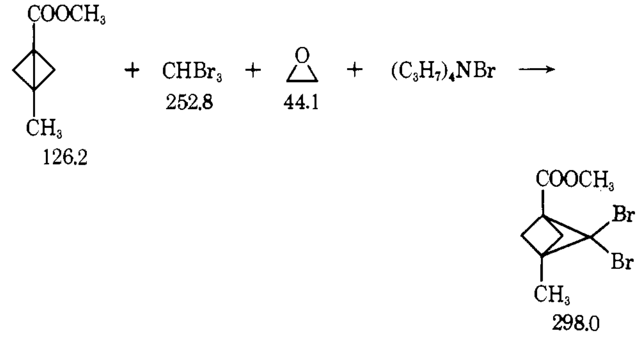

the pressure dropped from 190 to 30 psi. The crude product was received as 44 g of nonvolatile liquid. Two distillations yielded 9.71 g of liquid in four fractions, bp 61-90° (0.15 mm). Preparative gc of the two early cuts, bp 61-67° (0.15 mm), gave 1.4 g with retention time 15.3 min.

Anal. Calcd for $C_8H_{10}O_2Br_2$: C, 32.40; H, 3.42. Found: C, 32.37; H, 3.60.

The nmr and ir spectra were identical with that of the dichloro derivative within experimental error. As for the dichloride, the ir spectrum showed apparent $C{=}C$ but either this is characteristic for the bicyclo[1.1.1]pentanes or a trace of intensely absorbing cyclobutene, undetected by nmr, is present.

Acknowledgments. We are indebted to Dr. A. Cairncross for the synthesis of methyl 3-methyl-1-bicyclobutanecarboxylate, to Dr. W. P. Baker of the Du Pont Film Department for the high-pressure polymerizations of it and the corresponding *tert*-butyl ester, to Dr. E. L. Martin for the synthesis of 3-chloro-3-methylcyclobutanecarboxylic acid, to Dr. G. N. Milford of the Du Pont Textile Fibers Department for an acrylonitrile copolymer, and to Dr. E. Bromels for the thermodynamic properties of bicyclobutane.

Bicyclo[1.1.0]butanes from Ketene and Vinyl Ethers

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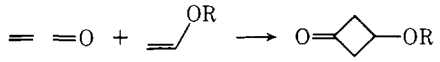
Experimental Station, E. I. du Pont de Nemours and Company,
Wilmington, Delaware 19898. *Received March 12, 1970*

Abstract: Four 3-alkoxycyclobutanones were prepared from ketene and vinyl ethers. Five bicyclobutanes, **4**, **7**, **12**, **16**, and **25**, were prepared from these ketones. The syntheses described provide easy access to large quantities of a variety of bicyclobutanes.

