Carbanionic Rearrangements of Halomethylenecyclobutanes. The Role of the Halogen

Zhengming Du, Melissa J. Haglund, Lauri A. Pratt, and Karen L. Erickson*

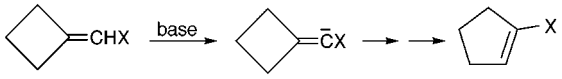
Carlson School of Chemistry, Clark University, Worcester, Massachusetts 01610

Received June 8, 1998

The carbanionic ring enlargement of (halomethylene)cyclobutanes to 1-halocyclopentenes has been extended to the fluoro analogues. At 180 °C, 3-hexyl-1-(fluoromethylene)cyclobutane provides better yields of rearranged product than the corresponding chloride, bromide, or iodide. At temperatures < 100 °C, the yield of ring-enlarged product follows the order I > Br > Cl, and the fluoride does not react. Experiments with labeled substrates show that, in general, the larger the halide and the higher the reaction temperature, the greater the preference for double migration over single migration as a mechanistic pathway. The trifluormethyl group is ineffective in promoting anionic rearrangement.

Introduction

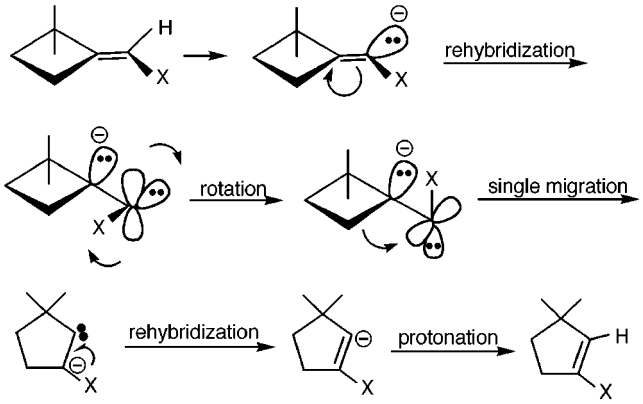
The base-induced regio- and stereospecific rearrangement of halomethylenecyclobutanes to 1-halocyclopentenes[1] is a unique and intriguing reaction as it appears to be an example of a "forbidden" 1,2-alkyl-to-carbanion shift.[2] To explain the accumulated experimental data on



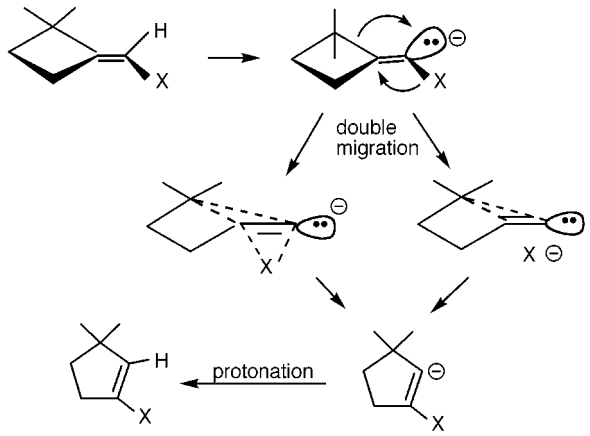
this reaction, two competing mechanistic pathways were postulated, both proceeding from an initially formed vinyl anion.[1] In Scheme 1 rehybridization of the vinyl anion to a 1,2-carbene anion occurs. After suitable bond rotation to align orbitals, ring enlargement ensues by single migration of a ring carbon. Alternately, Scheme 2 depicts a double migration process where both the halide and a ring carbon migrate analogous to the Beckmann rearrangement of oximes. Experimental evidence supports the simultaneous operation of both of these processes.[1] (Bromo-, (chloro-, and (iodomethylene)cyclobutane all undergo base-induced rearrangement to the corresponding 1-halocyclopentenes,[3] but the extent of double and single migration as a function of the halogen is not known, and the fluoro analogue has never been investigated. The present study was undertaken to determine what influence the nature of the halogen has on the mechanistic course of the reaction, and whether fluorines placed β to the negative charge facilitate the rearrangement process.

We are aware of only one instance where a vinyl carbanion has been pictured as a resonance hybrid with a 1,2-carbene anion as a contributing form. In 1985 Shainyan and co-workers[4] postulated the intermediacy of a 1,2-carbene anion to explain the rearrangement of

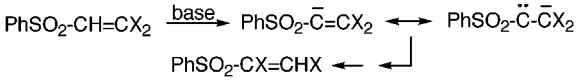
Scheme 1



Scheme 2



β,β-dihalovinyl sulfones to α,β-dihalovinyl sulfones, a process akin to that outlined in Scheme 1 with halide



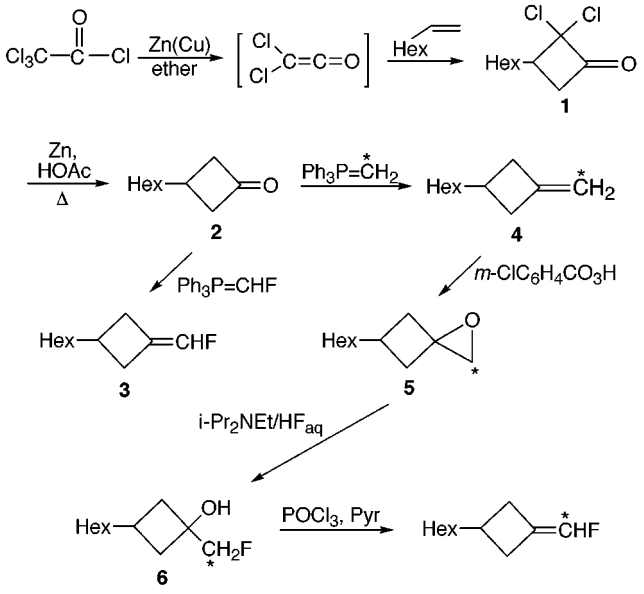
rather than carbon migrating. Also possible, but not considered by these authors, is a Beckmann type of double migration analogous to that shown in Scheme 2. Shainyan attributes stabilization of the 1,2-carbene anion

(1) Samuel, S. P.; Niu. T−Q.; Erickson, K. L. *J. Am. Chem. Soc.* **1989**, *111*, 1429 and references therein.
(2) For a theoretical study of such reactions and leading references, see: Borosky, G. *J. Org. Chem.* **1998**, *63*, 3337.
(3) Erickson, K. L.; Markstein, J.; Kim, K. *J. Org. Chem.* **1971**, *36*, 1024.
(4) Shainyan, B. A.; Mirskova, A. N.; Vitkovskii, V. Yu. *J. Org. Chem., USSR* (*Engl. Transl.*) **1985**, *21*, 877.

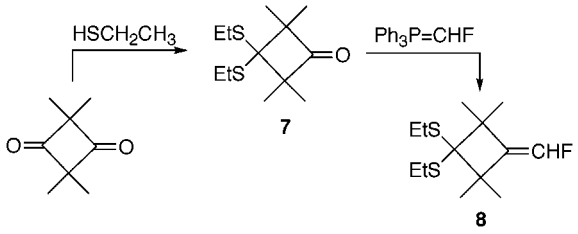
10.1021/jo9810866 CCC: $15.00
Published on Web 11/05/1998

form to the two halo substituents α to the negative charge. In the (halomethylene)cyclobutane case (Scheme 1) the carbene anion form should be favored if the halogen is effective at stabilizing an α-carbene and a *β*-carbanion and rearrangement then becomes possible. If the halide is a poor migrating/leaving group, single migration should be favored and double migration should be minimized as well as irreversible halide loss. When the halide dissociates from the organic moiety, a vinylidene carbene is formed which undergoes polymerization and/or trapping by base to give halide-free products.[1] The extent of single migration is expected to increase in the order F > Cl > Br > I with the Beckmann-like process increasing in the opposite direction. To determine the ratio of single to double migration as a function of the halide substituent, a series of 3-hexyl-1-(halomethylene)-^{13}C-cyclobutanes was examined. These compounds do not have any α-substituents to influence the reaction, and, with the fluoro compound in particular, the reduced volatility allows for easier handling. The effect of allylic fluoro substituents was also investigated.

