# The Base-Induced Ring Enlargement of Halomethylenecyclobutanes. A Carbon Analog of the Beckmann Rearrangement

K. L. ERICKSON

*Jeppson Laboratory, Clark University, Worcester, Massachusetts 01610*

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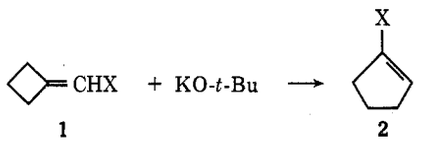
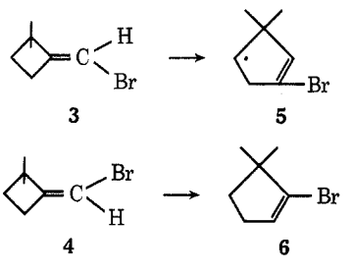
1-Chloromethyl-1-methylcyclobutane (**9**) and ethylthiomethylenecyclobutane (**15**) do not undergo ring enlargement with potassium *tert*-butoxide, although the latter compound does form the vinyl anion. Bromomethylenecyclobutane (**37**) rearranges in DMF in the presence of potassium *tert*-butoxide and potassium iodide to give *tert*-butoxymethylcyclobutene (**39**), 1-bromocyclopentene (**38**), and 1-iodocyclopentene (**40**). The formation of **40** is taken as evidence for the intermediacy of a carbene–bromide complex and a cyclopentyne–bromide complex in analogy to the Beckmann rearrangement of imine derivatives.

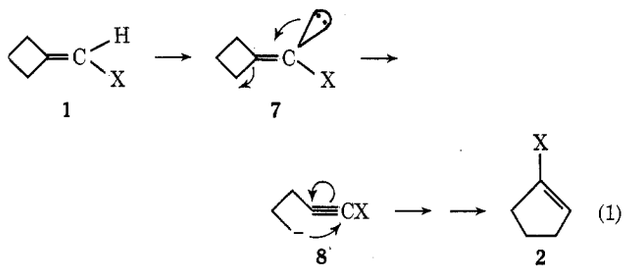
The base-induced rearrangement of 1-halomethylenecyclobutanes (**1**) to 1-halocyclopentenes (**2**) has been



under investigation in our laboratory for the past few years.[1] The stereospecificity of the rearrangement of the two unsymmetrical isomers **3** and **4** to **5** and **6**, re-



spectively, led us to postulate a cleavage–recombination mechanism for the ring enlargement process (eq 1).[1c]

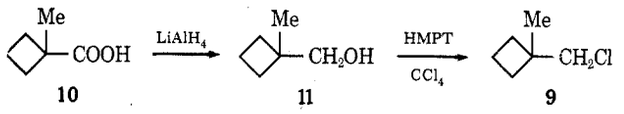


(1)

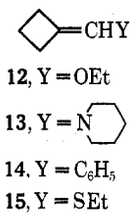
In attempts to provide further evidence in support of this mechanism, we have instead cast doubt upon its validity and have accumulated data more in agreement with an alternate mechanism. In addition, we have examined the sulfur analog of **1** and a nonvinyl analog to further delineate the generality of this reaction.

## Results and Discussion

The only systems to date which have been found to undergo the ring-enlargement reaction are those with a vinyl halide substituent.[1b] To determine if the vinyl system is necessary, 1-chloromethyl-1-methylcyclobutane (**9**) was synthesized from 1-methylcyclobutanecarboxylic acid (**10**)[2] as shown below and subjected to

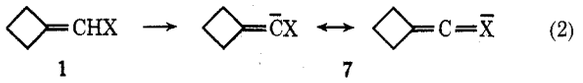


the rearrangement reaction conditions (potassium *tert*-butoxide at 100°). Compound **9** showed no tendency to react with potassium *tert*-butoxide even at 200°. After 6 days in refluxing *tert*-butyl alcohol-*O*-*d* in the presence of potassium *tert*-butoxide, no deuterium exchange had occurred. Chloride **9** thus fails to form a carbanion, without which no rearrangement is possible. The vinyl system is apparently necessary to sufficiently acidify the exocyclic hydrogens, but it alone is not adequate, as shown by the lack of rearrangement of compounds **12**, **13**, and **14**.[1b] In the case of 1-ethoxy-



methylenecyclobutane (**12**), this unreactivity has also been shown to be due to an inability to form the anion. Thus, after 6 days in refluxing *tert*-butyl alcohol-*O*-*d* and potassium *tert*-butoxide, no deuterium incorporation into **12** could be detected (nmr, mass spectrum).

While chloride, bromide, and iodide substituents would be expected to stablize vinyl anion **7** (see eq 2),



(2)

first-row elements (such as oxygen and nitrogen) cannot expand their octets and consequently cannot contribute any resonance stablization to the system. Presumably any methylenecyclobutane derivative with a vinyl substituent capable of stablizing the anion is a viable candidate for ring enlargement (providing other reactions do not compete). Since sulfur is known to be a good stabilizer of an adjacent negative charge, we undertook the synthesis of ethylthiomethylenecyclobutane (**15**) to determine if it would undergo the rearrangement.

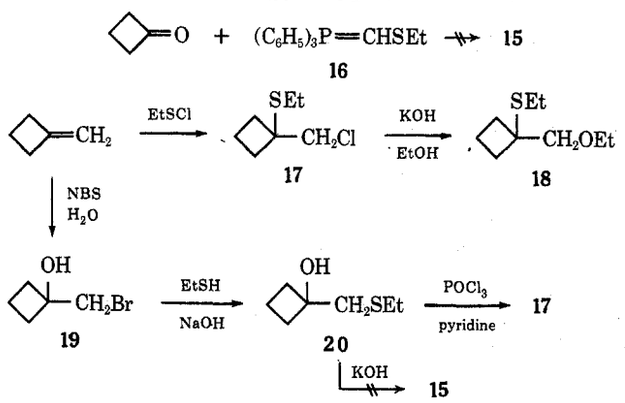
A variety of routes to **15** were simultaneously investigated (Schemes I and II). The most direct method, a Wittig reaction with cyclobutanone and ethylthiomethylenetriphenylphosphorane (**16**),[3] did not

(1) (a) K. L. Erickson, B. E. Vanderwaart, and J. Wolinsky, *Chem. Commun.*, 1031 (1968); (b) K. L. Erickson, J. Markstein, and K. Kim, *J. Org. Chem.*, **36**, 1024 (1971); (c) K. L. Erickson, *ibid.*, **36**, 1031 (1971).