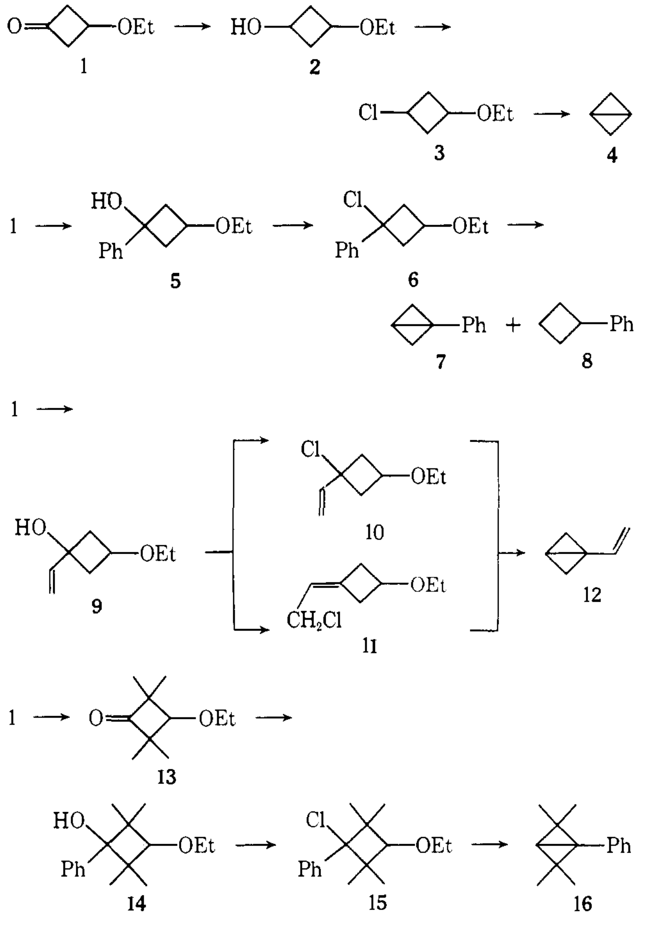
The addition of ketene to vinyl ethers has been known for some time, although the reported yields are not encouraging.[1] We found that ketene undergoes thermal cycloaddition to simple vinyl ethers in yields which are synthetically acceptable. The products of these additions were the expected 3-alkoxycyclobutanones,[1] which are convenient entries into the 1,3-disubstituted cyclobutane series and particularly the bicyclobutane series.

3-Alkoxycyclobutanones. Four vinyl ethers were heated with ketene at 100° for 4 hr in the absence of solvent. The crude reaction mixtures required distillation as the only purification step. Diketene in varying amounts and about 10% (based on ketene charged) of higher boiling, unidentified material were present in every case. The reactivity of the vinyl ethers toward ketene, as measured by the alkoxycyclobutanone:diketene ratio, was qualitatively in the order R = *tert*-Bu ≫ Et > Me > CH$_2$Ph. This order corresponds to the relative ability of R to stabilize a partial positive charge on oxygen in the transition state.[2] The 3-alkoxycyclobutanones are suitable intermediates for the preparation of bicyclobutanes, and Scheme I illustrates the generality of the method for the preparation of the hydrocarbon series.



R = Me, Et, *tert*-Bu, CH$_2$Ph

Scheme I



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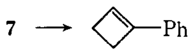
(1) C. D. Hurd and R. D. Kimbrough, Jr., *J. Amer. Chem. Soc.*, **82**, 1373 (1960); J. C. Martin, U. S. Patent, 3,285,915 (1966).

(2) R. Huisgen, L. A. Feiler, and P. Otto, *Tetrahedron Lett.*, **43**, 4485 (1968); W. T. Brady and H. R. O'Neal, *J. Org. Chem.*, **32**, 612 (1967).

Bicyclobutane (4). Compound **1** was reduced with lithium aluminum hydride to **2**, which was largely (~95%) the expected cis isomer. This was converted with thionyl chloride to **3**, which was ~95% trans. The stereochemistry of **2** and **3** was inferred from glpc retention times and nmr spectra. The methylene hydrogens of **2** appear as two complex multiplets spanning a total of 1.3 ppm. The methylene hydrogens of **3**, however, appear as a triplet (splitting = 6 Hz). Similar differences in the nmr spectra of cis and trans 1,3-disubstituted cyclobutanes have been described.[3] Treatment of **3** with magnesium in tetrahydrofuran or sodium in dioxane gave **4** in 70% yield.[4a] The nmr spectrum of **4** which had been purified by trap-to-trap distillation showed no absorption attributable to cyclobutene, and glpc showed one peak of 99.3–99.7 area %. In contrast, treatment of 1,3-dihalocyclobutanes with sodium has been reported to give bicyclobutane contaminated with 5–20% of cyclobutene.[4b] A possible explanation of the difference in product purity is that side reactions causing elimination of HX in the dihalocyclobutanes lead to 3-halocyclobutenes, which are easily reduced to cyclobutene,[5] whereas elimination of HX from the halo ethers leads to compounds not volatile in the bicyclobutane range.