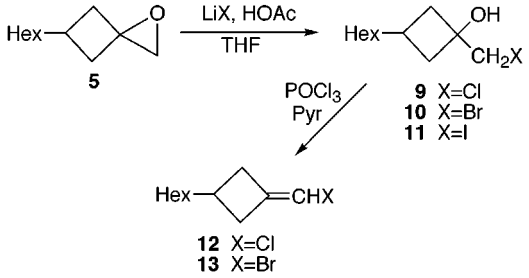
Synthesis of Methylenecyclobutanes. Fluoromethylenecyclobutanes (3 and 8). The cycloaddition reaction between dichloroketene and 1-octene mediated by ultrasound[5] formed 2,2-dichloro-3-hexylcyclobutanone (**1**) quantitatively, and dechlorination[6] occurred in >90% yield to give 3-hexylcyclobutanone (**2**). The Wittig reaction of **2** with (fluoromethylene)triphenylphosporane[7,8] afforded 1-(fluoromethylene)-3-hexylcyclobutane (**3**) in 91% yield. The Wittig reaction of **2** with (methylene-^{13}C)-triphenylphosphosporane gave 3-hexyl-1-(methylene-^{13}C)-cyclobutane also in >90% yield. This was converted to epoxide **5** which was then cleaved with *N*-ethyldiisopropylamine tris(hydrofluoride) ("Hunig's base")[9] in the presence of a 5-fold excess of *N*-ethyldiisopropylamine. Under these conditions, fluorohydrin **6** was formed quantitatively. When lesser amounts of *N*-ethyldiisopropylamine were used, the yield of **6** dropped and 3-hexylcyclobutanecarboxaldehyde was produced, presumably from formation of the isomeric fluorohydrin and its subsequent dehydrofluorination. Dehydration of **6** gave an 87% yield of 1-(fluoromethylene-^{13}C)-3-hexylcyclobutane.



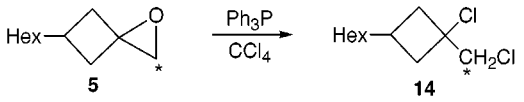
3,3-Bis(ethylthio)-2,2,4,4-tetramethyl-1-(fluoromethylene)cyclobutane (**8**) was easily prepared by a Wittig reaction on monoprotected 2,2,4,4-tetramethylcyclobutane-1,3-dione **7**.[10]



(Chloro-, (Bromo-, and (Iodomethylene)cylcobutanes (12, 13, and 18). The application of the above epoxide sequence for the preparation of the other labeled (halomethylene)cyclobutanes was not entirely satisfactory. Although (unlabeled) epoxide **5** underwent quantitative ring opening with lithium chloride, bromide, or iodide[11] to give the corresponding halohydrins **9**−**11**, dehydration of the chloro- and bromohydrins afforded the halomethylene compounds **12** and **13** in only modest yields, and iodohydrin **11** did not dehydrate but reformed the epoxide.

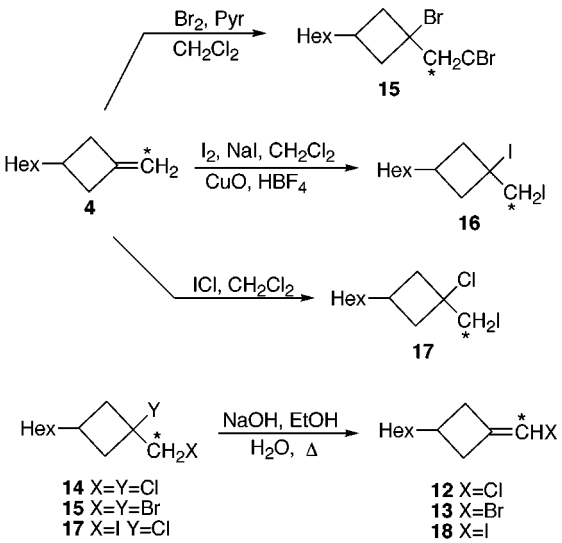


The labeled (chloro-, (bromo-, and (iodomethylene)-cyclobutanes were prepared more efficiently by dehydrohalogenation of the 1,2-dihalides. 1-Chloro-1-(chloromethyl-^{13}C)-3-hexylcyclobutane (**14**) was made from the reaction of labeled epoxide **5** with Ph_3P/CCl_4.[12]

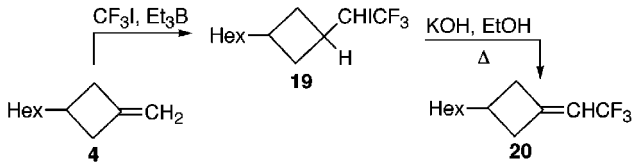


1-Bromo-1-(bromomethyl-^{13}C)-3-hexylcyclobutane (**15**) and 1-iodo-1-(iodomethyl-^{13}C)-3-hexylcyclobutane (**16**) were prepared by halogenation of 3-hexyl-1-(methylene-^{13}C)-cyclobutane (**4**). Dehydrohalogenation with alcoholic hydroxide afforded the chloro- (**12**) and bromomethylene (**13**) compounds, but the diiodide reverted to alkene **4** under these conditons. Addition of iodine monochloride to **4** gave 1-chloro-3-hexyl-1-(iodomethyl-^{13}C)cyclobutane (**17**), which underwent dehydrochlorination to give 3-hexyl-1-(iodomethylene-^{13}C)cyclobutane (**18**).

(5) (a) Bak, D. A.; Brady, W. T. *J. Org. Chem.* **1979**, *44*, 107. (b) Mehta, G.; Rao, H. S. P. *Synth. Commun.* **1985**, *15*, 991.
(6) Jeffs, P. W.; Molina, G.; Cass, M. W.; Cortese, N. A. *J. Org. Chem.* **1982**, *47*, 3871.
(7) Burton, D. J.; Wiemers, D. M. *J. Fluorine Chem.* **1985**, *27*, 85.
(8) Burton, D. J.; Greenlimb, P. E. *J. Org. Chem.* **1975**, *40*, 2796.
(9) Suga, H.; Hamatani, T.; Schlosser, M. *Tetrahedron* **1990**, *46*, 4247.
(10) Paquer, D.; Reffet, D.; Vazeux, M. *Recl. Trav. Chim. Pays-Bas* **1978**, *97*, 284.
(11) Bajwa, J. S.; Anderson, R. C. *Tetrahedron Lett.* **1991**, *32*, 3021.
(12) Isaacs, N. S.; Kirkpatrick, D. *Tetrahedron Lett.* **1972**, 3869.

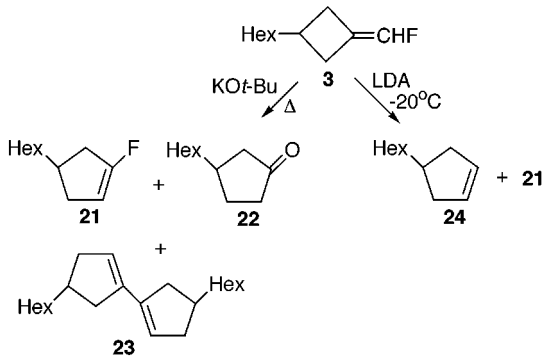


1-(Trifluoroethylidene)-3-hexylcyclobutane (20). This compound was prepared from 3-hexyl-1-(methylene)-cyclobutane (**4**). Triethylborane-catalyzed addition of trifluoroiodomethane[13] gave **19** as a mixture of diastereomers which were directly dehydroiodinated to give **20**.