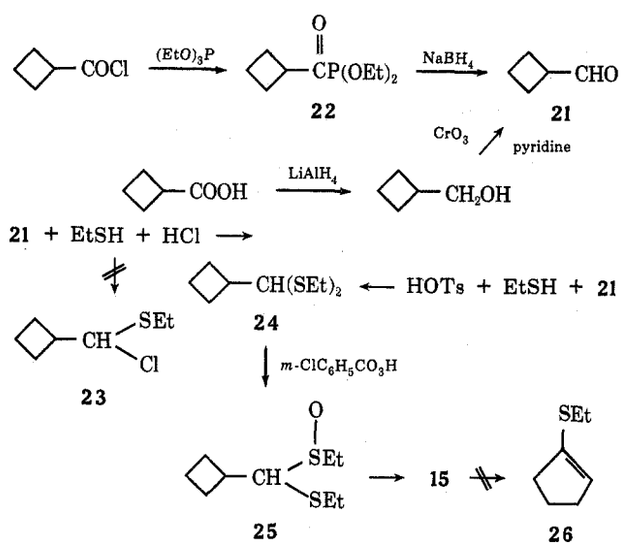
(2) D. G. Pratt and E. Rothstein, *J. Chem. Soc. C*, 2548 (1968).

(3) T. Mukaiyama, S. Fukuyama, and T. Kumamoto, *Tetrahedron Lett.*, 3787 (1968).

SCHEME I



SCHEME II



give any vinyl sulfide. Addition of ethanesulfenyl chloride to methylenecyclobutane proceeded in the wrong direction for our purposes, giving 1-chloromethyl-1-ethylthiocyclobutane (**17**), which readily afforded 1-ethoxymethyl-1-ethylthiocyclobutane (**18**) on treatment with alcoholic potassium hydroxide. Attempted phosphorus oxychloride dehydration of 1-(ethylthiomethyl)cyclobutanol (**20**), not unexpectedly, resulted in sulfur participation, affording **17** as the major product. Powdered potassium hydroxide[4] was likewise ineffective in eliminating water from **20**.

Other possible routes to **15** necessitated a more efficient synthesis of cyclobutanecarboxaldehyde (**21**) than we had previously used.[1b] Johnson and Rickborn[5] report such a synthesis, but we found their route lengthy compared to the two shown in Scheme II. Of these, the method of choice on a yield basis is the chromium trioxide–pyridine oxidation of cyclobutylmethanol.

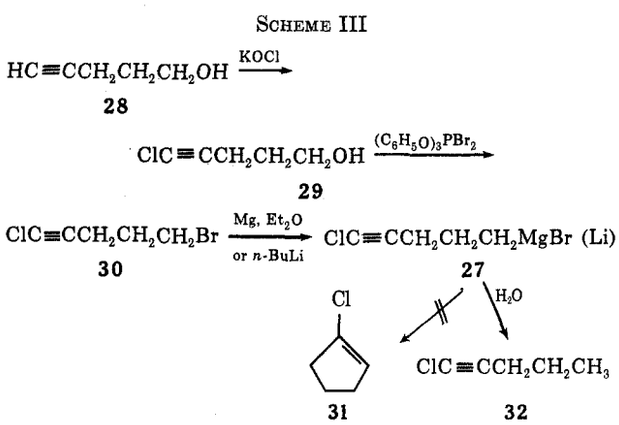
An attempt to prepare $\alpha$-chloro thioether **23** from **21** gave instead thioacetal **24**. This material was prepared in better yield using *p*-toluenesulfonic acid in catalytic amounts. Direct elimination of ethanethiol from **24** by heating with catalytic phosphoric acid[6] resulted in extensive decomposition. Conversion to the monosulfoxide **25** followed by pyrolysis[7] was effective, however, in generating ethylthiomethylenecyclobutane (**15**). Surprisingly, this compound showed no tendency to react with potassium *tert*-butoxide either at 100° or at 200°. 1-Ethylthiocyclopentene (**26**), independently synthesized, was not produced, and the starting vinyl sulfide was recovered in good yields.

When **15** was treated with potassium *tert*-butoxide in refluxing *tert*-butyl alcohol-*O*-*d* (3 days), exchange of the vinyl (and allyl) hydrogen occurred, indicating that the vinyl anion can form in this system. Its failure to rearrange demonstrates that anion formation is not the only requirement which must be met before ring enlargement will occur. Thus, the halomethylenecyclobutanes remain unique in their ability to undergo this reaction.

Turning now to the mechanism of the ring enlargement, the major objections to the postulated cleavage–recombination mechanism are cyclobutyl ring opening to an unstabilized ion (**8**) and the lack of any acyclic product formation. This latter fact requires that ring closure of **8** be faster than any external attack on it (such as protonation).

Evidence for the intermediacy of acyclic ion **8** could be provided by generating it independently and demonstrating its facile ring closure to a cyclopentene system. The most direct method of achieving this is *via* the organometallic derivative, **27**, which was synthesized in three steps from 4-pentyn-1-ol (**28**) (Scheme III).

SCHEME III

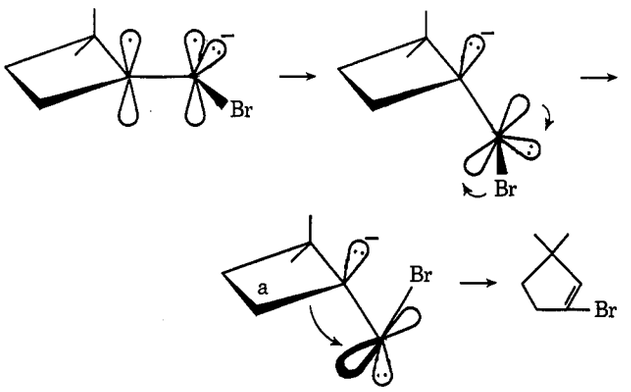


Ring closures of acyclic acetylenic Grignard and lithium derivatives have been reported to give five-membered rings quite readily in certain systems.[8] However, in our case, the cyclized product, 1-chlorocyclopentene (**31**), did not form. Both the Grignard and the lithium derivative gave large amounts of higher boiling material. The major volatile product was 1-chloro-1-pentyne (**32**), indicating that the proper organometallic derivative had indeed formed. If **27** is considered a reasonably good model for acyclic ion **8**, then its failure to close implies that the cleavage–recombination mechanism is incorrect.

