Base-Induced Reactions of Methylenecyclobutane Derivatives

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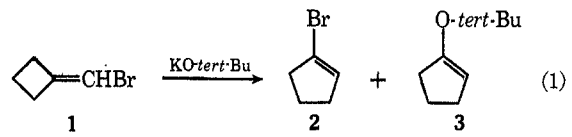
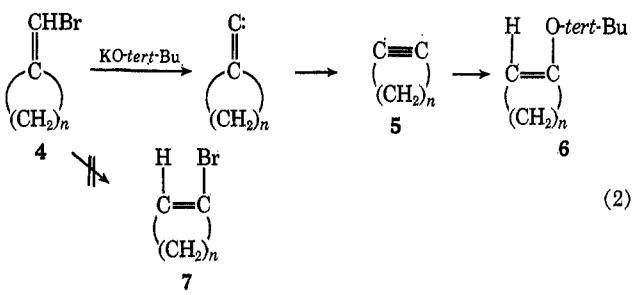
The reaction of substituted methylenecyclobutane derivatives with potassium *tert*-butoxide is examined. Halomethylenecyclobutanes rearrange to the corresponding 1-halocyclopentenes. Oxygen-, nitrogen-, and phenyl-substituted derivatives are essentially inert under the reaction conditions. Cyclobutylideneacetonitrile and *tert*-butyl cyclobutylideneacetate dimerize to Michael addition products.

We have previously reported on the unusual rearrangement of bromomethylenecyclobutane (**1**) to 1-bromocyclopentene (**2**) and 1-*tert*-butoxycyclopentene (**3**) in the presence of potassium *tert*-butoxide (eq 1).[2,3]



(1)

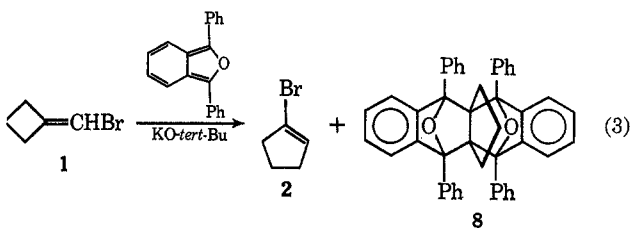
Unlike **1**, its larger ring homologs **4** undergo rearrangement leading to ring-enlarged enol ethers **6** and/or ring-enlarged acetylenes **5** *via* a carbenoid pathway (eq 2),



(2)

but no ring-enlarged vinyl bromides **7** are found. With the larger rings ($n > 6$), the cyclic acetylenes **5** and their base-isomerized products, allenes and dienes, are isolated in good yields; the smaller rings ($n \leq 6$) give rise to moderate yields of ring-enlarged enol ethers (**6**). Curiously, when $n = 5$, no ring-enlarged products whatsoever are found.[3]

In the rearrangement of bromomethylenecyclobutane (**1**), the major volatile product is the ring-enlarged vinyl bromide **2**. The ring-enlarged enol ether **3** is formed in low yields (2–4%) and apparently *via* the carbene–cycloalkyne mechanism described above. Evidence for this is obtained by carrying the reaction out in the presence of 1,3-diphenylisobenzofuran wherein the cyclopentyne intermediate is trapped in 12% yield as a 1:2 adduct **8**, the yield of 1-*tert*-butoxycyclopentene (**3**) drops to zero, and the yield of 1-bromocyclopentene (**2**) remains unchanged (eq 3).[3] The fact that the



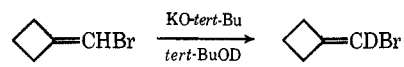
(3)

yield of 1-bromocyclopentene (**2**) is not affected by the presence of the trapping agent negates the possibility of a free cyclopentyne precursor for the ring-enlarged bromide. Rather, an alternate mechanism, not operative in the larger ring systems, must be involved here. In order to establish the generality of this reaction and provide some insight into its mechanism, we have investigated in greater detail the base-catalyzed rearrangement reaction of bromomethylenecyclobutane and some of its simple analogs. Our results are reported in this and the following paper.[4]

Results and Discussion

The original work with the bromomethylenecyclobutane system involved high reaction temperatures (250°) and no solvent; under these conditions rearrangement was instantaneous. We have now found that the reaction will proceed at much lower temperatures (even at room temperature) with a variety of strong bases. Thus, *n*-butyllithium, sodium amide, and molten potassium hydroxide all behave similiarly to potassium *tert*-butoxide but offer no special advantage over it. Unexpectedly, sodium hydride does not effect the rearrangement, nor do weaker bases, such as piperidine. Aprotic solvents may be used to achieve a homogeneous reaction medium. When protic solvents such as *tert*-butyl alcohol are used, the rate of the reaction is slowed appreciably.

The function of the base in this reaction is presumably that of abstraction of a vinylic proton. Evidence that the vinyl anion is indeed formed was obtained by exchange studies with bromomethylenecyclobutane (**1**). When this material was stirred with potassium *tert*-butoxide in refluxing *tert*-butyl alcohol-*O*-*d* for 1 hr, 45% exchange of the vinylic hydrogen occurred with no detectable allylic exchange (eq 4). The fact that the



(4)

vinyl anion is formed under the reaction conditions suggests, but does not prove, that it is involved in the rearrangement reaction. Its formation is undoubtedly facilitated by the electron-withdrawing nature of the bromine substituent. Replacement of the bromine by other electronegative groups should, therefore, give analogs which will undergo a similar ring-enlargement reaction. Accordingly, the construction of methylenecyclobutane derivatives bearing electronegative substituents other than bromine at the methylene carbon was undertaken. Synthetic accessibility was a prime consideration in choosing which analogs to study.

(1) Author to whom correspondence should be addressed.

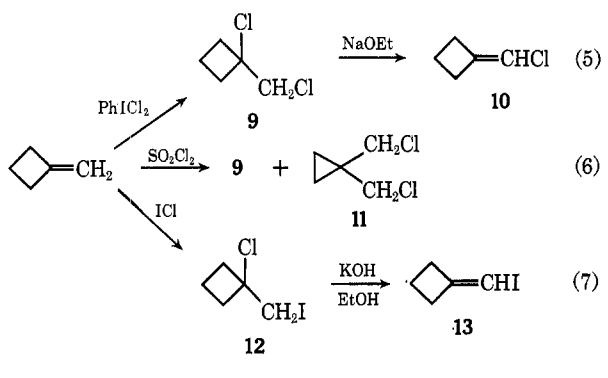
(2) K. L. Erickson, B. E. Vanderwaart, and J. Wolinsky, *Chem. Commun.*, 1031 (1968).

(3) K. L. Erickson and J. Wolinsky, *J. Amer. Chem. Soc.*, **87**, 1142 (1965).

