($MgSO_4$), and concentrated. Distillation of the residue (Kugelrohr, 90 °C (15 mm)) gave 1.32 g (93%) of the pure bromide: $^1$H NMR ($CDCl_3$) $\delta$ 0.85 (s, 9H), 1.52 (s, 6H), 3.43 (s, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 25.86, 29.32, 35.18, 36.70, 46.24, 47.30. Anal. Calcd for $C_{10}H_{17}Br$: C, 55.31; H, 7.89. Found: C, 55.0; H, 8.1.

**1-*tert*-Butyl-3-methylbicyclo[1.1.1]pentane (9).** A solution of 0.40 g (1.8 mmol) of 3-*tert*-butyl-1-(bromomethyl)bicyclo[1.1.1]pentane and 0.18 g of sodium borohydride in 15 mL of dry HMPA was stirred at 24 °C under a nitrogen atmosphere for 48 h. After addition of water, the mixture was extracted with 50 mL of pentane, and the extracts were washed with three 20-mL portions of water before being dried ($MgSO_4$). The solvent was removed carefully under vacuum at room temperature and the residue was distilled (Kugelrohr, 100 °C (70 mm)) affording 0.19 g (74%) of the title hydrocarbon: $^1$H NMR ($CDCl_3$) $\delta$ 0.80 (s, 9H), 1.13 (s, 3H), 1.39 (s, 6H); $^{13}$C NMR ($CDCl_3$) $\delta$ 18.60, 25.95, 29.38, 33.15, 47.48, 48.25. Anal. Calcd for $C_{10}H_{18}$: C, 86.88; H, 13.12. Found: C, 86.6; H, 13.1.

**Preparation of 2-*tert*-Butyl-4-methyl-1,4-pentadiene by Radical-Mediated Ring-Opening of 1-(Bromomethyl)-3-*tert*-butylbicyclo[1.1.1]pentane.** A stirred solution of 0.4182 g (1.926 mmol) of 1-(bromomethyl)-3-*tert*-butylbicyclo[1.1.1]pentane in 50 mL of dry benzene was heated at reflux under an atmosphere of nitrogen and a solution of 0.6201 g (2.131 mmol) of tri-*n*-butyltin hydride and AIBN (~5 mg) in 9 mL of dry benzene was added over a period of 5 h. The

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[7] Bailey, W. F.; Khanolkar, A. D.; Gavaskar, K. ; Ovaska, T. V.; Rossi, K.; Thiel, Y.; Wiberg, K. B. *J. Am. Chem. Soc.* **1991**, *113*, 5720.

[8] Van Geet, A. L. *Anal. Chem.* **1970**, *42*, 679.

[9] Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165.

[10] Crossland, R. K.; Servis, K. L. *J. Org. Chem.* **1970**, *35*, 3195.

[11] Kaplan, L. *J. Org. Chem.* **1968**, *33*, 2531.

[12] Della, E. W.; Taylor, D. K. *J. Org. Chem.* **1994**, *59*, 2986.

reaction mixture was heated at reflux for an additional 2 h after the addition was complete and then cooled to room temperature. GC analysis on a 19-m × 0.20-mm 20% methyl phenyl silicone (0.33-$\mu$m film thickness) fused-silica capillary column using temperature programming (50 °C for 5 min, 20 °C/min to 250 °C, 250 °C for 5 min) revealed that three products had formed in a 20:4:1 ratio. Solvent was removed at room temperature under a stream of nitrogen and the components were separated by preparative GC on a 10-ft, 10% SE-30 on Anachrom A (60–80 mesh) column at 65 °C. The major product (0.1501 g, 56%) was identified as 2-*tert*-butyl-4-methyl-1,4-pentadiene on the basis of the following spectroscopic properties: $^1$H NMR (CDCl$_3$) $\delta$ 1.07 (s, 9H), 1.69 (s, 3H), 2.77 (s, 2H) , 4.71–4.93 (m, 4H); $^{13}$C NMR (CDCl$_3$) $\delta$ 21.92, 29.20, 36.21, 40.76, 108.06, 112.75, 144.80, 155.01; IR (gas) 3085, 2970, 1795, 1636, 1473, 1374, 1205, 1023, 898 cm$^{-1}$; HRMS calcd for C$_{10}$H$_{18}$ 138.1409, found 138.1404.

The minor products, 0.0110 g (4%) of 1-*tert*-butyl-1-methyl-3-methylidenecyclobutane (**8**) and a trace of 1-*tert*-butyl-3-methylbicyclo[1.1.1]pentane (**9**), were identified by comparison of GC retention times and mass spectra with those of authentic samples.