There are at least two alternative mechanisms that can be considered which fit the available data and which avoid an acyclic intermediate. The first (Scheme IVa) involves a rehybridization of the vinyl system followed

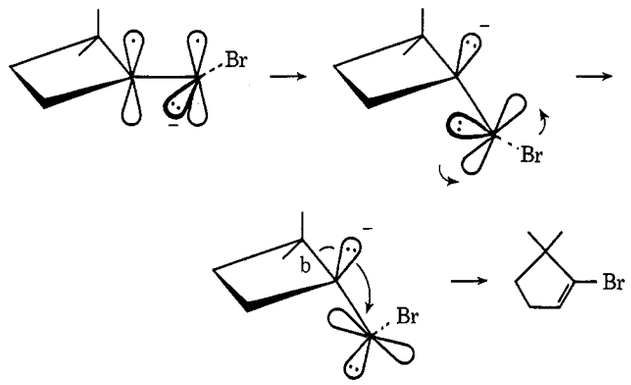
(4) C. C. Price and R. G. Gillis, *J. Amer. Chem. Soc.*, **75**, 4750 (1953).
(5) M. R. Johnson and B. Rickborn, *Org. Syn.*, **51**, 11 (1971).
(6) H. J. Boonstra, L. Brandsma, A. M. Wiegman, and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, **78**, 252 (1959).
(7) A. Deljac, Z. Stefanac, and K. Balenovic, *Tetrahedron, Suppl.*, **8**, 33 (1966).
(8) S. A. Kandil and R. E. Dessy, *J. Amer. Chem. Soc.*, **88**, 3027 (1966); H. G. Richey and A. M. Rothman, *Tetrahedron Lett.*, 1457 (1968).

SCHEME IVa

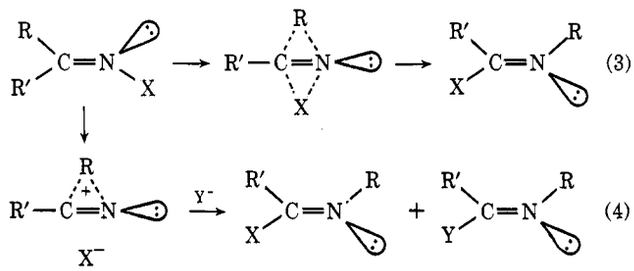


by rotation about the exocyclic bond in the direction indicated in order to avoid eclipsing of the two free-electron pairs and resulting in their maximum separation. At this point, the ring bond a is parallel to the empty lobe on the exocyclic carbon, and bond migration can occur. This migration involves transfer of an electron pair from an electron-rich site (carbanion) to an electron-poor site (carbene) and is analagous to a simple Wagner–Meerwein shift. Rehybridization and protonation give the final product. Using the same rationale, one obtains the proper product from the other isomer as well (Scheme IVb).

SCHEME IVb



A second possible mechanism is one analagous to the Beckmann rearrangement[9] (Scheme V). The Beckmann rearrangement proceeds with simultaneous trans migration of two groups (eq 3). Apparent cis migrations are



(3)

(4)

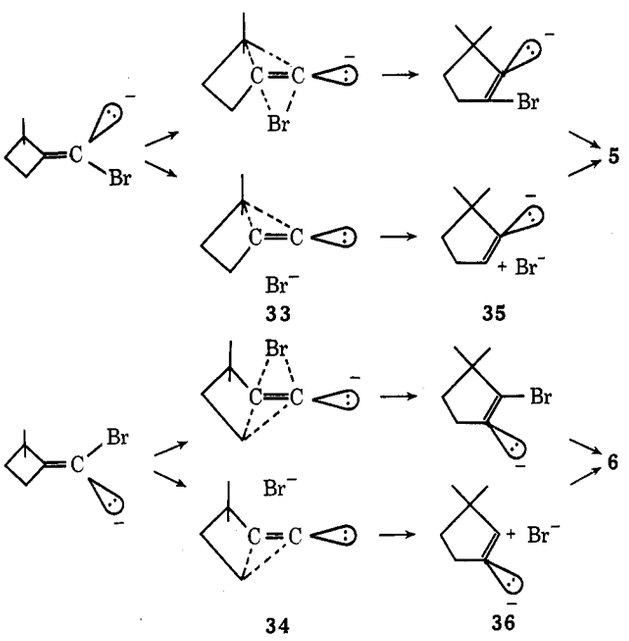
attributed to prior isomerization of starting materials.[10] In good solvents ion pairs are formed which may be trapped by extraneous counterions (eq 4).[11] If the

(9) L. G. Donaruma and W. F. Heldt, *Org. React.*, **11**, 1 (1960); P. A. Smith in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, p 483.

(10) P. T. Lansbury and N. R. Mancuso, *Tetrahedron Lett.*, 2445 (1965).

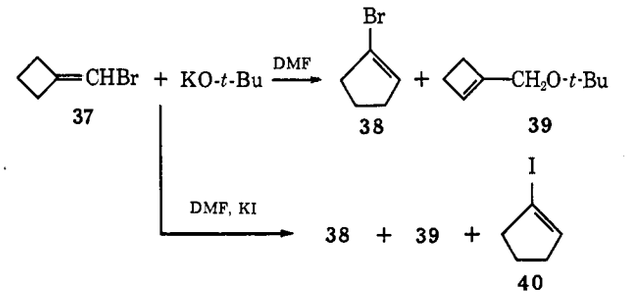
(11) C. A. Grob, H. P. Fischer, W. Raudenbusch, and J. Zergenyi, *Helv. Chim. Acta*, **47**, 1003 (1964).

SCHEME V



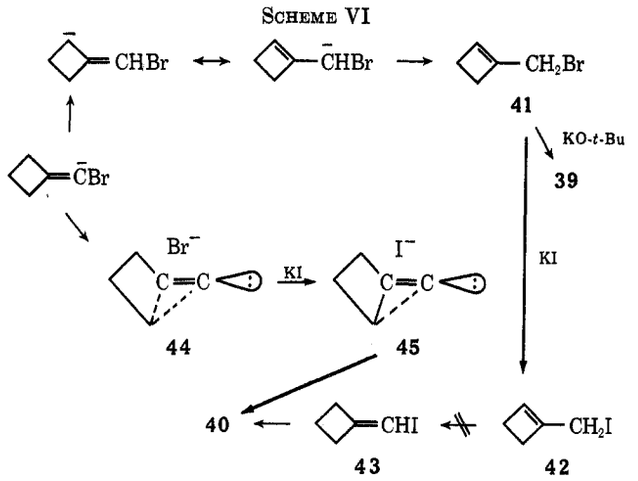
analogy holds for the vinyl bromide case, a carbene–bromide complex (**33**, **34**) would form in good solvents, leading directly to a cyclopentyne–bromide complex (**35**, **36**). In poor solvents or no solvent (as the reaction is normally run) the migration of the two groups may be synchronous with no apparent intermediates other than the initial and final carbanions. In this mechanism the ring carbon migrating for a given isomer is different from the one migrating in the rehybridization mechanism (Scheme IV), but the bromide also migrates here, and the end result is the same.

When bromomethylenecyclobutane (**37**) is allowed to react with potassium *tert*-butoxide in DMF (80°), the course of the reaction changes from that observed in the absence of solvent. With DMF the volatile products consist of a mixture of 20–25% 1-bromocyclopentene (**38**) and 75–80% 1-*tert*-butoxymethylcyclobutene (**39**). If the DMF reaction is run in the presence of added bromide ion (as KBr), the ratio of **38** to **39** rises to 35:65, and, when iodide ion is present (as KI), roughly equal quantities of **38** and **39** are produced, and the major product (35–55% of the volatile product mixture) is 1-iodocyclopentene (**40**).