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

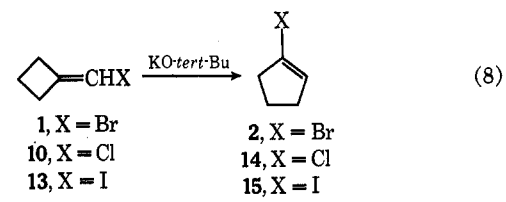
Attention was first directed toward the other halogen derivatives, chloromethylenecyclobutane (**10**) and iodomethylenecyclobutane (**13**). Attempts to prepare chloromethylenecyclobutane (**10**) directly *via* a Wittig reaction with cyclobutanone and chloromethylenetriphenylphosphorane failed. Whether the ylide was generated from chloromethyltriphenylphosphonium bromide[5] or phenyl(bromochloromethyl)mercury and triphenylphosphine,[6] large amounts of ketone were recovered from the reaction, and no more than trace quantities of the vinyl chloride were produced. Chloromethylenecyclobutane (**10**) was conveniently prepared, however, by the chlorination–dehydrochlorination of methylenecyclobutane in analogy with the preparation of bromomethylenecyclobutane (**1**).[7] Chlorination was effected with iodobenzene dichloride, and the resultant dichloride **9** was converted to the vinyl chloride **10** by treatment with sodium ethoxide (eq 5). When sulfuryl chloride was used as the chlorination agent, a 60:40 mixture of 1-chloro-1-chloromethylcyclobutane (**9**) and 1,1-bis(chloromethyl)cyclopropane (**11**) was produced (eq 6). Variations in the reaction conditions had little effect on the ratio of products formed.

Iodomethylenecyclobutane (**13**) was prepared by iodochlorination of methylenecyclobutane followed by dehydrochlorination of the intermediate dihalide **12** (eq 7). The iodochlorination step proceeded smoothly



although the reaction appeared to be freely reversible. The dehydrochlorination step produced low yields of iodomethylenecyclobutane (**13**), the main course of the reaction seemingly being elimination of iodine monochloride to re-form methylenecyclobutane. Excess base was necessary in order to destroy the iodine produced and to obtain pure iodomethylenecyclobutane.

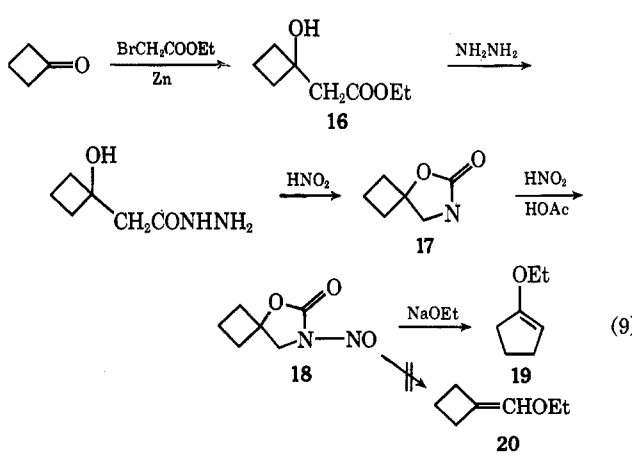
When treated with potassium *tert*-butoxide at 100°, chloromethylenecyclobutane (**10**) rearranged to 1-chlorocyclopentene (**14**) in yields ranging from 48–52%. There were no other volatile products formed, and the remainder of the organic material was accounted for as nonchlorine-containing polymeric material. Ionic chloride was found in the aqueous phase of the reaction mixture to the extent of 46%. These results are very similiar to those obtained with bromomethylenecyclobutane (**1**) where yields of 1-bromocyclopentene (**2**) ranged from 45–55% and ionic bromide (aqueous phase) from 47–52%.[2] Iodomethylenecyclobutane (**13**) gave very cleanly 64–70% yields of 1-iodocyclopentene (**15**) upon treatment with potassium *tert*-butoxide under the same conditions (eq 8). Ionic iodide was produced in



yields of 31–37%. The somewhat higher yields of rearranged iodide **15** and lower yields of ionic iodide produced from iodomethylenecyclobutane (**13**) suggest that fewer diversionary side reactions are occurring in this case.

Each of the 1-halocyclopentenes produced displayed reasonable stability under the reaction conditions. Thus, on small scale runs, 1-chlorocyclopentene (**14**) was recovered from potassium *tert*-butoxide treatment at 100° in yields of 92% with 4% ionic chloride produced. Similarly, 82% of 1-bromocyclopentene (**2**) and 84% of 1-iodocyclopentene (**15**) were recovered when subjected to the reaction conditions (3% ionic bromide and 2.5% ionic iodide were formed).

Electronegative substituents other than halogen which were selected for study were oxygen, nitrogen, and phenyl. The construction of an oxymethylenecyclobutane derivative was somewhat more difficult than was that of the halomethylenecyclobutanes. Initial attempts to prepare methoxymethylenecyclobutane *via* elimination of methanol from the dimethyl acetal of cyclobutanecarboxaldehyde met with no success. The lengthy, yet efficient, synthesis of exocyclic vinyl ethers described by Newman and Okorodudu[8] led to 1-ethoxycyclopentene (**19**) rather than ethoxymethylenecyclobutane (**20**) (eq 9). In view of the nature of the



intermediates postulated in this base-induced decomposition, such a result was not unexpected. Ethoxymethylenecyclobutane (**20**) was eventually prepared

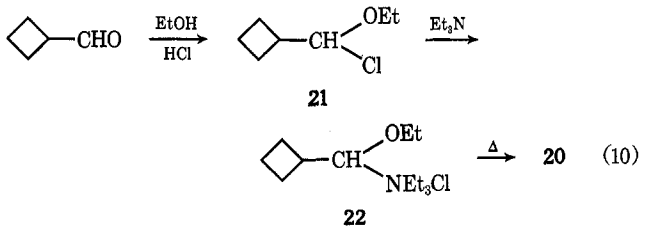
(5) D. Seyferth, S. O. Grim, and T. O. Read, *J. Amer. Chem. Soc.*, **83**, 1617 (1961); G. Koebrich, W. E. Breckoff, and W. Drischel, *Justus Liebigs Ann. Chem.*, **704**, 51 (1967); G. Koebrich, H. Trapp, K. Flory, and W. Drischel, *Ber.*, **99**, 689 (1966).

(6) D. Seyferth and H. D. Simmons, Jr., *J. Organometal. Chem.*, **6**, 311 (1966).

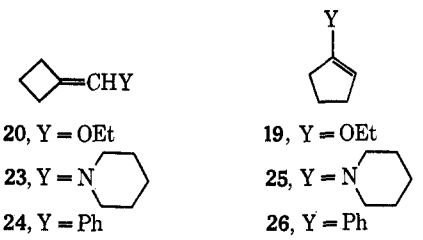
(7) J. Wolinsky and K. L. Erickson, *J. Org. Chem.*, **30**, 2208 (1965).

(8) M. S. Newman and A. O. M. Okorodudu, *ibid.*, **34**, 1220 (1969).

from chloro ether **21** by converting it to the quaternary amine salt **22** and pyrolyzing (eq 10).[9,10]

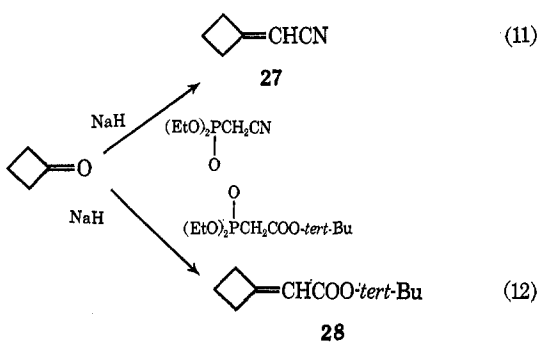


Piperidinomethylenecyclobutane (**23**) was prepared from cyclobutanecarboxaldehyde and piperidine in the usual fashion for disubstituted acetaldehydes.[11] Benzylidenecyclobutane (**24**) was prepared by the method of Graham and Williams.[12] Compounds **20**, **23**, and **24**

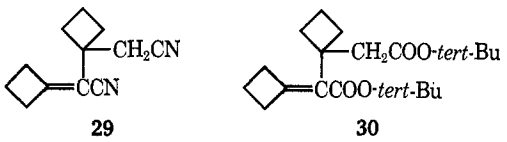


were essentially inert to potassium *tert*-butoxide. The expected rearrangement products, **19**, **25**, and **26**, were not formed even in small quantities as demonstrated by vpc examination with authentic, independently synthesized cyclopentene derivatives. A variety of reaction conditions were used (see Experimental Section), but in no case was any rearranged product found.