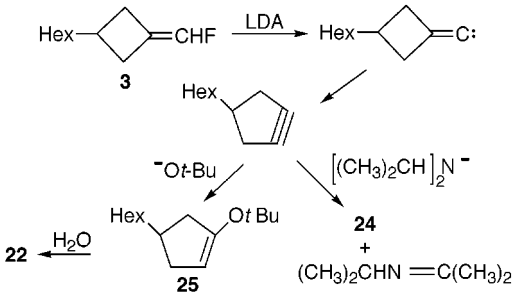


Results and Discussion

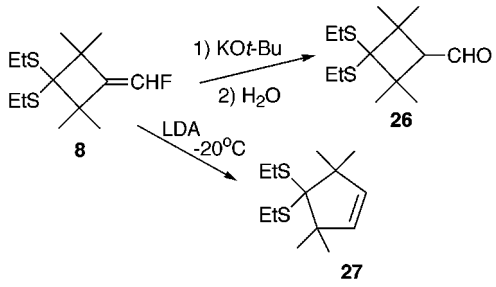
Compared to the other halogens, fluorine is a much weaker stabilizer of an adjacent negative charge,[14] and harsher reaction conditions were necessary to generate the initial fluorovinyl carbanion. Complete reaction of 1-(fluoromethylene)-3-hexylcyclobutane (**3**) with potassium *tert*-butoxide was effected in a sealed tube at 180−185 °C in 10−15 min. Two major volatile products were isolated after hydrolysis, 1-fluoro-4-hexylcyclopentene (**21**) and 3-hexylcyclopentanone (**22**), in ∼2:1 ratio. A trace of a hydrocarbon tentitatively identified as dimer **23** was also produced. When **3** was treated with lithium diisopropylamide (LDA)−THF complex in cyclohexane at −20 °C, rearranged fluoride **21** and 4-hexylcyclopentene (**24**) were produced in a relative ratio of 1:2.



Control studies established that **22**−**24** do not come from 4-hexyl-1-fluorocyclopentene (**21**). 3-Hexylcyclopentanone (**22**) is the hydrolysis product of the corresponding *tert*-butoxy enol ether **25**, which arises when *tert*-butoxide traps the cyclopentyne.[3,15] 4-Hexylcyclopentene (**24**) likely arises from hydride transfer from the LDA[16] to 4-hexylcyclopentyne. With LDA as the base, carbene formation from the halovinyl anion becomes more competitive, a consequence of the strong Li−F interaction favoring metal-assisted ionization.[17] The cyclopentene dimer (**23**) is not produced with other (halomethylene)cyclobutanes and the high reaction temperature necessary for the vinyl fluoride rearrangement may account for the dimer's formation.[18]



Tetramethyl(fluoromethylene)cyclobutane **8** failed to produce the ring-enlarged fluoride. This was surprising, as the analogous bromo compounds (with an ethoxy group at the 3-position) gave excellent yields of the ring-enlarged bromides.[1,19] Vinyl fluoride **8** with *tert*-butoxide gave only the *tert*-butyl enol ether substitution product, leading to 3,3-bis(ethylthio)-2,2,4,4-tetramethylcyclobutane carboxaldehyde (**26**) after hydrolysis. With LDA the carbene−cyclpentyne pathway afforded 4,4-bis(ethylthio)-3,3,5,5-tetramethylcyclopentene (**27**), but no ring-enlarged fluoride.



Rearrangement of 3-hexyl-1-(fluoromethylene)cyclobutane (**3**) did not occur after 1 h in refluxing heptane (98 °C), conditions under which all of the other (halomethylene)cyclobutanes reacted to give the rearrangement products shown below. A comparison of the product mixtures as a function of halide and reaction conditions

(13) Takeyama, Y.; Ichinose, Y.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1989**, *30*, 3159.

(14) Chambers, R. D.; Bryce, R. In *Comprehensive Carbanion Chemistry, Part C. Ground and Excited-State Reactivity*; Buncel, E., Durst, T., Eds.; Elsevier: New York, 1987; Chpt. 5.

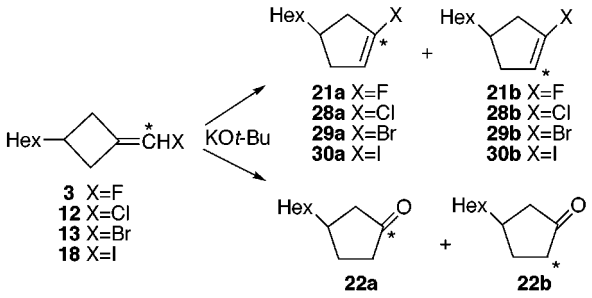
(15) Erickson, K. L.; Wolinsky, J. *J. Am. Chem. Soc.* **1965**, *87*, 1142.

(16) Newcomb, M.; Burchill, M. T.; Deeb, T. M. *J. Am. Chem. Soc.* **1988**, *110*, 6528.

(17) Topolski, M.; Duraisamy, M.; Rachon, J.; Gawronski, J.; Gawronska, K.; Goedken, V.; Walborsky, H. M. *J. Org. Chem.* **1993**, *58*, 546 and references therein.

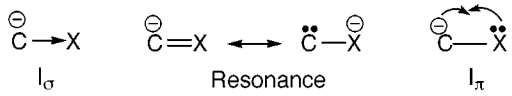
(18) 1-Cyclopentenylcyclopentene has been reported when cyclopentyne is generated from 1,2-dibromocyclopentene and n-BuLi: Wittig, G.; Heyn, J. *Liebigs Ann. Chem.* **1969**, *726*, 57.

(19) Erickson, K. L. *J. Org. Chem.* **1971**, *36*, 1031.



is shown in Table 1. The ratio of single migration (Scheme 1) to double migration (Scheme 2) was detected by ^{13}C NMR. In all cases studied, the label was found in the rearranged products at both vinyl carbons. The relative amount of label at each, however, was a function of the reaction temperature and the nature of the halide.

There are several factors operating in the stabilization/destabilization of the halovinyl anion: inductive withdrawal effects (I_σ), resonance effects, and electron-pair repulsion effects (I_π).[14] The first two effects stabilize the vinyl carbanion and the last, aggravated by the planar nature of the vinyl carbanion, destabilize it. In the case of the vinyl fluoride, with a short C−X bond, the



destabilizing I_π effect cancels the stabilizing I_σ effect. Moreover, resonance stabilization is prohibited here by the inability of fluorine to expand its octet. This is reflected in the higher temperature needed to generate the fluorovinyl anion. The temperature is important in controlling the ratio of single to double migration. Double migration, where two bonds must be broken, is preferred at higher temperatures.

Both single and double migration mechanisms involve rehybridization of the initial vinyl anion in order to permit free rotation and attainment of the proper geometry required for rearrangement.[1,20] Scheme 3 illustrates the Newman projection of the rehybridized halovinyl anion and the two pathways for it to rearrange to the halocyclopentene system. Counterclockwise rotation by 45° gives conformer **31** in which both the empty p-orbital and the carbon−halide bond are coplanar with the two ring carbon bonds. Migration of the halide and the ring carbon may be synchronous or involve an intermediate carbene−halide complex (**33**), as depicted in Schemes 2 and 4.[1,21] Alternately, a 45° clockwise rotation gives conformer **32** where the empty p-orbital is aligned with a ring carbon bond, but the carbon−halide bond is not. Here, the ring carbon migrates, but the halide does not.

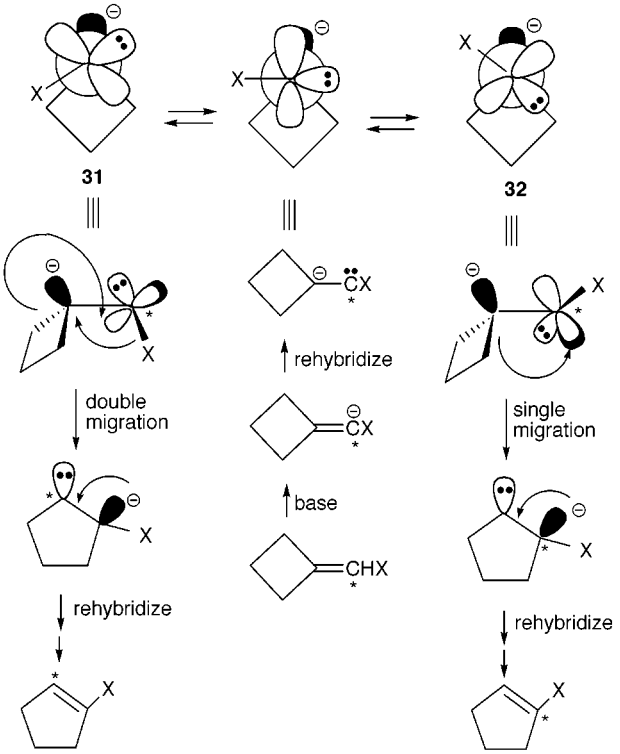
Because of electron pair repulsion, conformer **31** is expected to require higher temperatures for its formation than conformer **32**. However, **31** can undergo halide-assisted carbon migration while **31** must undergo unassisted carbon migration. If conformer **31** rearranges faster than **32**, then the increase in the ratio of double to single migration at higher temperatures shown in Table 1 becomes understandable. Table 1 also shows that the ratio of double to single migration decreases in the order I > Br, Cl > F which reflects the decreasing

(20) Du, Z.; Erickson, K. L. Manuscript in preparation.
(21) Erickson, K. L. *J. Org. Chem.* **1973**, *38*, 1463.