1-*tert*-Butoxymethylcyclobutene (**39**) most likely arises from isomerization of the vinylic ion to the allylic ion followed by displacement of the bromide (Scheme VI). The presence of a good solvent permits isomerization to take place. In the absence of solvent, or in poor solvents, no isomerization occurs and **38** is the sole volatile product.

SCHEME VI

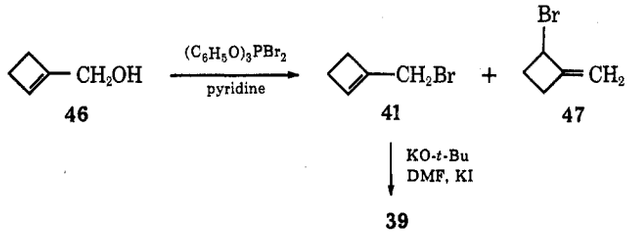



The critical question is whether 1-iodocyclopentene (**40**) arises simply from allyl bromide **41** giving allyl iodide **42** followed by isomerization back to the vinyl system **43** and then rearrangement, or whether **40** arises from trapping of an intermediate carbene–bromide complex (**44**) as postulated for the Beckmann mechanism (see Scheme VI).

Allylic halides **41** and **42** are not found in the product mixture; their conversion to **39** would be expected to be rapid. Once formed, **39** persists; it is stable to the reaction conditions. Other possible sources of 1-iodocyclopentene similiarly can be ruled out. Thus, 1-bromocyclopentene with potassium iodide and potassium *tert*-butoxide under the reaction conditions is recovered unchanged, and bromomethylenecyclobutane does not react with potassium iodide in DMF in the absence of potassium *tert*-butoxide. It remains, then, to determine whether allylic bromide **41** can revert to the vinyl system, and, with added iodide, whether **41** can give rise to **43** and thence **40**.

The synthesis of 1-bromomethylcyclobutene (**41**) was carried out as shown in Scheme VII. 1-Cyclobutene-

SCHEME VII




methanol (**46**) was prepared by the multistep method of Heyns and coworkers.[12] Various attempts were made to convert this alcohol to **41**, all of which resulted in mixtures of **41** and **47**. The method shown gave the best ratios of **41** to **47** (75:25).

These isomers did not resolve on the vpc (Carbowax), but nmr readily showed the presence of both. No serious attempt was made to achieve vpc separation, however, as it was expected that **41** would open to diene **48** on the instrument. This assumption is based upon the fact that cyclobutenes **39** and **46** both undergo partial ring opening to **49** and **50**, respectively, when collected from the vpc.

(12) K. Heyns, K. Molge, and W. Walter, *Ber.*, **94**, 1015 (1961).


**48**, X = Br
**49**, X = O-*t*-Bu
**50**, X = OH

Upon reaction with potassium *tert*-butoxide in DMF, with or without added iodide, **41** (25% **47**) gave good yields of 1-*tert*-butoxymethylcyclobutene (**39**). No bromomethylenecyclobutane (**37**) or 1-bromocyclopentene (**38**) were observed in the product mixture, nor were any organic iodides isolated when iodide ion was present. These results show that the allylic system does not revert to the vinylic system. Hence the formation of iodocyclopentene (**40**) from bromomethylenecyclobutane (**37**) and potassium iodide under the rearrangement reaction conditions is evidence for an intermediate whose halide can become detached. A carbene–bromide complex such as **44** postulated for the Beckmann mechanism is such an intermediate.

In the absence of solvent, bromomethylenecyclobutane (**37**) reacts with a mixture of potassium *tert*-butoxide and potassium iodide to give only the ring-enlarged bromide **38** in addition to recovered starting material. The presence of the additional solid (KI) hinders contact between **37** and the base with consequent slowing of the reaction. That no 1-iodocyclopentene is formed may be attributed to the heterogeneity of the reaction mixture and/or lack of formation of a carbene–ion complex. In the absence of a good stabilizing solvent, the rearrangement probably proceeds with simultaneous migration of both the ring carbon and the bromide as in the Beckmann rearrangement.

With molten potassium hydroxide serving as both the solvent and the base, bromomethylenecyclobutane (**37**) rearranges to **38** with about 50% conversion. With added iodide, product mixtures consist of 65% recovered **37**, 30% rearranged bromide (**38**), and 5% 1-iodocyclopentene (**40**). The allylic alcohol **46** was not found.

In summary, the uniqueness of halomethylenecyclobutanes to rearrange to 1-halocyclopentenes has been further demonstrated. This ring-enlargement reaction appears to proceed *via* the mechanism established for the Beckmann rearrangement rather than the cleavage–recombination mechanism originally postulated. Labelling experiments would provide definitive evidence for the double-migration mechanism.

## Experimental Section

Melting and boiling points are uncorrected. Infrared spectra were recorded on Perkin-Elmer Models 137 and 337 spectrophotometers. The nmr spectra were recorded with a Jeolco Model C-60H spectrometer, using tetramethylsilane as an internal standard. Mass spectra were determined on a Hitachi Perkin-Elmer RMU-6D mass spectrometer. Vapor phase chromatographic analyses were performed on a Varian Aerograph Model 90-P3 chromatograph with the following columns: Carbowax 20M, QF-1, SE-30, SF-96, and FFAP (all columns were 20% stationary phase on a 60/80 Chromosorb W A/W DMCS support) and on a Varian Aerograph Model 600-D with the following columns: 5% QF-1 on 60/80 Chromosorb W and 3% SE-30 on 100/120 Chromosorb W. Elemental analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn., and Atlantic Microlab, Inc., Atlanta, Ga.

**1-Methylcyclobutanemethanol** (11).—In a 500-ml flask equipped with a dropping funnel, overhead stirrer, condenser, and drying tube were placed 200 ml of anhydrous ether and 6.46 g (0.170 mol) of lithium aluminum hydride. The resultant suspension was stirred while 15.60 g (0.136 mol) of 1-methylcyclobutanecarboxylic acid[2] in 60 ml of anhydrous ether was added at a rate to maintain gentle reflux. After all of the acid was added, the mixture was refluxed for 3 hr. While the reaction mixture was cooled in ice, a saturated solution of sodium sulfate was added dropwise until the magnesium salts coagulated. The mixture was then filtered, the solid was washed well with ether, and the filtrate was dried over $MgSO_4$. The ether was removed, and the residue was distilled to give 11.5 g (85%) of product: bp 70–71° (32 mm); ir (neat) 2.91, 3.35, 6.86, 7.27, 9.55, 9.77 $\mu$; nmr ($CDCl_3$) $\delta$ 1.13 (s, 3 H), 1.80 (m, 6 H), 1.98 (s, 1 H), 3.47 (s, 2 H).