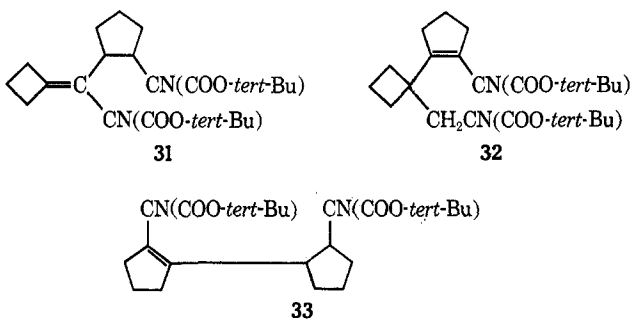
Because of their accessibility, the nitrile and ester functions were also examined as substituents, although special problems were anticipated with these unsaturated groups. Both cyclobutylideneacetonitrile (**27**) and *tert*-butyl cyclobutylideneacetate (**28**) were prepared in good yield by condensation of cyclobutanone with the appropriate phosphonate esters (eq 11 and 12).



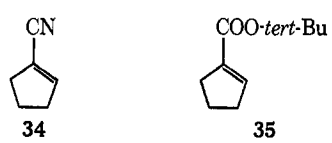
Both compounds reacted vigorously with potassium *tert*-butoxide, cyclobutylideneacetonitrile (**27**) so violently that the reaction had to be carried out in the presence of a solvent at ice temperature to prevent spontaneous ignition. In each case no ring-enlarged products were formed. Instead, Michael dimers **29** and **30** were isolated in good yields (80%). These dimers can be accounted for by simple Michael addition of the initially formed anion to the starting materials which are good Michael acceptors.



Structural assignments for **29** and **30** were made unambiguously from their spectral data. Thus, **29** displayed bands at 4.45, 4.55, and 6.06 μ in the infrared arising from the unconjugated nitrile, conjugated nitrile, and conjugated double bond exo to a four-membered ring. The nmr spectrum for **29** was consistent with its structure with allylic and nonallylic absorptions and a singlet at δ 2.72 ascribed to the isolated methylene group bearing the nitrile function. Similarly, **30** displayed bands at 5.75, 5.86, and 6.04 μ in the infrared (unconjugated carbonyl, conjugated carbonyl, and conjugated double bond exocyclic to a four-membered ring) and an nmr spectrum very similar to that of **29** except for the added presence of methyl absorption from the *tert*-butyl group. The singlet for the isolated methylene group appeared at δ 2.75. The spectral data rule out all other possible dimeric structures for these compounds. Since there are no vinylic hydrogens in the nmr, dimers arising from an allylic anion are excluded. Dimers **31**, **32**, and **33**, where rearrangement would precede dimerization, are likewise excluded. Dimers **31** and **33** would display no isolated methylene



group in the nmr, and dimers **32** and **33** would display double bond absorption in the infrared at higher wavelength than that observed for the products. Thus, 1-cyanocyclopentene (**34**) shows double bond absorption at 6.20 μ and *tert*-butyl cyclopentene-1-carboxylate (**35**)



at 6.17 μ (compared to the Michael product values of 6.06 and 6.04 μ). The ultraviolet spectra of **27**, **29**, and **34** and of **28**, **30**, and **35** are very similar and of no use in structural assignment.

Both 1-cyanocyclopentene (**34**) and *tert*-butyl cyclopentene-1-carboxylate (**35**) were subjected to the reaction conditions to test their stability. Each reacted vigorously with potassium *tert*-butoxide to give dimeric and polymeric material, which was not identified, but which was clearly different in spectral and chromatographic properties from those products obtained with the methylenecyclobutane derivatives.

(9) H. R. Henze and J. T. Murchison, *J. Amer. Chem. Soc.*, **53**, 4077 (1931); B. H. Shoemakers and C. E. Boord, *ibid.*, **53**, 1505 (1931).
(10) D. K. Black and S. R. Landor, *J. Chem. Soc.*, 5225 (1965).
(11) G. Stork, A. Brizzolara, H. Landesman, J. Szmeszkovicz, and R. Terrell, *J. Amer. Chem. Soc.*, **85**, 207 (1963).
(12) S. H. Graham and A. J. S. Williams, *J. Chem. Soc. C*, 655 (1966).

It is clear from these results that conjugated methylenecyclobutanes which are Michael acceptors rapidly undergo a Michael reaction when treated with potassium *tert*-butoxide to the virtual exclusion of the ring-enlargement reaction. With the unreactivity of the oxygen-, nitrogen-, and phenyl-substituted derivatives, it appears that the rearrangement reaction to a five-membered ring is facile only with halomethylenecyclobutanes. Why this unusual reaction is limited to the vinyl halide series is an intriguing question for which we presently have no answer, but the fact that none of these halides were first row elements may be an important point. We are currently investigating this possibility.

Experimental Section[13]

Bromomethylenecyclobutane (1).—This material was prepared by slight modifications of the literature procedures.[7,14] To 5.0 g (0.074 mol) of technical grade methylenecyclobutane (Aldrich Chemical Co., contaminated with *ca.* 5% spiropentane and 2-methyl-1-butene) in 30 ml of methylene chloride at ice temperature was added 2.5 g (0.037 mol) of anhydrous pyridine and then, dropwise with stirring, 11.75 g (0.074 mol) of bromine. The mixture was stirred for 15 min at ice temperature and then washed successively with aqueous sodium bisulfite, 6 *M* hydrochloric acid, water, and brine; the organic layer was dried over magnesium sulfate; and the solvent was removed *in vacuo*. The crude dibromide thus obtained was refluxed with 5.0 g of potassium hydroxide in 95% ethanol for 5 hr. The reaction mixture was taken up in water–pentane, and the pentane layer was washed repeatedly with water, dried over magnesium sulfate, and then fractionally distilled at atmospheric pressure to remove the solvent. Distillation of the residue at reduced pressure afforded 5.2 g (48% from methylenecyclobutane) of bromomethylenecyclobutane: bp 61–63° (60 mm) [lit.[7] bp 63° (60 mm)]; ir (neat) 3.22, 6.01, 7.92, 8.25, 12.58, 13.95 μ; nmr ($CDCl_3$) δ 2.00 (m, 2 H), 2.75 (m, 4 H), 5.70 (m, 1 H).

A small amount of a higher boiling fraction afforded 1,1-bis(ethoxymethyl)cyclopropane, identified by its spectral properties: ir (neat) 3.35, 3.48, 7.24, 9.00 μ; nmr ($CDCl_3$) δ 0.50 (s, 4 H), 1.19 (t, 6 H), 3.37 (s, 4 H), 3.51 (q, 4 H).