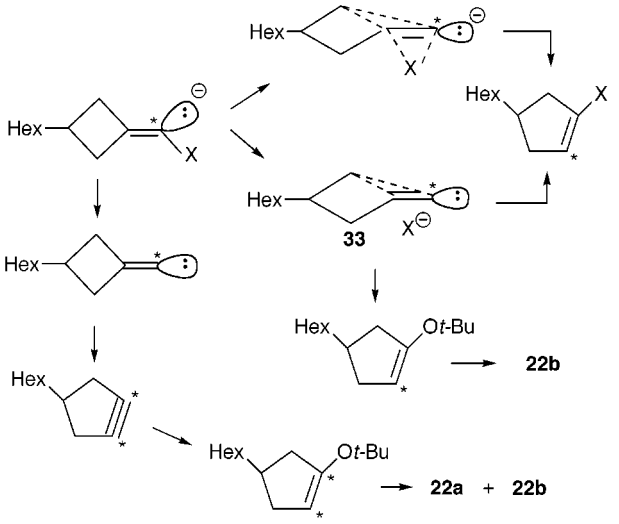
Table 1. Rearrangement Products of 3-Hexyl-1-(halomethylene)cyclobutanes

compd	temp (°C) (Solvent)	% yield of halocyclopentene (**b**/**a** ratio)	% yield of cyclopentanone (**b**/**a** ratio)
3	180 (none)	40 (1.52)	18 (2.08)
	98 (heptane)	0	trace
12	180 (none)	32 (2.80)	10 (1.05)
	98 (heptane)	58 (1.45)	8 (1.37)
13	180 (none)	20 (2.84)	0
	160 (pentadecane)	18 (2.54)	0
	98 (heptane)	63 (1.35)	5 (1.40)
18	180 (none)	21 (3.88)	0
	98 (heptane)	83 (2.10)	0
	69 (hexane)	86 (1.85)	0

Scheme 3



Scheme 4

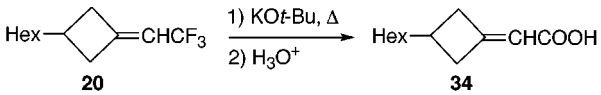


effectiveness of the halogen as a neighboring group and increasing C−X bond strength. Complete dissociation of the halide from the organic moiety (α-elimination) leads

to nonhalogenated products, and this becomes the major reaction pathway at 180 °C.

The label distribution in the cyclopentanone **22** is also a function of the halide and the reaction temperature. 3-Hexylcyclopentanone comes from hydrolysis of *tert*-butyl enol ether **25**; **25** may be generated by attack of the *tert*-butoxy anion on the intermediate vinyl carbene−halide complex **33** as well as on the cyclopentyne. At 180 °C, the vinyl carbene−fluoride complex (**33**, X = F) persists longer than the vinyl carbene−chloride complex (**33**, X = Cl), leading to larger amounts of **22b**. At 98 °C, the vinyl carbene−chloride and bromide complexes are of comparable stability. No cyclopentanone was detected in reactions of the vinyl iodide; in this case double migration apparently occurs rapidly enough to preclude butoxide trapping.

Because fluorine is very effective at stabilizing a β-negative charge, methylenecylcobutanes with allylic fluoro groups were synthesized and examined for their ability to undergo carbanionic rearrangement. Exocyclic allylic fluorides **20** stabilize the initially formed vinyl anion. However, 3-hexyl-1-(trifluoromethylmethylene)-cyclobutane (**20**) did not undergo base-induced rearrangement. When treated with potassium *tert*-butoxide at 100 °C, **20** gave only recovered starting material together with hydrolysis product 3-hexylcyclobutylidene acetic acid (**34**). With phenyllithium at 25 °C only **20** was recovered, and with *n*-butyllithium in refluxing hexane (14 h) **20** was recovered as part of a complex product mixture but no rearranged material was detected.



20 **34**

NMR Spectral Parameters of (Halomethylene)-cyclobutanes. A comparison of the ^{1}H and ^{13}C chemical shift values of the 1-(halomethylene)-3-hexylcyclobutanes and the 1-halo-4-hexylcyclopentenes provides a good illustration of the effect of the halogen on the electronic distribution at the vinylic carbons. C-1 is deshielded by the I_σ effect, and C-2 is shielded by the I_π effect. Table 2 gives the chemical shift values for the vinyl carbons and the vinyl hydrogens of 3-hexyl-1-(methylene)cyclobutane (**4**) and the fluoro- (**3**), chloro- (**12**), bromo- (**13**), and iodo- (**18**) derivatives. Also listed are the corresponding values for halocyclopentenes **21**, **28**, **29**, and **30**. Both deshielding and shielding trends follow the order F ≫ Cl > Br > I except for H-1 in the methylenecyclobutane series where there is negligible difference in deshielding by Cl, Br, and I. In acyclic vinyl halides this same order is followed.[22]

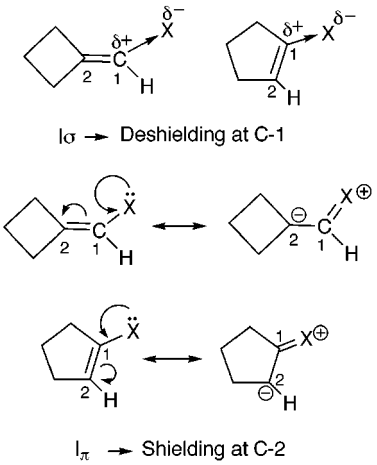


Table 2. NMR Chemical Shift Values of the Vinyl Carbons and Vinyl Hydrogens of 1-(Halomethylene)-3-hexylcyclobutanes and 1-Halo-4-hexylcyclopentenes

X	^{1}H (ppm) H_a	^{13}C (ppm) C_a	^{13}C (ppm) C_b	^{1}H (ppm) H_b	^{13}C (ppm) C_a	^{13}C (ppm) C_b
H	4.71	105.2	148.0	5.37	130.0	130.0
F	6.35	141.4	118.6	4.89	161.1	101.2
Cl	5.71	108.2	140.6	5.58	131.3	125.7
Br	5.77	96.4	143.8	5.76	119.6	130.2
I	5.70	68.7	151.1	6.04	91.8	139.4

Conclusions

The base-induced rearrangement of (halomethylene)-cyclobutanes to 1-halocyclopentenes has been extended to vinyl fluorides, but high temperatures are required in order to form the fluorovinyl anion. Of the two pathways leading to ring enlargement, double migration is favored over single migration at higher temperatures and with increasing halide size. Fluorines β to the negative charge are not sufficient to induce the rearrangement.

Experimental Section

General Procedures. Chemical reagents were purchased from commercial sources and were used without purification unless noted otherwise. Reaction solvents were reagent grade. Ether and tetrahydrofuran were dried by distillation from sodium benzophenone ketyl in an inert atmosphere. Pyridine was dried by distillation from CaH_2. All reactions were carried out with oven-dried glassware. $MgSO_4$ was the drying agent used in all standard reaction workups. Solvent removal was effected by rotary evaporation unless specified otherwise. All melting and boiling points are uncorrected.

Analytical thin-layer chromatography (TLC) was performed on commercial BakerFlex (silica gel IB2F) plates, and preparative TLC was done on Brinkmann HF 254+366 type 60 silica gel. Visualization was by UV light, exposure to I_2 vapors, and/or H_2SO_4 spray. Vacuum liquid chromatography (VLC) was performed with silica gel (EM no. 7736, type 60). Flash column chromatography (FCC) was performed on J. T. Baker 40 μm silica gel under a positive pressure of nitrogen. Analytical and preparative vapor phase chromatography (VPC) was carried out with 10% Carbowax 20M on Anakrom Q, 80/100 columns (10 ft × 1/8 in. or 10 ft × 1/4 in.).