*Anal.* Calcd for $C_6H_{12}O$: C, 71.95; H, 12.08. Found: C, 72.13; H, 12.07.

**1-Chloromethyl-1-methylcyclobutane** (9).—The procedure of Downie and coworkers[13] was adapted for the preparation of this compound. A mixture of 8.0 g (0.08 mol) of 1-methylcyclobutanemethanol, 17 g (0.12 mol) of reagent grade carbon tetrachloride, and 20 ml of anhydrous ether was cooled in an ice bath with stirring while 13.0 g (0.08 mol) of hexamethylphosphorus triamide in 20 ml of anhydrous ether was added dropwise. An immediate reaction occurred with the formation of an orange-brown color. Toward the end of the addition, a brown oil separated. The mixture was warmed to room temperature and the ether was distilled, leaving a one-phase residue which was flash distilled. The distillate was then fractionated at atmospheric pressure to give a forerun of chloroform and carbon tetrachloride and 8.0 g (85%) of product: bp 122–123°; ir (neat) 3.36, 6.90, 7.01, 7.30, 7.82, 7.90, 13.0–14.4 $\mu$; nmr ($CCl_4$) $\delta$ 1.21 (s, 3 H), 1.85 (m, 6 H), 3.52 (s, 2 H).

*Anal.* Calcd for $C_6H_{11}Cl$: C, 60.76; H, 9.35. Found: C, 60.73; H, 9.34.

On passage through the vpc, the chloride was partially converted to a hydrocarbon identified as 1-methylcyclopentene by comparison with authentic material.

**Reaction of 1-Chloromethyl-1-methylcyclobutane (9) with Potassium *tert*-Butoxide.**—In a flask equipped with a condenser, drying tube, and rubber serum cap was placed 0.62 g (0.0055 mol) of potassium *tert*-butoxide. This was heated to a bath temperature of 100–105°, and 0.59 g (0.0050 mol) of the chloride was injected by syringe through the serum cap. There was no obvious reaction. The mixture was kept at 100–105° for 30 min and then cooled, and water was added. Extraction with pentane gave an organic phase which was washed five times with water, and then dried, and the pentane was distilled. The residue consisted solely of starting alkyl chloride.

The reaction was repeated at a bath temperature of 200–205° for 30 min with the same results.

**Deuterium Exchange Studies with 1-Chloromethyl-1-methylcyclobutane (9).**—A mixture of 1.18 g (0.010 mol) of the chloride, 1.68 g (0.015 mol) of potassium *tert*-butoxide, and 5 ml of *tert*-butyl alcohol-*O*-*d* was refluxed for 3 days. Work-up as above gave recovered alkyl chloride with no detectable deuterium incorporation and 10% of a new compound which was not identified, but the ir ($CCl_4$) strongly suggests that it is 1-*tert*-butoxymethyl-1-methylcyclobutane (3.36, 6.84, 7.20, 7.33, 8.32, 9.19 $\mu$).

**Attempted Wittig Reaction of Ethylthiomethylenetriphenylphosphorane[3] with Cyclobutanone.**—A THF suspension of 8.57 g (0.024 mol) of methyltriphenylphosphonium bromide was treated with 11.4 ml (0.024 mol) of 2.1 *M* phenyllithium solution. The mixture was stirred at 25° for 3 hr and then 0.012 mol of ethanesulfenyl chloride was added, and stirring was continued for 3 hr. To this mixture was added 0.84 g (0.012 mol) of cyclobutanone dropwise. The mixture was refluxed for 15 hr, poured onto ice, and extracted with ether. The ether was dried and removed to give a residue which was flash distilled. The distillate consisted of diethyl disulfide, cyclobutanone, and aromatic compounds. No ethylthiomethylenecyclobutane was detected.

**Addition of Ethanesulfenyl Chloride to Methylenecyclobutane.**—Ethanesulfenyl chloride was prepared by the method reported for the methyl isomer.[14] To 3.05 g (0.025 mol) of diethyl disulfide at −15 to −20° was added dropwise 3.38 g (0.025 mol) of sulfuryl chloride. The solution turned orange. It was warmed to 25° and distilled at 65 mm; the material boiling at 35–40° was collected [lit.[15] bp 39° (58 mm)].

Ethanesulfenyl chloride was added dropwise to 0.8 g (0.0117 mol) of methylenecyclobutane dissolved in methylene chloride cooled to −40° until a slight orange color persisted. The solvent was removed and the residue was distilled to give material boiling over a 10° range (49–59° at 10 mm). Vpc showed it to be one major product (~90%) contaminated with two other materials. The major compound **17** partially rearranged on the vpc (forming 1-ethylthio-1-cyclopentene), and spectral data were gathered directly on the distillates: ir (neat) 3.38, 6.89, 6.97, 7.23, 7.79, 7.89, 12.74, 13.60, 14.20 $\mu$; nmr ($CCl_4$) $\delta$ 1.23 (t, 3 H), 1.6–2.8 (m, 8 H), 3.58 (s, 2 H). Because of the difficulty of purifying this material, an analysis was not obtained.

**1-Ethoxymethyl-1-ethylthiocyclobutane** (18).—Chlorosulfide **17** (0.82 g, 0.005 mol) was added to a solution of 0.4 g of KOH in 95% ethanol. The mixture was stirred at 25° for 2 hr and was then poured into ice and extracted with pentane. The pentane layer was washed with water and dried, and the pentane was removed. Distillation of the residue afforded 0.5 g (66%) of **18**: bp 52–54° (1.3 mm); ir (neat) 3.38, 3.50, 6.95, 7.29, 7.41, 7.92, 8.55, 9.02 $\mu$; nmr ($CCl_4$) $\delta$ 1.22 (t, 6 H), 1.6–2.8 (m, 8 H), 3.35 (s, 2 H), 3.51 (q, 2 H).

*Anal.* Calcd for $C_9H_{18}OS$: C, 62.02; H, 10.41. Found: C, 62.21; H, 10.46.

**1-(Ethylthiomethyl)cylcobutanol** (20).—To 33 ml (0.0082 mol) of 10% NaOH was added 0.51 g (0.0082 mol) of ethanethiol. To this was then added dropwise 1.35 (0.0082 mol) of 1-(bromomethyl)cyclobutanol (**19**).[1b] The opaque mixture was stirred at 25° for 30 min, at the end of which time the oil had migrated from the bottom of the water layer to the top. The mixture was extracted with ether, the ether layer was dried, and the ether was removed. Distillation afforded 0.90 g (73%) of **20**: bp 51–53° (0.5 mm); ir (neat) 2.89, 3.36, 6.8–7.5, 7.7–8.2, 8.5–8.9, 9.20, 10.34, 10.88, 13.44 $\mu$; nmr ($CDCl_3$) $\delta$ 1.22 (t, 3 H), 1.7–2.3, and 2.5–3.0 (m, 9 H).