1-Chloro-1-chloromethylcyclobutane (9).—Freshly prepared iodobenzene dichloride[15] (from 17.0 g of iodobenzene) was suspended in 80 ml of methylene chloride in a 200-ml flask equipped with a magnetic stirrer, condenser addition funnel, drying tube, and nitrogen inlet tube. Methylenecyclobutane (5.1 g, 0.075 mol) in 20 ml of methylene chloride was added rapidly. The mixture was stirred at room temperature for 30 min and then heated at reflux for 1 hr during which time the crystals dissolved and the color changed from yellow to orange. Petroleum ether was added to precipitate excess iodobenzene dichloride which was then removed by filtration. Excess solvent was removed by distillation, and the residue was taken up in pentane and washed with aqueous sodium bisulfite and water and dried, and the solvent removed by atmospheric distillation. Vacuum distillation of the residue afforded 6.2 g (60%) of 1-chloro-1-chloromethylcyclobutane (slightly contaminated with chlorobenzene), bp 60–64° (30 mm) [lit.[16] bp 49–50° (14 mm)]. Higher boiling fractions yielded iodobenzene.

An analytical sample of the dichloride displayed the following spectral properties: ir (neat) 3.40, 7.00, 7.75, 8.01, 9.43, 10.62, 11.03, 12.43, 12.84, 13.4–14.1, 14.40 μ; nmr ($CDCl_3$) δ 2.00 (m, 2 H), 2.50 (m, 4 H), 3.76 (s, 2 H).

Anal. Calcd for $C_5H_8Cl_2$: C, 43.16; H, 5.75; Cl, 51.07. Found: C, 43.40; H, 5.72; Cl, 51.33.

Chlorination of Methylenecyclobutane with Sulfuryl Chloride.—In a 25-ml flask equipped with a magnetic stirrer, condenser, addition funnel, and drying tube was placed 2 ml of carbon tetrachloride, two drops of benzaldehyde, and 2 g (0.03 mol) of methylenecyclobutane. Sulfuryl chloride (1.65 ml, 0.02 mol) in 2 ml of carbon tetrachloride was added dropwise over a 1-hr period after which the reaction mixture was refluxed for 1.5 hr. The mixture was then distilled at reduced pressure to give one fraction, bp 31–32° (8 mm), which by vpc (10% Carbowax 20M, 80°) was shown to be a 60:40 mixture of 1-chloro-1-chloromethylcyclobutane (9) and 1,1-bis(chloromethyl)cyclopropane (11).[17] The latter was identified by its spectral properties: ir (neat) 3.31, 3.40, 3.56, 7.07, 7.57, 7.98, 9.88, 11.18, 13.54, 14.00, 14.50 μ; nmr ($CDCl_3$) δ 0.82 (s, 4 H), 3.60 (s, 4 H). Variation of the reaction conditions did not appreciably affect the ratio of products formed.

Chloromethylenecyclobutane (10).—1-Chloro-1-chloromethylcyclobutane (6.0 g, 0.043 mol) was added to a solution of 2.8 g of sodium in 30 ml of anhydrous ethanol. The mixture was refluxed for 6 hr and then water was added, and the mixture was extracted with pentane. The pentane extracts were washed several times with water and dried, and the pentane was removed by distillation through a short Vigreux column. The residue was distilled at atmospheric pressure to give 2.7 g (66%) of chloromethylenecyclobutane (10): bp 110–112°; ir (neat) 3.34, 3.40, 5.98, 7.05, 7.80, 10.42, 11.40, 12.40, 13.78, 14.80 μ; nmr ($CDCl_3$) δ 2.00 (m, 2 H), 2.75 (m, 4 H), 5.75 (m, 1 H).

Anal. Calcd for C_5H_7Cl: C, 58.82; H, 6.86; Cl, 34.31. Found: C, 58.54; H, 6.79; Cl, 34.55.

Iodomethylenecyclobutane (13).—Iodine monochloride (4.86 g, 0.03 mol) in 10 ml of methylene chloride was added dropwise over 30 min to an ice-cooled, stirred solution of 2.04 g (0.03 mol) of methylenecyclobutane in 30 ml of methylene chloride. Stirring was continued for 30 min at ice temperature and then at room temperature for 2 hr. The mixture (deep red) was washed with aqueous sodium bisulfite to remove excess iodine monochloride, but the color reappeared as soon as the methylene chloride layer was dried. The methylene chloride was removed *in vacuo*, and the residue (generally dark red or brown) was poured into a hot solution of 5 g of potassium hydroxide in 50 ml of 95% ethanol and refluxed for 2 hr. The reaction mixture was then cooled, poured into ice, and extracted with pentane. The pentane layer was dried and then distilled through a short Vigreux column. Fractionation of the residue afforded 1.5 g (27% from methylenecyclobutane) of iodomethylenecyclobutane: bp 68–70° (20 mm); ir (neat) 3.22, 6.03, 7.97, 8.28, 9.52, 12.62, 14.15 μ; nmr (CCl_4) δ 1.97 (m, 2 H), 2.58 (m, 4 H), 5.64 (m, 1 H).

Anal. Calcd for C_5H_7I: C, 30.96; H, 3.64. Found: C, 31.12; H, 3.80.

If only 1 equiv of base is used in the dehydrochlorination step, it is completely used in about 10 min of refluxing, and the mixture takes on the brown color of iodine. Under these conditions, numerous products are formed.

Cyclobutanecarboxaldehyde Dimethyl Acetal.—In a 10-ml flask equipped with a condenser, drying tube, nitrogen inlet tube, and magnetic stirrer was placed 0.5 g (0.006 mol) of cyclobutanecarboxaldehyde (prepared by chromic acid oxidation of cyclobutyl methanol), 1.07 g (0.007 mol) of tetramethoxysilane, 0.5 ml of anhydrous methanol, and two drops of 85% phosphoric acid. This mixture was stirred at 75° for 2.5 hr when it turned into a gelatinous semisolid. An additional 5 ml of anhydrous methanol was added and refluxing was continued for 16 hr. The mixture was then extracted with ether, the ether extracts were washed with 10% sodium hydroxide and then water, and the solvent was removed by distillation. Flash distillation of the residue afforded the acetal: ir (CCl_4) 3.40, 3.51, 8.00, 8.09, 8.25, 8.80, 8.98, 10.16 μ; nmr ($CDCl_3$) δ 1.8–2.8 (m, 7 H), 3.32 (s, 6 H), 4.33 (d, 1 H).

Anal. Calcd for $C_7H_{14}O_2$: C, 64.58; H, 10.84. Found: C, 64.58; H, 10.74.

(13) Melting 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. Ultraviolet spectra were run using a Perkin-Elmer Model 202 spectrophotometer. Vapor phase chromatographic analyses were performed on a Varian Aerograph Model 90-P3 chromatograph (thermal conductivity detector) or Varian Aerograph Model 600-D chromatograph (flame ionization detector). The following columns were used: 10 ft × 1/8 in., 10% Carbowax 20M on 60–80 Chromosorb W, AWDMCS; 10 ft × 0.25 in. 20% Carbowax 20M on 60–80 Chromosorb P; 10 ft × 0.25 in., 10% QF-1 on 60–80 Chromosorb W, AWDMCS; and 10 ft × 3/8 in., 3% SE-30 on 60–80 Chromosorb W. Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich., Galbraith Microanalytical Laboratories, Knoxville, Tenn., and Chemalytics, Inc., Tempe, Ariz.