IR spectra of liquid samples were run neat, and solids were run as KBr pellets. ^{1}H NMR spectra were determined at 200 MHz in $CDCl_3$ with TMS (0.00 ppm) as the internal reference. ^{13}C NMR spectra were recorded at 50.3 MHz with $CDCl_3$ as the solvent and reference (77.0 ppm). ^{13}C NMR assignments were made on the basis of chemical shifts and proton multiplicities (from APT spectra). Chemical shifts of ^{19}F NMR spectra were recorded at 188.1 MHz in $CDCl_3$ with $CFCl_3$ as the internal reference (0.0 ppm). Quantitative ^{13}C NMR analyses of ^{13}C-enriched compounds were carried out as described previously.[1] Elemental analyses were performed by Desert Analytics, Tucson, AZ.

(22) Pretsch, E.; Clerc, T.; Seibel, J.; Simon, W. In *Tables of Spectral Data for Structure Determination of Organic Compounds*, 2nd ed.; Fresenius, W., Huber, J. F. K., Pungor, E., Rechnitz, G. A., Simon, W., West, T. S., Eds.; Springer-Verlag: New York, 1989.

3-Hexylcyclobutanone (2). A mixture of 6.5 g (0.10 mol) of Zn powder, 5.6 g (0.05 mol) of 1-octene, and 250 mL of dry ether under N_2 was placed in an ultrasonic water bath maintained at 15−20 °C.[4] With sonication, a solution of trichloroacetyl chloride (12.7 g, 0.075 mol) in 135 mL of dry ether was added dropwise over 1 h; sonication was continued for an additional 30 min. The reaction mixture was treated with 10 mL of H_2O and filtered through Celite. The filtrate was extracted with ether and washed with H_2O, saturated $NaHCO_3$, and saturated NaCl. After the solvent was dried and removed, 2,2-dichloro-3-hexylcyclobutanone (**1**) was obtained as a yellow brown oil (10.4 g, ∼100%), IR (neat) 2925, 1808 cm^{-1}. Crude **1** was diluted with HOAc (10 mL) and added dropwise to a rapidly stirred mixture of Zn dust (21 g, 0.32 mol) in HOAc (30 mL). After complete addition, the mixture was stirred at 80 °C for 2 h and then cooled and 5 mL of H_2O was added. The mixture was filtered through Celite, the filtrate was then washed with water, saturated $NaHCO_3$, and saturated NaCl and dried, and the solvent was removed. Vacuum distillation gave 3-hexylcyclobutanone (**2**), $bp_{1.8}$ = 87−88 °C (7.01 g, 91%). The spectral properties of **2** were identical to those previously reported.[23]

3-Hexyl-1-(methylene-^{13}C)cyclobutane (4). Potassium *tert*-butoxide (2.24 g, 20.0 mmol) and (methyl-^{13}C)triphenylphosphonium iodide (10% enriched, 7.90 g, 19.5 mmol) in 20 mL of dry THF was stirred at 25 °C under N_2 for 1 h, during which time the color of the solution became yellow. 3-Hexylcyclobutanone (**2**) (3.00 g, 19.5 mmol) was added dropwise, and the reaction mixture was stirred for an additional 24 h at 25 °C. Vacuum filtration removed the solids, and distillation removed the THF. The residue was extracted with pentane, and the pentane layer was washed with 50% aqueous methanol and then dried. The solvents were removed by distillation, and the residue was chromatographed on silica gel with pentane:diethyl ether (15:1) to give 2.70 g (91%) of **4** as a colorless oil: IR 3073, 2921, 2853, 1676, 1466 873 cm^{-1}; ^{1}H NMR δ 0.88 (3H, t, J = 6.3 Hz), 1.26 (8H, m), 1.45 (2H, m), 2.28 (3H, m), 2.73 (2H, m), 4.71 (2H, m); ^{13}C NMR δ 14.1 (CH_3), 22.7 (CH_2), 27.5 (CH_2), 29.3 (CH_2), 30.3 (CH), 31.9 (CH_2), 36.6 (CH_2), 37.7 (CH_2, 2 carbons), 105.2 (=CH_2), 148.0 (=C).

1-(Fluoromethylene)-3-hexylcyclobutane (3). *Method A.* (Fluoromethyl)triphenylphosphonium tetrafluoroborate was prepared from triphenylphosphine, tribromofluoromethane, and sodium bromide as described by Burton and Wiemers.[7] The product was purified by VLC (EtOAc:MeOH, 95:5) followed by recrystallization from CH_2Cl_2. A solution of 0.46 g (1.2 mmol) of (fluoromethyl)triphenylphosphonium tetrafluoroborate in 8 mL of dry THF under Ar was cooled to −78 °C. To this stirred solution was added dropwise 0.75 mL of 1.6 M (1.2 mmol) n-BuLi in hexane. After complete addition, the mixture was stirred for 30 min at −78 °C, and then 0.185 g of 3-hexylcyclobutanone (**2**) was added dropwise. Stirring was continued at −78 °C for 2 h, the mixture was warmed to 0 °C, and 0.125 g of solid KO-*t*-Bu was added. The mixture was warmed to 25 °C and stirred for 2 h. Ether was added, and the mixture was filtered through Celite. The filtrate was washed with saturated NaCl until the washings were neutral. The organic layer was dried and the solvent removed. The dark brown residue was flash distilled and further purified by VPC to give 0.008 g of recovered **2** and 0.186 g (91%) l-(fluoromethylene)-3-hexylcyclobutane (**3**): IR 3089, 2955, 2923, 1711, 1093, 1067 cm^{-1}; ^{1}H NMR δ 0.88 (3H, t, J = 6.8 Hz, 1.26 (8H, m), 1.43 (2H, m), 2.25 (3H, m), 2.73 (2H, m), 6.35 (1H, d of quintets J = 85.6, 2.4 Hz); ^{13}C NMR δ 14.1 (CH_3), 22.6 (CH_2), 27.1 (CH_2), 29.2 (CH_2), 31.1 (d, J = 10.0 Hz, CH_2), 31.8 (CH), 31.8 (d, J = 5.1 Hz, CH_2), 31.9 (CH_2), 36.5 (CH_2), 118.6 (d, J = 11.4 Hz, C-1), 141.4 (d, J = 244.9 Hz, CHF); ^{19}F NMR δ −143.3 (d, J = 85.6 Hz). Anal. Calcd for $C_{11}H_{19}F$: C, 77.60; H, 11.25. Found: C, 77.38; H, 11.17.

Method B. A solution of *m*-chloroperoxybenzoic acid (4.58 g, 21.2 mmol) in CH_2Cl_2 (20 mL) was cooled to 0 °C. 3-Hexyl-1-(methylene-^{13}C)cyclobutane (**4**) (10% enriched, 2.70 g, 17.7 mmol) was added dropwise. After 3 h of stirring at 25 °C, the mixture was filtered, and the solid was washed with 20 mL of CH_2Cl_2. The combined washings and filtrate were washed with saturated $NaHCO_3$, H_2O, and saturated NaCl. After drying, the solvent was evaporated, and the pale yellow residue was chromatographed on silica gel with pentane:diethyl ether (5:1) to give 2.97 g (∼100%) of 5-hexyl-1-oxaspiro[2.3]hexane-2-^{13}C (**5**) (10% enriched), colorless oil, as a mixture of diastereomers: IR 3038, 2924, 1467, 1398 1131, 930 cm^{-1}; ^{1}H NMR δ 0.87 (t, J = 5.9 Hz), 1.28 (br s), 1.50 (m), 1.91−2.05 (m), 2.05−2.40 (m), 2.54 (m), 2.67 (s), 2.71 (s).

HF (48%, 12.5 g, 0.300 mmol) was added dropwise to a solution of *N*-ethyldiisopropylamine (12.0 g, 0.100 mol) in diethyl ether (30 mL) at 0 °C in a polyethylene flask. The mixture was stirred at 25 °C for 1 h. The solvent was removed by distillation, and the residue was transferred to a flask epuipped with a Dean−Stark trap. Benzene (40 mL) was added, and the solution was refluxed for 5 h. After 4.5 mL of H_2O had separated, the benzene was fractionally distilled, and the residue was distilled under reduced pressure to give *N*-ethyldiisopropylamine−tris(hydrofluoride) "Hunig's hydrofluoride", 14.3 g (76%): bp_4 = 93−95 °C; lit.[8] $bp_{4.0}$ = 93−95 °C; IR 2991, 2683 (br), 1807 (br), 1469 (br), 1134 cm^{-1}.