*Anal.* Calcd for $C_7H_{14}OS$: C, 57.49; H, 9.65. Found: C, 57.51; H, 9.68.

**Attempted Dehydration of 1-(Ethylthiomethyl)cyclobutanol (20).**—To a mixture of 0.760 g (0.0050 mol) of phosphorus oxychloride in 8 ml of anhydrous pyridine at ice temperature was added 0.68 g (0.0046 mol) of the alcohol. A precipitate formed readily. The mixture was stirred at 25° overnight and was then poured onto ice and extracted with pentane. The pentane was washed with water, dried, and removed. The residue was distilled to give 0.5 g (65%) of 1-chloromethyl-1-ethylthiocyclobutane (**17**). A small amount (~15%) of another compound was present in the distillate, possibly the isomer, 1-(ethylthiomethyl)cyclobutyl chloride. No olefin was detected.

A second attempt at dehydration of **20** was made with powdered potassium hydroxide at 250°.[4] No vinyl sulfide was produced.

**Cyclobutanecarboxaldehyde** (21). **Method A.**[16,17]—To 11.85 g (0.100 mol) of cyclobutanecarbonyl chloride was added dropwise 16.60 g (0.100 mol) of triethyl phosphite at a rate to keep the internal temperature below 35°. The reaction was run in a nitrogen atmosphere. After the phosphite was completely added, the mixture was stirred at 25° for 30 min. Distillation at 1.7 mm afforded 18.2 g (83%) of **22** boiling at 103–104°: ir (neat) 5.88, 7.95, 8.55, 9.0–10.8, 12.55, 13.25, 13.86 $\mu$; nmr ($CDCl_3$) $\delta$ 1.37 (t, 6 H), 1.7–2.7 (m, 6 H), 3.4–4.0 (m, 1 H), 4.25 (pentet, 4 H).

*Anal.* Calcd for $C_9H_{17}O_4P$: C, 49.90; H, 7.78. Found: C, 49.21; H, 7.86.

A suspension of 6.60 g (0.03 mol) of phosphonate **22** in 30 ml of water was cooled to 0°, and a solution of 0.76 g (0.02 mol) of sodium borohydride in 60 ml of water was added alternately with 6.26 g (0.046 mol) of potassium dihydrogen phosphate. The pH of the mixture was thus maintained between 6 and 7. The mixture was stirred for 20 min at 25°, and it was then made strongly basic with 10% NaOH and steam distilled. The aldehyde was extracted from the distillate with ether. Distillation at atmospheric pressure gave 1.2 g (46%) of aldehyde, bp 113–

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115° (lit.[5] bp 56–59° (120 mm). The aldehyde was not stored but was used immediately.

The steam distillation residue, upon acidification and ether extraction, gave 0.77 g (26%) of cyclobutanecarboxylic acid.

**Method B.**[18]—Cyclobutylmethanol was prepared by lithium aluminum hydride reduction of cyclobutanecarboxylic acid.

To an ice-cooled, stirred solution of 56.94 g (0.727 mol) of pyridine (dried over 4A molecular sieves) in 900 ml of methylene chloride (washed with concentrated $H_2SO_4$ and water, dried, and distilled onto 4A molecular sieves) was added portionwise 36.0 g (0.36 mol) of chromium trioxide (dried over $P_2O_5$). The red-brown suspension was warmed to 25° and stirred at this temperature for 15 min. Cyclobutylmethanol (5.16 g, 0.06 mol) was added all at once, and the mixture was stirred at 25° for 30 min.

The solution was decanted into a separatory funnel, and the gummy precipitate was washed several times with ether; the washings were added to the methylene chloride solution. This was washed with 5% NaOH (2 × 100 ml), 5% HCl (3 × 100 ml), 5% $NaHCO_3$ (2 × 100 ml), and brine. It was dried ($MgSO_4$), and the methylene chloride was distilled off through a 200-cm Vigreux column. The residue was distilled at atmospheric pressure to give a total of 4.0 g (80%) of cyclobutanecarboxaldehyde. Earlier boiling fractions were freed of methylene chloride by vpc collection (Carbowax, 125°).

**Reaction of Cyclobutanecarboxaldehyde with Ethanethiol and Hydrogen Chloride.**—The method of Boonstra and coworkers[6] was used. To 0.34 g (0.005 mol) of aldehyde cooled to −40° was added dropwise 0.31 g of ethanethiol while a rapid stream of hydrogen chloride was bubbled through the mixture. A solid formed. The mixture was taken up in ether and dried, and the ether was removed. The residue was not the chloro sulfide but instead the diethyl thioacetal of cyclobutanecarboxaldehyde (**24**).

**Attempted Elimination of Ethanethiol from Thioacetal 24.**—The procedure of Boonstra and coworkers[6] was followed. The thioacetal was placed in a minidistillation apparatus with a drop of 85% phosphoric acid. The system was evacuated to 110 mm and heated to an oil-bath temperature of 145°, at which point violent decomposition occurred. Very little distillate was obtained and much residue remained. The only component in the distillate identified was starting material.

**Diethyl Thioacetal of Cyclobutanecarboxaldehyde (24).**—To a mixture of 3.30 g (0.039 mol) of the aldehyde and 60 mg of *p*-toluenesulfonic acid cooled in an ice bath was added dropwise 5.27 g (0.085 mol) of thioethanol. An immediate reaction generally occurred with separation of water. The mixture was heated at an oil-bath temperature of 70° for 10 hr; it was then poured into 10% NaOH and extracted with ether. The ether extract was dried, and the ether was removed. Distillation of the residue gave 6.3 g (85%) of thioacetal: bp 69–70° (0.6 mm); ir (neat) 3.35, 6.90, 7.25, 7.88, 7.97, 10.23, 12.46, 12.73, 13.48 μ; nmr ($CCl_4$) δ 1.25 (t, 6 H), 1.6–2.3 (m, 7 H), 2.64 (q, 4 H), 3.72 (d, 1 H).

*Anal.* Calcd for $C_9H_{18}S_2$: C, 56.78; H, 9.53. Found: C, 56.91; H, 9.62.

**Ethylthiomethylenecyclobutane (15).**—The general method of Deljac and coworkers[7] was used. To an ether solution of 4.9 g (0.0257 mol) of **21** cooled in ice was added dropwise an ether solution of 5.10 g (0.0257 mol) of 85% *m*-chloroperbenzoic acid. The ether was then stripped off, and methylene chloride was added to precipitate most of the *m*-chlorobenzoic acid, which was then filtered. The filtrate was washed with $NaHCO_3$ solution and dried, and the methylene chloride was removed to give 4.9 g (93%) of crude sulfoxide **25**: ir (neat) 3.36, 6.91, 7.39, 7.95, 9.52, 9.83, 10.31, 12.80, 13.60, 14.22 μ. It was not purified but was pyrolyzed directly.