1-Phenylbicyclobutane (7). Treatment of **1** with phenylmagnesium bromide gave **5**, which was not purified but was converted to **6** by contact with 12 *N* aqueous hydrochloric acid. Treatment of **6** with magnesium in refluxing tetrahydrofuran gave **7** in 40% yield, contaminated with 10–15% of phenylcyclobutane (**8**), apparently formed by reduction of the 1,3 bond of **7**.[6a] The use of lower temperatures to circumvent this side product led to much lower yields of **7**, possibly because at lower temperatures the initially formed organomagnesium compound undergoes other reactions in preference to expelling ethoxide. A similar temperature effect has been observed in the formation of cyclopropanes from various haloethers.[6b]

Although samples of **7** prepared from **6** are suitable for most purposes, pure **7** was desired for polymerization studies. Attempts to remove **8** from samples of **7** by distillation at high reflux ratios and a pot temperature of 50°, led to extensive conversion of **7** to 1-phenylcyclobutene (**17**). Collection of the major components after glpc separation of **7** and **8** revealed that **7** had completely isomerized to **17**. Mixtures of **7** and **17** showed only one peak on a glpc trace and hence could not be assayed under the conditions used (see Experimental Section).

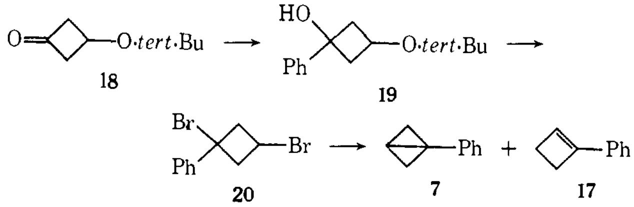


17

Purification of **7** *via* a 1,3-dihalo compound, which could be converted back to **7** under conditions mild enough to preclude formation of **8**, was attempted. Addition of iodine to a mixture of **7** and **8** gave 1,3-diiodo-1-phenylcyclobutane as a crystalline solid. However, dissolution of this solid in tetrahydrofuran caused iodine to be liberated, and treatment of this solution with magnesium gave no **7**. Addition of bromine to a mixture of **7** and **8** gave a material whose nmr spectrum was identical with the nmr spectrum of the material prepared by adding bromine to **17**. Although the material was not characterized, it appeared to be a mixture of *cis*- and *trans*-1,2-dibromo-1-phenylcyclobutane, as indicated by two methine multiplets at δ 4.4 and 5.0 in its nmr spectrum. An authentic sample of 1,3-dibromo-1-phenylcyclobutane (see below) exhibits an nmr spectrum very different from the material just described.

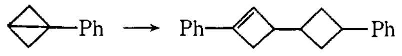
The desired 1,3-dibromo-1-phenylcyclobutane (**20**) was finally synthesized by Scheme II. This route was satisfactory for reducing the quantity of **8** (~<1%), since much milder conditions (Mg, THF, 20–25°) could be used for the ring closure. However, nmr spectra of crude product mixtures showed detectable amounts (~5%) of **17**, which was not detected in crude reaction mixtures of **7** prepared by Scheme I. All the above results concerning **7** point to an acid-catalyzed rearrangement of **7** to **17**. Small amounts of hydrogen bromide formed during the addition of bromine to **7** could cause rearrangement to **17** followed by bromination, and differences in acidity and solubility of magnesium bromide and magnesium chloroethoxide could cause rearrangement of **7** to **17** in the presence of the former but not the latter. Also supporting the acid-catalyzed reaction is the fact that when **7** was flash distilled at 70° in the presence of small amounts of unreacted 1,3-dibromo-1-phenylcyclobutane (**20**), much larger quantities of **17** were formed (~20%). Apparently, the generation of hydrogen bromide from **20** resulted in a much faster rate of rearrangement. Analogy exists for the acid-catalyzed conversion of bicyclobutanes to cyclobutenes.[7]

Scheme II



18 19 20 7 17

On standing for several days at 25°, or when heated neat with peroxides, **7** was converted to a mixture of polymer and a dimer, which was assigned structure **21** primarily on nmr and mass spectral evidence (see Experimental Section).