(14) H. Normant and P. Maitte, *Bull. Soc. Chim. Fr.*, 1424 (1960).

(15) H. J. Lucas and E. R. Kennedy, *Org. Syn.*, **22**, 69 (1942).

(16) J. G. Traynham and O. S. Pascual, *Tetrahedron*, **7**, 165 (1959).

(17) B. Chambourx, P. Y. Etienne, and R. Pollaud, *C. R. Acad. Sci.*, **251**, 255 (1960); H. E. Simmons, Jr., E. P. Blanchard, Jr., and H. D. Hartzler, *J. Org. Chem.*, **31**, 295 (1966).

Ethyl 1-Hydroxycyclobutylacetate (16).—In a three-neck flask equipped with a mechanical stirrer, condenser, drying tube, and dropping funnel was placed 15 ml of anhydrous benzene and 3.8 g of activated zinc dust (prepared by washing successively with 20% hydrochloric acid, water, acetone, and anhydrous ether and then air-drying). The mixture was heated to reflux with vigorous stirring, the heat was removed, and a mixture of 2.5 g (0.0356 mol) of cyclobutanone and 7.8 g of ethyl bromoacetate was added dropwise at a rate to maintain vigorous reflux after initiation of the reaction. The mixture was refluxed for an additional 15 min and then cooled thoroughly in ice, and an ice-cold solution of 5% sulfuric acid (50 ml) was added dropwise. The mixture was filtered, and the benzene layer was separated and combined with an ether extract of the aqueous layer. After drying (magnesium sulfate) the mixture, the benzene and ether were removed *in vacuo*, and the residue was distilled to give 2.9 g (57%, not an optimum yield) of ethyl 1-hydroxycyclobutylacetate (16): bp 50–51° (0.35 mm); ir (neat) 2.82, 5.74, 8.35, 9.03, 9.42, 9.67 μ; nmr (CD_3COCD_3) δ 1.23 (t, 3 H), 1.5–2.3 (m, 6 H), 2.61 (s, 2 H), 3.00 (s, 1 H), 4.12 (q, 2 H).

Anal. Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 60.72; H, 8.60.

Cyclobutanespiro-1-oxa-3-azacyclopentan-2-one (17).—The hydrazide of 1-hydroxycyclobutylacetic acid was prepared from 16 and 85% hydrazine hydrate by refluxing in several drops of methanol for 2 hr. Without purification, the hydrazide, mp 120–122.5° (1.44 g, 0.01 mol), was dissolved in 6 ml of 2 *N* hydrochloric acid and cooled to 8–12°. To this stirred solution was added dropwise 0.76 g of sodium nitrite dissolved in 1 ml of water. After complete addition of the nitrite solution, 6 ml of hexane was added, and the mixture was gradually heated to reflux (68°) when nitrogen evolution became rapid. The mixture was then cooled, and 1.1 g (86%) of the oxazolidone crystallized, mp 113–115°. An analytical sample was prepared by recrystallization from benzene–hexane: mp 115–116°; ir (Nujol) 3.08, 5.78, 8.87, 9.19, 10.29, 10.62, 13.90, 14.5–15.0 μ; nmr ($CDCl_3$) δ 1.3–2.8 (m, 6 H), 3.69 (s, 2 H), 6.70 (broad s, 1 H).

Anal. Calcd for $C_6H_9NO_2$: C, 56.68; H, 7.13; N, 11.02. Found: C, 56.75; H, 6.91; N, 10.97.

Cyclobutanespiro-3-nitroso-1-oxa-3-azacyclopentan-2-one (18).—To a stirred mixture of oxazolidone (17) (1.0 g, 0.0079 mol) in a mixture of 1 ml each of concentrated hydrochloric acid, glacial acetic acid, and water at 0–5° was added dropwise a solution of 0.58 g of sodium nitrite in 4 ml of water. The mixture was kept in ice for an additional 15 min after complete addition of the nitrite solution. The yellow crystalline solid was then filtered and dried to give 1.1 g (90%) of 18, mp 83–85°. An analytical sample was prepared by recrystallization from benzene–hexane: mp 84–85°; ir (Nujol) 5.53, 9.08, 10.35, 13.20 μ; nmr ($CDCl_3$) δ 1.5–2.1 (m, 6 H), 4.00 (s, 2 H).

Anal. Calcd for $C_6H_8N_2O_3$: C, 46.16; H, 5.16; N, 17.94. Found: C, 46.01; H, 4.98; N, 17.89.

Reaction of Cyclobutanespiro-3-nitroso-1-oxa-3-azacyclopentan-2-one (18) with Sodium Ethoxide.—To a suspension of 0.5 g (0.0032 mol) of nitrosooxazolidone 18 in 2 ml of anhydrous ethanol at 0–5° was added slowly a slight excess of sodium ethoxide dissolved in absolute ethanol. The mixture was stirred in ice for an additional 15 min and then poured into water and extracted with pentane. The pentane extracts were dried (magnesium sulfate), and the pentane was removed by distillation through a short Vigreux column. Flash distillation of the residue afforded 0.25 g (75%) of 1-ethoxycyclopentene (19):[18] ir (neat) 3.22, 6.01, 8.02, 9.50, 13.01 μ; nmr (CCl_4) δ 1.27 (t, 3 H), 1.80 (m, 2 H), 2.23 (m, 4 H), 3.69 (q, 2 H), 4.25 (broad s, 1 H).

Conversion to the 2,4-dinitrophenylhydrazone derivative gave needles (ethanol–water), mp 143–144°, mmp (with authentic cyclopentanone 2,4-dinitrophenylhydrazone) 143–144°.

Ethoxymethylenecyclobutane (20).—Chloro ether 21 was prepared by the literature procedures.[9] To a solution of 0.5 g (0.006 mol) of cyclobutanecarboxaldehyde and 0.28 g (0.006 mol) of absolute ethanol cooled in an ice–salt bath was added hydrogen chloride gas over a 30-min period. The reaction mixture was then stirred for 3.5 hr in ice. At the end of this time two layers had formed. Magnesium sulfate was added to remove any water, and the excess hydrogen chloride was removed *in vacuo*. The crude chloro ether was taken up in ether and cooled in an ice–salt bath while 2 ml of anhydrous triethylamine was added. The mixture was allowed to stand in ice for 2 hr and then at room temperature for 1.5 hr. The amine salt 22 was very hygroscopic and was pyrolyzed directly.[10] It was heated at 120° (22 mm), and the distillate [bp 57° (22 mm)] was trapped in a Dry Ice cooled receiver. The distillate contained some cyclobutanecarboxaldehyde and its diethyl acetal in addition to the vinyl ether 20. The latter was purified by vpc (10% Carbowax 20M, 60°). An analytical sample displayed ir (CCl_4) 5.88, 8.40, 8.60, 8.81, 9.84 μ; nmr (CCl_4) δ 1.19 (t, 3 H), 2.00 (m, 2 H), 2.58 (m, 4 H), 3.65 (q, 2 H), 5.63 (m, 1 H).

Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.79. Found: C, 75.32; H, 10.99.