The sulfoxide (1 g) was placed in a 5-ml round-bottom flask stuffed with glass wool and attached to a minidistillation setup. The pressure was reduced to 15 mm, and the flask was heated to a bath temperature of 150–160°. The distillate (0.45 g, 71%) generally contained ~10% impurities. The vinyl sulfide was purified by vpc (Carbowax, 125°): ir (neat) 3.38, 6.02, 6.88, 7.01, 7.25, 7.90, 12.18, 13.04, 13.76 μ; nmr ($CCl_4$) δ 1.24 (t, 3 H), 1.8–2.4 (m, 2 H), 2.4–3.0 (m, 6 H), 5.57 (m, 1 H).

*Anal.* Calcd for $C_7H_{12}S$: C, 65.56; H, 9.44. Found: C, 65.54; H, 9.49.

**Reaction of Ethylthiomethylenecyclobutane (15) with Potassium *tert*-Butoxide.**—The reaction was run as described for **9**. In no case was there any 1-ethylthiocyclopentene (**26**) produced. The starting material was recovered unchanged.

**1-Ethylthio-1-cyclopentene (26).**—This material was prepared by the method of Brandsma.[19] The vinyl sulfide was purified by vpc (Carbowax, 125°): ir (neat) 3.26, 3.38, 6.22, 6.89, 7.24, 11.7–13.5 μ; nmr ($CCl_4$) δ 1.26 (t, 3 H), 1.8–2.2 (m, 2 H), 2.2–2.8 (m, 4 H), 2.75 (q, 2 H, overlapping allylic H's), 5.28 (m, 1 H).

**Deuterium Exchange Studies with Ethoxymethylenecyclobutane (12).**—The vinyl ether[1b] (150 mg) and 200 mg of potassium *tert*-butoxide were dissolved in 2 ml of *tert*-butyl alcohol-*O*-*d*, and the mixture was refluxed for 3 hr to 6 days. In no case was there any detectable vinyl (or allylic) hydrogen exchange (nmr, mass spectrum).

**Deuterium Exchange Studies with Ethylthiomethylenecyclobutane (15).**—The vinyl sulfide (150 mg) and 300 mg of potassium *tert*-butoxide were dissolved in 3 ml of *tert*-butyl alcohol-*O*-*d* and the mixture was refluxed for 3 days. Both nmr and mass spectrum indicated vinylic and allylic H exchange. The predominant isomers were $d_4$ and $d_3$, but some $d_5$ and $d_6$ were also formed.

**5-Chloro-4-pentyn-1-ol (29).**—A solution of potassium hypochlorite was prepared from 39.0 g of HTH[20] and was cooled in an ice bath. To this was added all at once 11.04 g (0.093 mol) of 4-pentyn-1-ol[21] and 60 ml of pyridine. The two-phase reaction mixture was stirred vigorously at 10–20° for 8 hr, and then it was extracted with ether. The ether extract was washed with water, 6 *N* HCl, water, and $NaHCO_3$ solution and was dried over $MgSO_4$, and the ether was removed *in vacuo*. On distillation, the residue afforded a forerun of starting material (1.1 g) and 7.6 g (50%) of 5-chloro-4-pentyn-1-ol (**29**): bp 86–87° (10 mm); ir (neat) 3.00, 3.38, 4.46, 9.46 μ; nmr ($CDCl_3$) δ 1.75 (pentet, 2 H), 2.23 (s, 1 H), 2.40 (m, 2 H), 3.77 (t, 2 H).

*Anal.* Calcd for $C_5H_7ClO$: C, 50.65; H, 5.95. Found: C, 50:51; H, 5.97.

**1-Chloro-5-bromo-1-pentyne (30).**—Triphenyl phosphite dibromide[22] was prepared as follows. To 22.32 g (0.072 mol) of triphenyl phosphite cooled in an ice bath was added dropwise 11.52 g (0.072 mol) of bromine. An instantaneous reaction occurred with the formation of a yellow-orange solid. After complete addition of the bromine, the mixture was stirred at ice temperature until the bromine color disappeared.

A mixture of 7.80 g (0.066 mol) of 5-chloro-4-pentyn-1-ol (**29**) and 5.70 g (0.073 mol) of pyridine was added dropwise to the ice-cooled triphenyl phosphite dibromide. The mixture was allowed to warm slowly (1 hr) to room temperature while the orange solid became a white paste. The mixture was poured into ice and extracted with ether. The ether extracts were washed with cold 6 *N* HCl and water, then dried over $MgSO_4$. After removal of the ether, the residue was distilled to give 5.9 g (50%) of 1-chloro-5-bromo-1-pentyne (**30**): bp 79–80° (12 mm); ir (neat) 3.40, 4.45, 6.97, 7.84, 8.01, 11.73, 12.5–13.3 μ; nmr ($CCl_4$) δ 1.8–2.6 (m, 4 H), 3.50 (t, 2 H).

*Anal.* Calcd for $C_5H_6BrCl$: C, 33.10; H, 3.33. Found: C, 33.34; H, 3.41.

**1-Chloro-1-pentyne (32).**—A solution of potassium hypochlorite was prepared from 9.7 g of HTH.[20] To this was added at ice temperature 2.21 g (0.032 mol) of 1-pentyne and 15 ml of pyridine. The mixture was then stirred vigorously at 25° for 4 days. It was worked up in the same manner as 5-chloro-4-pentyn-1-ol (**29**). Atmospheric distillation afforded a forerun of starting material and 0.9 g (28%) of 1-chloro-1-pentyne (**32**): bp 92° (lit.[23] bp 92°); ir ($CCl_4$) 3.34, 4.42, 6.83, 6.98, 7.23, 9.15, 9.24, 11.33, 14.28 μ.

**Reaction of 1-Chloro-5-bromo-1-pentyne (30) with Magnesium and Lithium Reagents.**—To 0.24 g (0.01 g-atom) of magnesium in anhydrous ether in a nitrogen atmosphere was added 1.8 g (0.01 mol) of 1-chloro-5-bromo-1-pentyne dropwise. Some difficulty was experienced in initiating the reaction and in keeping it going once it had started. When vpc indicated that most of the starting material had reacted, the mixture was poured into ice water and was extracted with ether. The ether extracts were dried, and the ether was removed by distillation. The volatile

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products were isolated by flash distillation and examined by vpc (Carbowax, 70°). The major product was identified as 1-chloro-1-pentyne, and no 1-chlorocyclopentene[24] could be detected. A substantial amount of higher molecular weight material was produced which was not investigated further. This reaction was repeated several times with the same results.