7 21

1-Vinylbicyclobutane (12). Treatment of **1** with vinylmagnesium bromide gave **9**, which was converted to a mixture of **10** and **11** by shaking with 12 *N* aqueous

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(3) I. Lillien and R. A. Doughty, *J. Amer. Chem. Soc.*, **89**, 155, (1967); I. Lillien and R. A. Doughty, *Tetrahedron*, **23**, 3321 (1967).

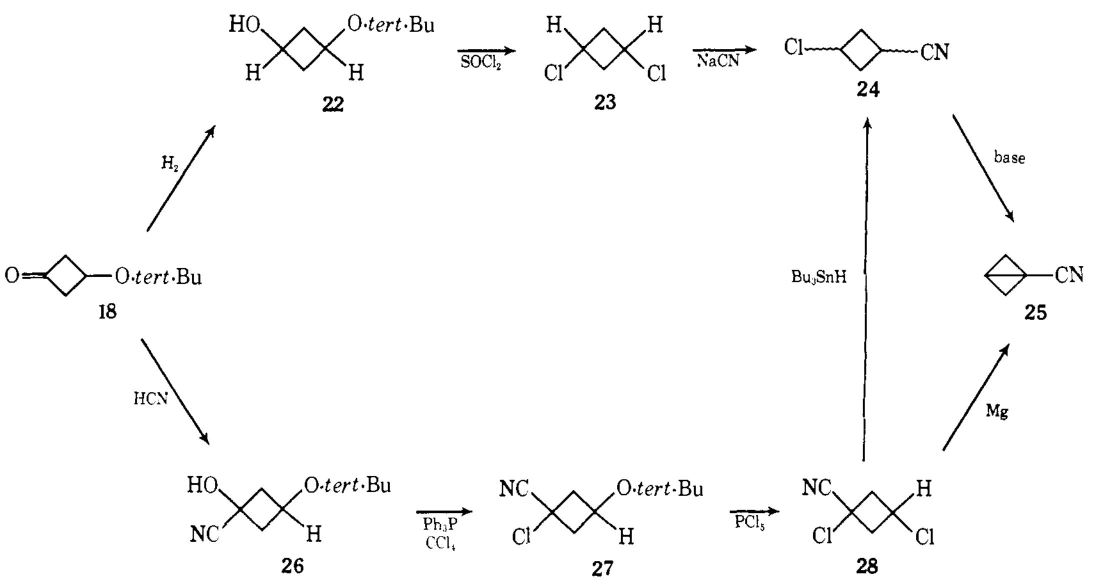
(4) (a) One other bicyclobutane has been prepared from a halo ether: D. P. G. Hamon, *Tetrahedron Lett.*, 3143 (1969); (b) K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965); K. B. Wiberg and G. M. Lampman, *Tetrahedron Lett.*, 2173 (1963).

(5) M. R. Rifi, *J. Amer. Chem. Soc.*, **89**, 4442 (1967). Due caution should be exercised when working with bicyclobutanes, since they form explosive peroxides readily.

(6) (a) W. R. Moore, S. S. Hall, and C. Largman, *Tetrahedron Lett.*, 4353 (1969); (b) N. Rabjohn and M. S. Cohen, *J. Amer. Chem. Soc.*, **74**, 6290 (1952); L. H. Slaugh, *ibid.*, **83**, 2734 (1960); J. T. Grayson, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Org. Chem.*, **20**, 275 (1955).