A mixture of epoxide **5** (2.97 g, 17.7 mmol), *N*-ethyldiisopropylamine (15.0 g, 116 mmol), and Hunig's hydrofluoride (3.40 g, 18.0 mmol) was heated for 3 h at 150 °C. After dilution with diethyl ether (50 mL), the organic layer was washed with 10% HCl, H_2O, and saturated NaCl and dried and the solvent removed. The residue was flash chromatographed on silica gel with hexane:ethyl acetate (3:1) to give 3.27 g (98%) of 1-(fluoromethyl-^{13}C)-3-hexylcyclobutanol (**6**) (10% enriched), colorless oil, as a mixture of diastereomers: IR 3382, 2925, 1462, 1287, 1020 cm^{-1}; ^{1}H NMR δ 0.86 (t, J = 6.5 Hz), 1.24 (br s), 1.38 (m), 1.6−1.8 (m), 2.1−2.5 (m), 4.19 (d J = 51.5 Hz), 4.43 (d J = 51.5 Hz); ^{19}F NMR δ −228.4 (t, J = 51.4 Hz), −228.6 (t, J = 51.6 Hz).

To **6** (1.62 g, 8.60 mmol) in 20 mL of dry pyridine at 0−5 °C was added 4 mL of $POCl_3$. The mixture was stirred for 20 h at 25−30 °C, diluted with petroleum ether (40 mL), and slowly quenched with H_2O (20 mL). The mixture was extracted with petroleum ether and washed with dilute HCl followed by brine. After the solvent was dried and removed, the residue was chromatographed on silica gel with pentane:diethyl ether (5:1) to give 1.28 g (87%) of 1-(fluoromethylene-^{13}C)-3-hexylcyclobutane (**3**) (10% enriched).

3,3-Bis-(ethylthio)-2,2,4,4-tetramethylcylobutanone (7). The method of Paquer and co-workers[10] was followed, but the reaction time was extended to two weeks to provide an 88% yield of **7**: $bp_{0.07}$ = 62−64 °C; lit.[9] $bp_{2.5}$ = 100 °C; IR and ^{1}H NMR agreed with those in ref 9 (note that the number of hydrogens at δ 1.35 is quoted as 9 rather than 12 in ref 10); ^{13}C NMR δ 13.7 (CH_3), 22.2 (CH_3), 25.6 (CH_2), 67.0 (C-2, C-4), 70.2 (C-3), 219.2 (C-1).

3,3-Bis-(ethylthio)-1-(fluoromethylene)-2,2,4,4-tetramethylcyclobutane (8). Ketone **7** was converted to **8** with (fluoromethylene)triphenyphosphorane as described for **3** above (method A). The product was purifed by VLC on silica gel (pentane) followed by VPC to give a 33% yield of **8**: IR 2964, 2929, 1698, 1086, 1035 cm^{-1}; ^{1}H NMR δ 1.22 (6H, t, J = 7.5 Hz), 1.38 (6H, s), 1.49 (6H, s), 2.57 (4H, q, J = 7.5 Hz), 6.36 (1H, d, J = 83.2 Hz); ^{13}C NMR δ 13.8 (CH_3), 25.6 (CH_3), 25.7 (CH_2), 27.4 (CH_3), 47.8 (d, J = 10.2 Hz, C-2 or C-4), 50.1 (d, J = 2.6 Hz, C-2 or C-4), 75.1 (C-3), 136.6 (d, J = 4.8 Hz, C-1), 142.2 (d, J = 251.8 Hz, CHF); ^{19}F NMR δ −147.2 (d, J = 83.9 Hz); HRMS calcd for $C_{11}H_{18}FS_2$ [(M − C_2H_5)$^+$] 233.0830. Found 233.0847.

1-(Halomethylene)-3-hexylcyclobutanes (9, 10, 11). To a solution of unlabeled epoxide **5** (168 mg, 1.00 mmol) and acetic acid (180 mg, 3.00 mmol) in dry THF (10 mL) was added anhydrous LiX (X = Cl, Br, I, 1.60 mmol), and the reaction mixture was stirred at 25 °C. After completion of the reaction (TLC monitoring: I, 30 min; Br, 6 h; Cl, 24 h), the reaction mixture was diluted with H_2O and extracted with ether. The organic layer was washed with H_2O and dried and the solvent

(23) Schmit, C.; Falmagne, J. B.; Escudero, J.; Vanlierde, H.; Ghosez, L. *Org. Synth.* **1990**, *69*, 199.

evaporated. The residue was dissolved in ether and passed through a short columm of silica gel to remove traces of inorganic salts giving the halohydrins (**9**, **10**, and **11**) quantitatively.

To a stirred solution of crude halohydrin (1 mmol) in dry pyridine (5 mL) at 0−5 °C was added 1 mL of $POCl_3$, and the mixture was stirred 20 h at 25 °C. The reaction mixture was diluted with petroleum ether (10 mL) and slowly quenched with water (10 mL). The mixture was extracted with petroleum ether and washed with dilute HCl followed by brine. After drying and removal of the solvent, the residue was chromatographed on silica gel with pentane:diethyl ether (5:1) to give **12** (70 mg, 42%), **13** (90 mg, 40%), and starting epoxide **5** (80 mg) from **11**.

1-(Chloromethylene-^{13}C)-3-hexylcyclobutane (12). A mixture of epoxide **5** (1.0 g, 6.0 mmol), triphenylphosphine (2.3 g, 9.0 mmol), and CCl_4 (10 mL) was refluxed under N_2 for 2 h. The solution was diluted with ether and then washed with water and brine. The organic layer was dried and the solvent removed. The residue (crude **14**) was refluxed with a solution of 0.8 g of NaOH (20 mmol) in 10 mL of 95% EtOH for 30 min, and then H_2O was added. The mixture was extracted with pentane, and the pentane extracts were washed with H_2O and dried. The pentane was removed by fractional distillation, and the residue was flash distilled to give 0.7 g, 63% of **12**: IR 3073, 2924, 1674, 1467 cm^{-1}; ^{1}H NMR δ 0.89 (3H, t, J = 7.2 Hz), 1.27 (8H, br s), 1.50 (2H, m), 2.26 (3H, m), 2.81 (2H, m), 5.71 (1H, quintet, J = 2.4 Hz); ^{13}C NMR δ 14.1 (CH_3), 22.6 (CH_2), 27.2 (CH_2), 29.2 (CH_2), 30.3 (CH), 31.9 (CH_2), 35.1 (CH_2), 35.3 (CH_2), 36.5 (CH_2), 108.2 (=CHCl), 140.6 (=C). Anal. Calcd for $C_{11}H_{19}Cl$ (unlabeled sample): C, 70.66; H, 10.26. Found: C, 70.81; H, 10.36.

1-(Bromomethylene-^{13}C)-3-hexylcyclobutane (13). A solution of labeled alkene **4** (1.00 g, 6.60 mmol) in CH_2Cl_2 (30 mL) was cooled to 0 °C, and bromine (0.64 g, 8.0 mmol) was added dropwise. Stirring was continued at 0 °C for 15 min after the addition was complete. The solution was washed with aqueous $NaHSO_3$, 6 M HCl (until the washings were acidic), H_2O, and brine. The organic layer was dried, and the solvent was removed. The residue (crude **15**) was dehydrohalogenated as described above for **12** to give 0.88 g, 58% of **13**: IR 3074, 2922, 1664, 1466 cm^{-1}; ^{1}H NMR δ 0.88 (3H, t, J = 6.8 Hz), 1.26 (8H, br s), 1.46 (2H, m), 2.25 (3H, m), 2.72 (2H, m), 5.77 (1H, quintet, J = 2.4 Hz); ^{13}C NMR δ 14.1 (CH_3), 22.6 (CH_2), 27.2 (CH_2), 29.2 (CH_2), 29.5 (CH), 31.8 (CH_2), 36.4 (CH_2), 36.5 (CH_2), 37.1 (CH_2), 96.4 (=CHBr), 143.8 (=C). Anal. Calcd for $C_{11}H_{19}Br$ (unlabeled sample): C, 57.15; H, 8.28. Found: C, 57.14; H, 8.21.