Piperidinomethylenecyclobutane (23).—Cyclobutanecarboxaldehyde was refluxed with 1 equiv of piperidine in benzene under a water separator for 5 hr. The excess benzene was distilled off, and the residue was distilled *in vacuo* to give piperidinomethylenecyclobutane (23): bp 75–78° (3.2 mm): ir (neat) 3.38, 3.49, 3.55, 5.96, 8.93, 11.64, 12.53 μ; nmr (neat) 1.2–3.3 (m, 16 H), 5.15 (m, 1 H). The enamine was not stable and had to be stored under nitrogen in the cold.

1-Piperidinocyclopentene (25).—Freshly distilled cyclopentanone (3.7 g, 0.05 mol) and 10 ml of anhydrous piperidine were dissolved in 70 ml of anhydrous benzene and refluxed under a water separator for 12 hr. The benzene was then removed and the residue distilled *in vacuo* to give 1-piperidinocyclopentene (25):[19] ir (neat) 3.40, 3.50, 3.56, 6.12, 7.21, 8.05, 8.84, 13.09 μ; nmr (neat) δ 1.4–3.0 (m, 16 H), 4.24 (m, 1 H).

1-Phenylcyclopentene (26).—Freshly distilled cyclopentanone (20 g, 0.24 mol) was added dropwise to a solution of phenylmagnesium bromide (0.50 mol) in absolute ether. The reaction mixture was refluxed overnight, and then water was cautiously added. The mixture was extracted with ether, dried over magnesium sulfate, and concentrated. The residue was dissolved in anhydrous pyridine, and phosphorus oxychloride was added dropwise. Stirring was continued at room temperature for 1 hr and then the mixture was poured into ice and extracted with ether. The ether layer was washed with 6 *M* hydrochloric acid and then water and dried. The ether was removed and the residue vacuum distilled to give 16.0 g (46%) of 1-phenylcyclopentene: bp 88–90° (5 mm) [lit.[20] bp 122° (50 mm)]; $n^{20}D$ 1.5750 (lit.[20] $n^{25}D$ 1.5736).

Diethylphosphonoacetonitrile.—In a flask equipped with an addition funnel, condenser, drying tube, magnetic stirrer, and thermometer was placed 109 g (0.665 mol) of triethyl phosphite. To this was added dropwise 50.1 g (0.665 mol) of chloroacetonitrile. The reaction mixture was heated at 150–180° for 4 hr, after which it was distilled at reduced pressure to gave a forerun of triethyl phosphite and 104.3 g (90%) of diethylphosphonoacetonitrile: bp 130–133° (2.6 mm) [lit.[21] bp 101–102° (0.4 mm)]; ir (neat) 4.42, 7.18, 7.30, 7.88, 8.10, 9.3–10.0, 10.1–10.5, 11.80, 12.2–12.9, 14.15 μ; nmr ($CDCl_3$) δ 1.63 (t, 6 H), 3.33 (d, J = 24 Hz, 2 H), 4.90 (m, 4 H). Both sets of methylene protons were coupled to the phosphorus.

Cyclobutylideneacetonitrile (27).—A 50-ml flask was equipped with a magnetic stirrer, addition funnel, condenser, drying tube, nitrogen inlet tube, and thermometer. After flushing the system with nitrogen, 0.34 g (0.014 mol) of oil-free sodium hydride dispersion in 10 ml of anhydrous monoglyme (dried over lithium aluminum hydride, distilled from sodium hydride) was placed in the flask, and diethylphosphonoacetonitrile (2.48 g, 0.014 mol) in 5 ml of monoglyme was added dropwise keeping the temperature between 5 and 7° with an ice bath. The mixture was then stirred for 20 min. A solution of 1.0 g (0.014 mol) of cyclobutanone in 5 ml of monoglyme was added at a rate to keep the temperature below 10°. Toward the end of the addition, the mixture became opaque, and a gelatinous precipitate formed. The mixture was stirred at room temperature for 30 min and then poured into ice and extracted with ether. The ether extracts were washed well with water and dried over magnesium sulfate, and the ether was removed. The yellow residue was distilled at reduced pressure giving 0.96 g (75%) of cyclobutylideneacetonitrile (27): bp 70° (30 mm); ir (neat) 3.25, 3.40, 4.50, 6.06, 7.12, 12.23, 13.90 μ; nmr ($CDCl_3$) δ 2.10 (m, 2 H), 2.88 (m, 4 H), 5.12 (m, 1 H); uv (EtOH) λ_{max} 239, 225 mμ (sh).

(18) U. Schmidt and P. Grafen, *Justus Liebigs Ann. Chem.*, **656**, 97 (1962).

(19) G. Opitz, A. Griesinger, and H. W. Schubert, *ibid.*, **665**, 91 (1963).

(20) A. D. Ketley and J. L. McClanahan, *J. Org. Chem.*, **30**, 942 (1965).

(21) W. Stilz and H. Pommer, German Patent 1,108,208 (1959) [*Chem. Abstr.*, **56**, 11422*f* (1962)]; E. C. Ladd, U. S. Patent 2,632,019 (1953) [*Chem. Abstr.*, **48**, 1418*c* (1954)].

Anal. Calcd for C_6H_7N: C, 77.39; H, 7.57; N, 15.04. Found: C, 77.45; H, 7.42; N, 15.10.

tert-**Butyl Diethylphosphonoacetate.**—In a 50-ml flask equipped with a magnetic stirrer, condenser, drying tube, and addition funnel was placed 7.0 g (0.042 mol) of triethyl phosphite. *tert*-Butyl bromoacetate (8.2 g, 0.042 mol) was added slowly during the course of 2 hr. The mixture was heated overnight at 70° and then at 75–80° for an additional 10 hr. Distillation at reduced pressure afforded a forerun of triethyl phosphite followed by 7.2 g (68%) of product: bp 100–103° (1.5 mm); ir (neat) 5.77, 7.17, 7.30, 7.80, 7.95, 9.54, 9.74, 10.38 μ; nmr ($CDCl_3$) δ 1.32 (t, 6 H), 1.40 (s, 9 H), 2.80 (d, J = 22 Hz, 2 H), 4.10 (m, 4 H). Both sets of methylene protons were coupled to the phosphorus.

Anal. Calcd for $C_{10}H_{19}O_5P$: C, 47.62; H, 8.39. Found: C, 47.77; H, 8.25.

tert-**Butyl Cyclobutylideneacetate** (**28**).—Into a 50-ml flask equipped with a magnetic stirrer, addition funnel, condenser, nitrogen inlet tube, and thermometer was placed 30 ml of anhydrous monoglyme and 0.33 g (0.014 mol) of oil-free sodium hydride dispersion. The system was flushed with nitrogen and 3.6 g (0.014 mol) of *tert*-butyl diethylphosphonoacetate in 5 ml of monoglyme was added dropwise at a rate to keep the temperature below 35°. After complete addition of the phosphonate, the mixture was stirred at room temperature for 30 min and then cyclobutanone (1.0 g, 0.014 mol) in 5 ml of monoglyme was added dropwise at a rate to maintain the temperature below 30°. External cooling was necessary. Stirring was continued for 30 min and then the mixture was poured into ice and extracted with ether. The ether extracts were washed well with water and dried over magnesium sulfate, and the ether was removed. The residue was distilled at reduced pressure affording 2.0 g (83%) of product: bp 39–41° (1.5 mm); ir (neat) 5.88, 6.03, 7.22, 7.36, 8.68, 9.23, 10.15, 11.70, 13.19 μ; nmr ($CDCl_3$) δ 1.43 (s, 9 H), 2.02 (m, 2 H), 2.90 (m, 4 H), 5.45 (m, 1 H); uv (EtOH) λ_{max} 240, 222 mμ (sh).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.43; H, 9.52. Found: C, 71.45; H, 9.50.