This halide showed no tendency to react with elemental lithium. It did, however, react with *n*-butyllithium, giving much the same results as the magnesium reaction.

**1-Bromomethylcyclobutene (41).**[12,25]—1-Cyclobutenemethanol (**46**) was prepared by the multistep method of Heyns and coworkers.[12] On vpc it underwent some ring opening to 2-hydroxymethyl-1,3-butadiene (**50**).[26]

Triphenyl phosphite dibromide[22] was prepared from 2.08 g (0.013 mol) of bromine and 4.03 g (0.013 mol) of triphenyl phosphite. To this was added dropwise with ice cooling a mixture of 1.0 g (0.012 mol) of 1-cyclobutenemethanol and 1.03 g (0.013 mol) of anhydrous pyridine. After the mixture had been stirred for 1 hr at 25°, it was flash distilled to give 0.6 g of distillate. Nmr ($CCl_4$) showed it to be a mixture of 75% 1-bromomethylcyclobutene (**41**) and 25% 2-methylenecyclobutyl bromide[25] (**47**): δ 2.5 (m), 3.8 (broad singlet), 4.8–5.3 (m, $=CH_2$), 6.0 (m, =CH). The ratio of vinyl H's was used to determine the composition of the mixture.

The ratio of endo to exo isomer varied from run to run and the composition of the mixture appeared to change on standing. Some runs afforded the inverse ratio of 75% **41** to 25% **47**.

**Reactions of Vinylic and Allylic Bromides with Potassium *tert*-Butoxide in DMF. General Procedure.**—A slight excess of potassium *tert*-butoxide was dissolved in dry DMF and heated to a bath temperature of 80–90°. The bromide was injected beneath the surface of the hot solution and stirring was continued for 5–30 min.

The solution was cooled and water was added. The aqueous reaction mixture was extracted with pentane, and the pentane extracts were washed several times with water and finally with brine. The extracts were dried over $MgSO_4$, and the pentane was removed by distillation. The residue was generally flash distilled and the distillate was examined by vpc.

In reactions utilizing extraneous bromide or iodide ion, the DMF solution was saturated (80–90°) with powdered KBr or KI before injection of the vinyl or allyl bromide.

**A. With Bromomethylenecyclobutane (37).**—The vinyl bromide (40 μl) was injected into a solution of 60 mg of potassium *tert*-butoxide in 2 ml of dry DMF at a bath temperature of 80–90°. Work-up afforded a volatile product mixture consisting of 20–25% 1-bromocyclopentene[1b] and 75–80% 1-*tert*-butoxymethylcyclobutene (**39**). The latter compound displayed ir (neat) 3.28, 3.38, 6.05, 6.82, 7.20, 7.32, 8.33, 9.34, μ; nmr ($CCl_4$) δ 1.21 (s, 9 H), 1.40 (m, 4 H), 3.73 (m, 2 H), 5.73 (m, 1 H). On the vpc this compound underwent partial ring opening to 2-*tert*-butoxymethyl-1,3-butadiene (**49**): ir (neat) 3.22, 3.35, 5.51 (w), 6.28, 7.31, 7.37, 8.39, 9.06, 11.07 μ; nmr ($CCl_4$) δ 1.22 (s, 9 H), 3.98 (m, 2 H), 4.8–5.4 (m, 4 H), 6.31 (q, further split, 1 H).

*Anal.* Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found (mixture of **39** and **49**): C, 76.99; H, 11.55.

When the reaction was carried out in the presence of added KBr, the ratio of **39** to **38** was 65:35. With added KI, the ratio of **39** to **38** was ~50:50, and the total volatile product consisted of 35–55% 1-iodocyclopentene.[1b]

**B. With 1-Bromomethylcyclobutene (41).**—The allyl bromide (0.37 g), contaminated with 2-methylenecyclobutyl bromide, was injected into a solution of 0.42 g of potassium *tert*-butoxide and 2 ml of DMF at a bath temperature of 85°. Work-up afforded a volatile product mixture consisting of >90% 1-*tert*-butoxymethylcyclobutene (**39**). No 1-bromocyclopentene (**38**) or bromomethylenecyclobutane (**37**) were detected.

This reaction was carried out several times in the presence of KI. In no case was any 1-iodocyclopentene (**40**) observed as a product.

**C. With 1-Bromocyclopentene (38).**—The vinyl bromide (40 μl) was injected into a solution of 60 mg of potassium *tert*-butoxide and 1.2 g of KI in 3 ml of dry DMF at 85–90°. Work-up afforded only recovered starting material.

**Reaction of Bromomethylenecyclobutane (37) with Potassium Iodide in DMF.**—The vinyl bromide (20 μl) was injected into a DMF solution of 600 mg of KI at a bath temperature of 85–90°. The mixture was kept at this temperature for 10 min. Work-up as in the general procedure above afforded only recovered vinyl bromide.

**Reaction of Bromomethylenecyclobutane (37) with Potassium *tert*-Butoxide and Potassium Iodide in the Absence of Solvent.**—A mixture of 30 mg of potassium *tert*-butoxide and 300 mg of KI was ground together and heated to a bath temperature of 85°. The vinyl bromide (20 μl) was injected. Work-up afforded a mixture of 1-bromocyclopentene (**38**) and recovered starting material (**37**) in a ratio of 1:3. There was no 1-iodocyclopentene (**40**) detected.

**Reaction of Bromomethylenecyclobutane (31) with Molten Potassium Hydroxide. A. In the Absence of Potassium Iodide.**—The vinyl bromide (0.4 g) was injected into 1 g of molten KOH at a bath temperature of 180° and held at that temperature for 30 min. Work-up afforded about a 50:50 mixture of 1-bromocyclopentene (**38**) and recovered bromomethylenecyclobutane (**37**). No other volatile products were present.

**B. In the Presence of Potassium Iodide.**—This reaction was run several times in the same manner as for part A, but with added powdered KI (~500 mg). Work-up afforded product mixtures generally consisting of 30% 1-bromocyclopentene (**38**), 65% recovered bromomethylenecyclobutane (**37**), and 5% 1-iodocyclopentene (**40**).

**Registry No.**—**9,** 38401-40-0; **10,** 32936-76-8; **11,** 38401-41-1; **15,** 38401-42-2; **17,** 38401-43-3; **18,** 38401-44-4; **19,** 30800-70-5; **20,** 38401-46-6; **21,** 2987-17-9; **22,** 38401-48-8; **24,** 38401-49-9; **25,** 38401-50-2; **28,** 5390-04-5; **29,** 38401-51-3; **30,** 1192-04-7; **38,** 38401-52-4; **39,** 38401-53-5; **49,** 38401-54-6; cyclobutanecarbonyl chloride, 5006-22-4; *m*-chloroperbenzoic acid, 937-14-4.

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