3-Hexyl-1-(iodomethylene-^{13}C)cyclobutane (18). Iodine (0.64 g, 8.0 mmol), NaI (0.60 g, 4.00 mmol), CuO (0.30 g, 3.90 mmol), and 48% HBF_4 (0.73 g, 4.00 mmol) were added to a solution of alkene **5** (1.00 g, 6.60 mmol) in CH_2Cl_2 at 0 °C. Stirring was continued at 0 °C for 50 min after the addition was complete. The mixture was filtered and washed with CH_2Cl_2. The organic layer was washed with H_2O and brine and then dried and the solvent removed to give crude **16**. Attempted dehydrohalogenation of **16** as described for **12** gave only recovered alkene **4** in 58% yield.

A solution of labeled alkene **4** (1.00 g, 6.60 mmol) in CH_2Cl_2 (30 mL) was cooled to 0 °C. Iodine monochloride (1.22 g, 7.50 mmol) in CH_2Cl_2 (2 mL) was added dropwise, and stirring was continued at 20 °C for 30 min after the addition was complete. The solution was then washed with aqueous $NaHSO_3$, 6 M HCl (until the washings were acidic), H_2O, and brine. The organic layer was dried, and the solvent was removed. The residue (crude **17**) was dehydrohalogenated in the same manner as described above for **12** to give 0.90 g, 49% of **18**: IR 3076, 2925, 1651, 1458 cm^{-1}; ^{1}H NMR δ 0.88 (3H, t, J = 6.8 Hz), 1.26 (8H, br s), 1.44 (2H, m), 2.10 (1H, m), 2.17 (2H, m), 2.65 (2H, m), 5.70 (1H, quintet, J = 2.4 Hz); ^{13}C NMR δ 14.1 (CH_3), 22.6 (CH_2), 27.3 (CH_2), 28.3 (CH), 29.2 (CH_2), 31.9 (CH_2), 36.3 (CH_2), 37.7 (CH_2), 40.9 (CH_2), 68.7 (=CHI), 151.1 (=C). Anal. Calcd for $C_{11}H_{19}I$ (unlabeled sample): C, 47.49; H, 6.88. Found: C, 47.89; H, 6.70.

1-(2,2,2-Trifluoro-1-iodoethyl)-3-hexylcyclobutane (19). The method of Takeyama (et al.[13] was followed. Gaseous CF_3I (37 mL) was condensed into a vessel under Ar cooled to −35 °C. To this were added 135 mL of hexane and 2.70 g (0.0175 mol) of 3-hexyl-1-(methylene)cyclobutane (**4**). Triethylborane (19.55 mL) was added, and the mixture was stirred at −35 °C for 5 h. The solvent was removed to give a 79% yield of crude 1-(2,2,2-Trifluoro-1-iodoethyl)-3-hexylcyclobutane (**19**).[13]

To a solution of 9.0 g KOH in 120 mL of 95% EtOH was added 9.35 g of **19**, and the mixture was refluxed for 4 h. Water was added followed by ether extraction. After the solvent was dried and removed, the residue was subjected to vacuum flash distillation to give 4 mL of a yellow liquid containing three components. VPC separation afforded **20** as the major component: IR 2925, 1715, 1350, 1280, 1185, 1120, 1065 cm^{-1}; ^{1}H NMR δ 0.87 (3H, t), 1.25 (8H, br s), 1.48 (2H, m), 2.3−2.5 (2H, m), 2.52 (1H, heptet), 2.7−3.3 (2H, m), 5.34 (1H, m); ^{13}C NMR δ 14.0 (CH_3), 22.7 (CH_2), 27.3 (CH_2), 29.3 (CH_2), 31.0 (CH), 31.9 (CH_2), 36.5 (CH_2), 36.9 (CH_2), 37.1 (CH_2), 110.1 (CH, q, J = 33.6 Hz), 123.9 (CF_3, q, J = 270.0 Hz), 154.0 (C-1, q, J = 6.8 Hz); ^{19}F δ −60.4. Anal. Calcd for $C_{12}H_{19}F_3$: C, 65.41; H, 8.71. Found: C, 65.21; H, 8.69.

General Procedure for Potassium *tert*-Butoxide-Induced Rearrangement of (Halomethylene)cyclobutanes 3, 9, 10, and 11. The vinyl halides were treated with KO*t*-Bu under four different sets of reaction conditions: at 180 °C in absence of solvent, at 160 °C in pentadecane, at 98 °C in refluxing heptane, and at 69 °C in refluxing hexane. In all cases chromatographically pure samples were used.

Freshly sublimed KO*t*-Bu (0.28 g, 2.5 mmol) was suspended in solvent (5 mL) in a flask equipped with a reflux condenser, a drying tube, a magnetic stirrer, an N_2 inlet, and a septum cap. The system was heated in an oil bath to the desired temperature, and the vinyl halide (1.0 mmol) was injected by syringe. In the case of the vinyl fluoride with no solvent, the reactants were mixed at 25 °C, sealed in a reaction tube, and heated to the desired temperature. The temperature was maintained for 30 min, the mixture was cooled, and H_2O was added. The reaction mixture was extracted with pentane, the combined pentane layers were washed with H_2O, and the pentane was removed by fractional distillation. The residue was subjected to flash distillation under reduced pressure followed by preparative VPC purification of products. All yields reported are isolated yields of purified products. See Table 1.

1-Fluoro-1-^{13}C-4-hexylcyclopentene (21a) and 1-Fluoro-2-^{13}C-4-hexylcyclopentene (21b): IR 3084, 2924, 1682, 1179 cm^{-1}; ^{1}H NMR δ 0.88 (3H, t, J = 6.5 Hz), 1.27 (8H, br s), 1.42 (2H, m), 1.89 (m), 2.16 (m), 2.25−2.55 (m) 4.89 (1H, m); ^{13}C NMR δ 14.1 (CH_3), 22.6 (CH_2), 27.6 (CH_2), 29.3 (CH_2), 31.8 (CH_2), 33.3 (d, J = 8.4 Hz, CH_2), 35.2 (d, J = 19.1 Hz, CH_2), 35.3 (CH), 36.8 (CH_2), 101.2 (d, J = 10.7 Hz, CH), 161.1 (d, J = 276.4 Hz, CF); ^{19}F NMR δ −121.4. HRMS: Calcd for $C_{11}H_{19}F$ (M^+): 170.1471. Found: 170.1469.

3-Hexyl-1-^{13}C-cyclopentanone (22a) and 3-Hexyl-5-^{13}C-cyclopentanone (22b): IR 2925, 1744 cm^{-1}; ^{1}H NMR δ 0.88 (3H, t, J = 6.7 Hz), 1.28 (8H, m), 1.38 (2H, m), 1.78 (1H, dd, J = 8.9 Hz, further split), 2.0−2.5 (6H, m); ^{13}C NMR δ 14.1 (CH_3), 22.6 (CH_2), 27.8 (CH_2), 29.3 (CH_2), 29.5 (CH_2), 31.8 (CH_2), 35.7 (CH_2), 37.2 (CH), 38.6 (CH_2), 45.3 (CH_2), 220.2 (C-1). Anal. Calcd for $C_{11}H_{20}O$ (unlabeled sample): C, 78.51; H, 11.98. Found: C, 78.22; H, 11.90. 2,4-Dinitrophenylhydrazone derivative, mp 103.5−104.5 (EtOH).

1-(4-Hexylcyclopentenyl)-4-hexylcyclopentene (23): ^{1}H NMR (500 MHz) δ 0.88 (6H, t, J = 6.8 Hz), 1.24 (16H, br s), 1.39 (4H, m), 1.97 (2H, m), 2.17 (2H, m), 2.34 (2H, m), 2.47 (2H, m), 2.58 (2H, m), 5.58 (2H, m); ^{13}C NMR δ 14.1 (CH_3), 22.6 (CH_2), 27.8 (CH_2), 29.3 (CH_2), 31.8 (CH_2), 36.5 (CH_2), 37.4 (CH), 37.8 (CH_2), 43.6 (CH_2), 125.7 (CH), 131.3 (C-1).