Cyclopentene-1-carboxylic Acid.—In a 100-ml flask equipped with a magnetic stirrer and condenser was placed 5.5 g (0.06 mol) of 1-cyanocyclopentene (Frinton Chemical Co.) and 25 ml of 30% sodium hydroxide solution. The mixture was refluxed for 48 hr and then cooled and poured into water. The mixture was acidified with 20 ml of 50% sulfuric acid, and the 1-cyclopentene-1-carboxylic acid precipitated. The crude acid was extracted with ether and recrystallized from hot water affording 3.3 g (50%) of colorless product, mp 118–120° (lit.[22] mp 120–121°).

tert-**Butyl Cyclopentene-1-carboxylate** (**35**).—A 150-ml Pyrex narrow-mouthed pressure bottle was charged with 15 ml of anhydrous ether, 15 drops of concentrated sulfuric acid, 2.4 g (0.022 mol) of 1-cyclopentene-1-carboxylic acid, and *ca.* 6 ml of isobutylene. The latter was liquified by passage into a test tube immersed in a Dry Ice bath. The bottle was clamped shut and shaken mechanically for 22 hr. After the first 5 hr most of the solid had dissolved. The bottle was cooled in a Dry Ice bath and opened, and ether was added. The contents were then poured into a separatory funnel containing a mixture of 30 ml of water, 30 g of ice, and 6 g of sodium hydroxide. The phases were separated, and the aqueous phase was extracted several times with ether. The ether layers were washed and then dried over potassium carbonate. The solution was filtered into a dropping funnel attached to the neck of a 25-ml Claisen flask. The flask was heated to 100°, and the isobutylene and ether were removed by flash distillation effected by allowing the solution to run slowly from the dropping funnel into the flask. The residue was distilled at reduced pressure giving 2.2 g (63%) of *tert*-butyl cyclopentene-1-carboxylate (**35**): bp 39–40° (1.2 mm); ir (neat) 5.85, 6.17, 6.85, 7.30, 7.45, 8.23, 8.70, 9.44, 11.25 μ; nmr ($CDCl_3$) δ 1.00 (s, 9 H), 1.98 (m, 2 H), 2.47 (m, 4 H), 6.63 (m, 1 H); uv (EtOH) λ_{max} 239, 223 mμ (sh).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.43; H, 9.52. Found: C, 71.23; H, 9.75.

Reaction of Methylenecyclobutane and Cyclopentene Derivatives with Potassium *tert*-**Butoxide. General Procedure.**—In a flask equipped with a reflux condenser, drying tube, nitrogen inlet tube, and rubber septum was placed the potassium *tert*-butoxide. Generally a slight excess of unsublimed potassium *tert*-butoxide (MSA Corp.) was used although large excesses of the base did not alter the reaction course nor did the use of sublimed *tert*-butoxide. The system was flushed with nitrogen, and the butoxide was heated to 100° (oil bath temperature); the vinyl compound was injected *via* syringe under the surface of the hot butoxide. The bath temperature was maintained for the course of the reaction, anywhere from 2–60 min, and then the mixture was cooled, and water was added. Extraction with either ether or pentane followed, the aqueous phases being acidified and saved for classical halide determination with silver nitrate. The organic phase was washed well with water and dried over magnesium sulfate, and the solvent was removed by atmospheric distillation. In large scale runs, products were obtained by vacuum distillation and yields determined by isolation. In small scale runs, flash distillation at reduced pressure with Dry Ice cooled receivers afforded the products, and yields were determined by vpc (Carbowax 20M) with internal standards (toluene, *o*- or *p*-xylene).

When different bases were used in the absence of solvent, the procedure described above was followed. When solvents were used, generally the reflux temperature of the solvent determined the temperature at which the reaction was run, although in a number of cases lower temperatures were used (see text).

A. With Bromomethylenecyclobutane (**1**).—Bromomethylenecyclobutane (1.47 g, 0.010 mol) was injected beneath the surface of 1.23 g (0.011 mol) of potassium *tert*-butoxide at 100° under a nitrogen atmosphere. After 5 to 30 min at this temperature, the usual work-up procedure was followed. Inorganic bromide found in the aqueous phase varied from 47–52%. The volatile organic products were flash distilled at reduced pressure and then separated by vpc (10% Carbowax 20M, 80°). 1-*tert*-Butoxycyclopentene (**3**) was produced in yields varying from 2–4%, 1-bromocyclopentene (**2**) from 45–55%. The remaining material was nonvolatile residue. 1-*tert*-Butoxycyclopentene was identified by its ir spectrum (5.98, 7.22, 7.36, 8.66 μ) and conversion to the 2,4-dinitrophenylhydrazone derivative of cyclopentanone: mp 143°; mmp (with authentic cyclopentanone derivative) 143°. The ir and nmr spectra of both derivatives were superimposable.

1-Bromocyclopentene displayed $n^{18}D$ 1.5030 (lit.[23] $n^{18}D$ 1.5034); ir (neat) 6.18, 9.57, 10.55, 12.00, 12.50 μ; nmr ($CDCl_3$) δ 1.7–2.8 (complex m, 6 H), 5.74 (m, 1 H). This material was identical (n_D, ir, nmr) with authentic 1-bromocyclopentene prepared by the method of Abell and Chiao.[23]

B. With 1-Bromocyclopentene (**2**).—1-Bromocyclopentene (2.19 g, 0.013 mol) was injected under the surface of 3.0 g of potassium *tert*-butoxide at 100°, and the reaction mixture was kept at this temperature for 30 min. Work-up afforded an 82% recovery of 1-bromocyclopentene. Ionic bromide (3%) was found in the aqueous phase.

C. With Chloromethylenecyclobutane (**10**).—Chloromethylenecyclobutane (0.96 g, 0.008 mol) was injected into 2.0 g of potassium *tert*-butoxide at 100°, and heating was continued for 30 min. Work-up afforded a 46% yield of ionic chloride in the aqueous layer and 48–52% yields of 1-chlorocyclopentene (**14**) in the organic phase. The latter displayed ir and nmr spectra identical with those of authentic material prepared by the method of Roberts and coworkers.[24]

D. With 1-Chlorocyclopentene (**14**).—Chlorocyclopentene[24] (0.69 g, 0.006 mol) was injected into 1.8 g of potassium *tert*-butoxide at 100° and maintained at that temperature for 30 min. Work-up afforded a 4% yield of ionic chloride in the aqueous phase and a 92% recovery of 1-chlorocyclopentene.

E. With Iodomethylenecyclobutane (**13**).—Iodomethylenecyclobutane (0.97 g, 0.005 mol) was injected into 0.8 g of potassium *tert*-butoxide at 100°, and heating was continued for 10 min. Work-up afforded 31–37% yields of ionic iodide and 64–70% yields of 1-iodocyclopentene (**15**). The latter was identified by its spectral (practically identical with that of **2** and **14**) and analytical data: ir (neat) 3.24, 6.20, 6.95, 7.60, 7.74, 8.32, 9.66, 10.60, 12.13, 12.70 μ; nmr (CCl_4) δ 1.5–2.8 (m, 6 H), 6.02 (m, 1 H).