**1-*tert*-Butyl-1-methyl-3-methylidenecyclobutane (8).** Following the general protocol for lithium–iodine exchange,[4] 1.71 mL of a 2.88 M solution of *t*-BuLi (4.92 mmol) in *n*-pentane was added dropwise at −78 °C under an atmosphere of nitrogen to a 0.1 M solution of 0.5921 g (2.242 mmol) of 3-*tert*-butyl-1-(iodomethyl)bicyclo[1.1.1]pentane in *n*-pentane–diethyl ether (4:1 by vol). The solution was stirred for an additional 5 min at −78 °C after the addition was complete and the flask was then transferred to an ice bath. The mixture was allowed to stand at 0 °C for 15 min then rapidly quenched with 0.5 mL of oxygen-free methanol. The reaction mixture was washed with water and brine and dried (MgSO$_4$). GC analysis on a 19-m × 0.20-mm 20% methyl phenyl silicone (0.33-$\mu$m film thickness) fused-silica capillary column using temperature programming (50 °C for 5 min, 20 °C/min to 250 °C, 250 °C for 5 min) revealed three products in a 85:14:1 ratio. Solvent was removed at room temperature under a stream of nitrogen and the components were separated by preparative GC on a 10-ft, 10% SE-30 on Anachrom A (60–80 mesh) column at 65 °C. The major product (0.1424 g, 46%) was identified as the title compound (**8**) on the basis of the following spectroscopic properties: $^1$H NMR (CDCl$_3$) $\delta$ 0.88 (s, 9H), 1.14 (s, 3H), 2.06 (apparent doublet of quintets, $J$ = 14.40 Hz, $J$ = 2.20 Hz, 2H) , 2.70–2.79 (m, 2H), 4.80 (apparent quintet, $J$ = 2.40 Hz, 2H); $^{13}$C NMR (CDCl$_3$) $\delta$ 23.39, 25.11, 33.86, 39.17, 40.17, 106.84, 145.64; IR (gas) 3079, 2967, 1760, 1676, 1473, 1376, 1200, 1123, 877 cm$^{-1}$, HRMS calcd for C$_{10}$H$_{18}$ 138.1409, found 138.1404.

The minor products, 0.0248 g (8%) of 2-*tert*-butyl-4-methyl-1,4-pentadiene and a trace of 1-*tert*-butyl-3-methylbicyclo[1.1.1]pentane (**9**), were identified by comparison of GC retention times and mass spectra with those of authentic samples.

**Reaction of 3-*tert*-Butyl-1-(Iodomethyl)bicyclo[1.1.1]pentane with *t*-BuLi and Quench at −131 °C (Scheme 1).** A 0.1 M solution of 0.1389 g (0.5258 mmol) of 3-*tert*-butyl-1-(iodomethyl)bicyclo[1.1.1]pentane in *n*-pentane–diethyl ether (3:2 by vol) was cooled to −131 °C (liquid nitrogen–*n*-pentane bath) under nitrogen, and 0.43 mL of a 2.72 M solution of *t*-BuLi (1.2 mmol) in pentane was added dropwise. The solution was stirred for an additional 15 min after the addition followed by rapid quench with 0.5 mL of oxygen-free methanol. The reaction mixture was washed with water and brine and dried (MgSO$_4$). GC analysis on a 19-m × 0.20-mm 20% methyl phenyl silicone (0.33-$\mu$m film thickness) fused-silica capillary column using temperature programming (50 °C for 5 min, 20 °C/min to 250 °C, 250 °C for 5 min) revealed that a 2:1 ratio of 1-*tert*-butyl-1-methyl-3-methylidenecyclobutane (**8**) and 1-*tert*-butyl-3-methylbicyclo[1.1.1]pentane (**9**) had been produced; no other products were detected. The hydrocarbons were identified by comparison of the GC retention times and mass spectra with those of authentic samples.

**Kinetics of the Ring-Opening of [(1-*tert*-Butyl-3-methylidenecyclobutyl)methyl]lithium (6) to (4-*tert*-Butyl-2-methylidene-4-pentenyl)lithium (7).** A 0.1 M solution of **6** in *n*-pentane–diethyl ether (4:1 by vol) was generated under an atmosphere of nitrogen by allowing a solution of **5** (vide supra) to isomerize for 30 min at −78 °C. An aliquot of the supernatant solution was filtered through dry glass wool and transferred via cannula to an oven-dried 5-mm NMR tube that was precooled to −78 °C under inert atmosphere. The sample was loaded into an NMR probe that had been precooled to −7.7 °C. The acquisition parameters were as follows: acquisition time, 1 s; relaxation delay, 0 s; number of transients, 4; sweep width, 1800–2000 Hz; 32 K data points for the Fourier transform. The isomerization was followed for about two half-lives (20 data points) by observation of the CH$_2$-Li region of the spectrum in which **6** appears as a singlet at $\delta$ = +0.021 and **7** as a singlet a $\delta$ = −0.069. Chemical shifts were referenced with respect to the central line of diethyl ether triplet at $\delta$ = 1.07 and are reported relative to tetramethylsilane at $\delta$ = 0.00. The integrals were normalized and analyzed, as described above, by nonlinear fit to the exponential form of the first order rate law to give a rate constant for the conversion of **6** to **7** of $4.9 \pm 0.2 \times 10^{-4}$ s$^{-1}$ at −7.7 °C.

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**Supplementary Material Available:** Copies of the $^1$H and $^{13}$C NMR spectra for all new compounds for which combustion analytical data are not available (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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