1-Chloro-1-^{13}C-4-hexylcyclopentene (28a) and 1-Chloro-2-^{13}C-4-hexyl-cyclopentene (28b): IR 3070, 2926, 1628, 1466 cm^{-1}; ^{1}H NMR δ 0.88 (3H, t, J = 6.7 Hz), 1.27 (8H, br s), 1.39 (2H, m), 2.00 (1H, m), 2.21−2.70 (4H, m), 5.58 (1H, m); ^{13}C NMR δ 14.1 (CH_3), 22.6 (CH_2), 27.8 (CH_2), 29.3 (CH_2), 31.8 (CH_2), 36.5 (CH_2), 37.4 (CH), 37.7 (CH_2), 43.6 (CH_2), 125.7

(CH), 131.3 (CCl). Anal. Calcd for $C_{11}H_{19}Cl$ (unlabeled sample): C, 70.66; H, 10.26. Found: C, 70.33; H, 10.35.

1-Bromo-1-^{13}C-4-hexylcyclopentene (29a) and 1-Bromo-2-^{13}C-4-hexylcyclopentene (29b): IR 3066, 2924, 1622, 1463 cm^{-1}; ^{1}H NMR δ 0.87 (3H, t, J = 7.2 Hz), 1.25 (8H, br s), 1.38 (2H, m),1.94 (1H, m), 2.34 (3H, m), 2.66 (1H, m), 5.57 (1H, m); ^{13}C NMR δ 13.9 (CH_3), 22.5 (CH_2), 27.6 (CH_2), 29.2 (CH_2), 31.6 (CH_2), 36.2 (CH_2), 37.8 (CH), 38.6 (CH_2), 45.6 (CH_2), 119.6 (CBr), 130.2 (CH). Anal. Calcd for $C_{11}H_{19}Br$ (unlabeled sample): C, 57.15; H, 8.28. Found: C, 57.07; H, 8.40.

1-Iodo-1-^{13}C-4-hexylcyclopentene (30a) and 1-Iodo-2-^{13}C-4-hexylcyclopentene (30b): IR 3070, 2923, 1609, 1465 cm^{-1}; ^{1}H NMR δ 0.88 (3H, t, J = 6.7 Hz), 1.26 (8H, br s), 1.39 (2H, m), 1.98 (1H, m), 2.38 (3H, m), 2.70 (1H, m), 6.04 (1H, m); ^{13}C NMR δ 14.1 (CH_3), 22.6 (CH_2), 27.9 (CH_2), 29.4 (CH_2), 31.8 (CH_2), 36.2 (CH_2), 38.7 (CH), 40.4 (CH_2), 50.0 (CH_2), 91.8 (CI), 139.4 (CH). Anal. Calcd for $C_{11}H_{19}I$ (unlabeled sample): C, 47.49; H, 6.88. Found: C, 47.75; H, 6.60.

Reaction of 1-Fluoro-4-hexylcyclopentene (21) with Potassium *tert*-Butoxide. A 40 mg sample of a 1.52/1.00 mixture of **21b**/**21a** was allowed to react with excess KO*t*-Bu at 180 °C in a sealed tube for 30 min. Workup afforded an 80% recovery of **21** with the same **b**/**a** ratio.

Reaction of 1-Fluoro-4-hexylcyclopentene (21) with LDA. Lithium diisopropylamide mono(tetrahydrofuran), 1.5 M in cyclohexane (0.44 mL, 0.66 mmol), was cooled to −20 °C, and 110 mg (0.65 mmol) of **21** was injected. The mixture was stirred at −20 °C for 30 min. Aqueous HCl was added, the mixture was extracted with pentane and dried, and the solvents were removed. Following flash distillation, VPC purification afforded 4-hexylcyclopentene (**24**) (29% yield) and 1-fluoro-4-hexylcyclopentene (**21**) (15% yield). 4-Hexylcyclopentene (**24**): IR 3054, 2957, 1616 cm^{-1}, ^{1}H NMR δ 0.88 (3H, t, J = 6.8 Hz); 1.27 (10H, br s), 1.95 (2H, dd, further split), 2.24 (1H, heptet), 2.48 (2H, dd, further split), 5.65 (2H, br s); ^{13}C NMR δ 14.1 (CH_3), 22.7 (CH_2), 28.4 (CH_2), 29.5 (CH_2), 31.9 (CH_2), 36.6 (CH_2), 37.7 (CH), 39.0 (CH_2, 2C), 130.0 (CH, 2C); HRMS calcd for $C_{11}H_{20}$ 152.1560. Found 152.1533.

Reaction of 1-Fluoro-4-hexylcyclopentene (21) with Potassium *tert*-Butoxide. A 15 mg sample of **21** was subjected to the same reaction conditions as reported for **3**. Only recovered **21** was obtained.

Reaction of 3,3-Bis-(Ethylthio)-2,2,4,4-tetramethyl-1-(fluoromethylene)cyclobutane (8) with Potassium *tert*-Butoxide. A 13 mg (0.05 mmol) sample of **8** was heated at 150 °C in a sealed tube with excess KO*t*-Bu for 1 h. Water was added and the aqueous was extracted with pentane. After the pentane was dried and removed, **8** was recovered in 70% yield. The reaction was repeated with 26 mg (0.10 mmol) of **8** at 180−185 °C. Workup afforded 16 mg of product mixture which was subjected to preparative TLC to give 3,3-bis-(ethylthio)-2,2,4,4-tetramethylcyclobutanecarbaldehyde (**26**): IR 2964, 2745, 2705, 1711 cm^{-1}; ^{1}H NMR δ 1.23 (6H, t, J = 7.5 Hz), 1.36 (6H, s), 1.47 (6H, s), 2.56 (2H, q, J = 7.5 Hz), 2.56 (1H, d, J = 3.7 Hz), 2.58 (2H, q, J = 7.5 Hz), 9.92 (1H, d, J = 3.7 Hz); HRMS calcd for $C_{13}H_{25}OS_2$ [$(M + 1)^+$] 261.1349. Found 261.1347.

Reaction of 3,3-Bis-(ethylthio)-2,2,4,4-tetramethyl-1-(fluoromethylene)cyclobutane (8) with LDA. The reaction was carried out as described for **21** with 26 mg (0.10 mmol) of **8** and 0.11 mmol of LDA and a reaction time of 1 h. Workup afforded a 28% yield of 4,4-bis-(ethylthio)-3,3,5,5-tetramethylcyclopentene (**27**) isolated by preparative TLC: IR 3062, 2959, 2927, 1601, 1452, 878, 698 cm^{-1}; ^{1}H NMR δ 1.22 (6H, t, J = 7.5 Hz), 1.37 (12H, s), 2.58 (4H, q, J = 7.5 Hz), 4.74 (2H, s); ^{13}C NMR δ 13.9 (CH_3), 25.6 (CH_2), 26.7 (CH_3), 43.0 (C-3,C-5), 52.7 (C-4), 100.5 (CH); HRMS calcd for $C_{13}H_{25}S_2$ [$(M + 1)^+$] 245.1399. Found 245.1387.

Reaction of 3-Hexyl-1-(2,2,2-trifluoroethylidene)cyclobutane (20) with Potassium *tert*-Butoxide. Freshly sublimed KO*t*-Bu (0.10 g, 0.91 mmol) was heated to 100 °C, and then 200 mg (0.91 mmol) of **20** was injected into the base. The temperature was maintained for 10 min. Water was added, and the mixture was extracted with pentane. The aqueous layer was acidified and extracted with ether. The pentane extract gave recovered **20**, and the ether extract gave a 40% yield of (3-hexylcyclobutylidene)acetic acid (**34**) after purification by VLC (CH_2Cl_2:EtOAc, 75:25): IR 1690, 1660, 1250 cm^{-1}; ^{1}H NMR δ 0.88 (3H, t, J = 6.8 Hz), 1.27 (8H, br s), 1.48 (2H, m), 2.3−2.5 (3H, m), 2.64 (1H, m), 2.81 (1H, m), 3.25 (1H, m), 5.62 (1H, quintet, J = 2.2 Hz); ^{13}C NMR δ 14.1 (CH_3), 22.6 (CH_2), 27.3 (CH_2), 29.2 (CH_2), 31.2 (CH), 31.8 (CH_2), 36.5 (CH_2), 38.4 (CH_2), 39.8 (CH_2), 112.4 (=CH), 168.9 (=C), 172.2 (O=C).

Acknowledgment. We thank Dr. M. R. Brennan for assistance with some of the NMR experiments.

JO9810866