Anal. Calcd for C_5H_7I: C, 30.96; H, 3.64. Found: C, 31.04; H, 3.65.

F. With 1-Iodocyclopentene (**15**).—1-Iodocyclopentene (0.50 g, 0.0026 mol) was injected into 0.4 g of potassium *tert*-butoxide at 100° and maintained at that temperature for 10 min. Work-

(22) G. H. Alt and A. J. Speziale, *J. Org. Chem.*, **31**, 1349 (1966).

(23) P. I. Abell and C. Chiao, *J. Amer. Chem. Soc.*, **82**, 3619 (1960).

(24) L. K. Montgomery, F. Scardiglia, and J. D. Roberts, *ibid.*, **87**, 1917 (1965).

up gave a 2.5% yield of ionic iodide in the aqueous phase and an 84% recovery of 1-iodocyclopentene.

G. With Ethoxymethylenecyclobutane (20).—Ethoxymethylenecyclobutane (70 μl) was injected into excess potassium *tert*-butoxide at 100° and held at this temperature for 1 hr. Work-up afforded only recovered starting material as shown by vpc and ir analysis. Repetition of the reaction at 200° for 3 hr gave again only recovered starting material.

H. With Piperidinomethylenecyclobutane (23).—Piperidinomethylenecyclobutane (30 μl) was injected into excess potassium *tert*-butoxide at 100°, and the temperatue was held for 1 hr. Work-up gave only recovered starting material as shown by vpc and ir analysis. The use of longer reaction times, higher reaction temperatures, or DMF as solvent did not result in any rearrangement product being produced.

I. With Benzylidenecyclobutane (24).—Benzylidenecyclobutane (75 μl) was injected into 0.16 g of potassium *tert*-butoxide at 200°, and the temperature was maintained for 48 hr. The usual work-up procedure afforded only recovered starting material (vpc, ir analysis). The use of sodium amide or *n*-butyllithium as bases gave the same results.

J. With Cyclobutylideneacetonitrile (27).—When a small amount of **27** was injected directly into potassium *tert*-butoxide at room temperature or in an ice bath, the mixture ignited spontaneously. Accordingly, a lower temperature and a solvent were used in this reaction as well as a slower addition rate.

Cyclobutylideneacetonitrile (1.86 g, 0.02 mol) in 20 ml of dry hexane was added dropwise to an ice-cooled slurry of 4.4 g (0.04 mol) of potassium *tert*-butoxide in 40 ml of dry hexane. The reaction mixture was stirred at ice temperature for 1 hr and then worked up by the general procedure. The residue thus obtained gave *ca.* 50 mg of a precipitate (mp 253–256 dec) which was not identified, and an orange oil (1.6 g, 80%) which was identified as α-(1-cyanomethyl-1-cyclobutyl)-$\Delta^{1,\alpha}$-cyclobutaneacetonitrile (**29**). This material distilled at 140° (1.5 mm), but substantial decomposition occurred under these conditions. An analytical sample (vpc, QF-1, 198°) displayed ir (neat) 4.45, 4.55, 6.06, 7.07, 9.46, 9.70 μ; nmr ($CDCl_3$) δ 1.65–2.60 (complex m, 8 H), 2.72 (s, 2 H), 3.00 (m, 4 H); uv (EtOH) λ_{max} 237, 225 mμ (sh).

Anal. Calcd for $C_{12}H_{14}N_2$: C, 77.39; H, 7.57; N, 15.04. Found: C, 77.61; H, 7.27; N, 15.26.

K. With 1-Cyanocyclopentene (34).—1-Cyanocyclopentene (Frinton Chemical Co.) (1.86 g, 0.02 mol) in 20 ml of hexane was added dropwise to an ice-cooled slurry of 4.4 g of potassium *tert*-butoxide in 40 ml of hexane. The mixture was stirred at ice temperature for 1 hr and then worked up as usual. Only broad melting solids could be isolated whose spectral properties did not coincide with those of the products from **27**.

L. With *tert*-Butyl Cyclobutylideneacetate (28).—The reaction was run in the usual fashion—2.5 g (0.015 mol) of *tert*-butyl cyclobutylideneacetate was injected into 3.5 g of potassium *tert*-butoxide as 100°, and the temperature was maintained for 30 min. Usual work-up gave 2.0 g (80%) of a yellow oil which, by vpc analysis (SE-30, 190°), showed two components in a relative ratio of 85:15. The major component was shown to be *tert*-butyl α-(1-carbo-*tert*-butoxymethyl-1-cyclobutyl)-$\Delta^{1,\alpha}$-cyclobutylacetate (**30**): ir (neat) 5.82, 5.86, 6.04,7.24, 7.38, 7.60, 8.05, 8.70 μ; nmr ($CDCl_3$) δ 1.49 (s, 9 H), 1.6–2.5 (complex m, 8 H), 2.75 (s, 2 H), 3.13 (m, 4 H); uv (EtOH) λ_{max} 239, 225 mμ (sh).

Anal. Calcd for $C_{20}H_{32}O_4$: C, 71.42; H, 9.53. Found: C, 71.32; H, 9.33.

The minor component was not identified; spectral data indicated it was a mixture containing **30** and the anhydride derived from it. It is possible that the latter was forming on the gas chromatograph as the material was not completely stable under these conditions.

Vacuum distillation of the crude oil obtained in this reaction gave material boiling from 155–160° (1.5 mm), which was largely **30**, but substantial decomposition occurred during the distillation.

M. With *tert*-Butyl Cyclopentene-1-carboxylate (35).—*tert*-Butyl cyclopentene-1-carboxylate (0.90 g, 0.005 mol) was injected into 1.4 g of potassium *tert*-butoxide at 100°, and the temperature was maintained for 30 min. Work-up afforded yellow oil (thermally unstable) whose spectral and analytical data indicated mixtures of dimers, none of which corresponded to those obtained from the reaction of *tert*-butyl cyclobutylideneacetate.

Anal. Calcd for $C_{20}H_{32}O_4$: C, 71.43; H, 9.52. Found: C, 71.42; H, 9.55.

Exchange Studies with Bromomethylenecyclobutane (1).—Bromomethylenecyclobutane was stirred with a slight excess of potassium *tert*-butoxide in *tert*-butyl alcohol-*O*-*d* at reflux temperature for 1 hr. Work-up showed that less than 5% rearrangement had occurred under these conditions. The starting material was recovered (vpc, 10% Carbowax 20M, 60°) and subjected to both mass spectral and nmr analysis. Both methods showed 45% exchange had occurred. There was no detectable allylic exchange.

Registry No.—**1,** 1905-06-2; **9,** 27784-28-7; **10,** 27784-29-8; **13,** 27784-30-1; **15,** 17497-52-8; **16,** 27784-32-3; **16** hydrazide, 27784-34-5; **17,** 27784-33-4; **18,** 27784-35-6; **19,** 17065-24-6; **20,** 27784-66-3; **23,** 27784-67-4; **25,** 1614-92-2; **27,** 27784-69-6; **28,** 27784-70-9; **29,** 27784-71-0; **30,** 27784-72-1; **35,** 27784-73-2; cyclobutanecarboxaldehyde dimethyl acetal, 27784-74-3; diethylphosphonoacetonitrile, 2537-48-6; *tert*-butyl diethylphosphonoacetate, 27784-76-5.

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(25) NSF Undergraduate Research Participant, 1967–1968.