(7) S. Masamune, *Tetrahedron Lett.*, 945 (1965); V. V. Razin, M. I. Mostova, and I. A. D'yakonov, *Russ. J. Org. Chem.*, **4**, 524 (1968).

Scheme III



hydrochloric acid. Both **10** and **11** gave **12** on treatment with magnesium in refluxing ether under high dilution conditions[8] to prevent coupling reactions. Samples of **12** proved to be very reactive with certain alkenes and should be handled with care. For example, when a neat mixture of **12** and acrylonitrile was put in a capped vial, the vial exploded violently after about 5 min. A sample of this mixture which was diluted with chloroform had completely reacted in 7 hr at 25°. Similar reactivity has been found for other bicyclobutane hydrocarbons.[5]

1-Phenyl-2,2,4,4-tetramethylbicyclobutane (16). Polysubstituted bicyclobutanes are also available from the 3-alkoxycyclobutanones as demonstrated for **16**. Treatment of **1** with sodium hydride and methyl iodide gave **13** in 56% yield. This was then transformed into **16** by chemistry already described for **7**.

1-Cyanobicyclobutane (25). The 3-alkoxycyclobutanones are valuable for preparing not only a variety of bicyclobutane hydrocarbons but also various other 1-substituted bicyclobutanes (Scheme III). Reduction of **18** with lithium aluminum hydride or Raney nickel gave **22**, about 95% of which was the cis isomer. This was converted with thionyl chloride–DMF to **23**, again about 95% rich in the cis isomer. The stereochemistry of **22** and **23** was assigned on the basis of nmr spectra, as discussed previously for **2** and **3**.[9] Treatment of **23** with sodium cyanide gave **24**, which can easily be converted to **25** with base.[10]

A second route to **25** is shown in Scheme III. The cyanohydrin (**26**) was prepared from liquid hydrogen cyanide, and appeared to be largely the cis (OH, O-*tert*-Bu) isomer by its nmr spectrum. Treatment of **26** with triphenylphosphine in carbon tetrachloride gave a 65% yield of **27**, which appeared to be largely trans (Cl, O-*tert*-Bu) by its nmr spectrum (~95% by glpc).[11] Conversion of **27** to **28** was accomplished with phosphorus pentachloride. Compound **28** was largely cis (Cl, Cl) by its nmr spectrum. Treatment of **28** with magnesium in tetrahydrofuran gave **25**, but extensive polymerization occurred during work-up. Therefore, **28** was reduced to **24** with tributyltin hydride,[12] which could then be satisfactorily converted to **25** with base.[10]

The stereochemical assignments of **26**, **27**, and **28** are internally consistent. Thus, **26** would be expected to be predominantly cis (OH, O-*tert*-Bu) because of attack of cyanide from the least-hindered side. This being the case, **27** would be expected to be trans (Cl, O-*tert*-Bu), since the conversion of alcohols to halides with phosphines and halocarbons[13] has been shown to occur with inversion of configuration.[14] Transformation of the O-*tert*-Bu group of **27** to the chloride should also proceed with inversion to give *cis*-(Cl, Cl) **28**.

Summary. Scheme I represents a general route to 1-substituted bicyclobutane hydrocarbons, limited primarily by the availability of organometallic reagents. Scheme III provides a convenient route to other bicyclobutanes by proper utilization of the 1,3 difunctionality. Many of the compounds described, and potentially many others, provide interesting subjects for conformational, stereochemical, and spectroscopic studies in the cyclobutyl and bicyclobutyl systems.

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(8) A. C. Cope and E. C. Herrick, *J. Amer. Chem. Soc.*, **72**, 983 (1950).

(9) For comparison purposes, the trans isomer of **23** was obtained by separation of a mixture of *cis*- and *trans*-**23**, which was obtained by Bu_3SnH reduction of 1,1,3-trichlorocyclobutane. The latter compound was prepared directly from **18** and phosphorus pentachloride (see Experimental Section). The nmr spectra of *cis*- and *trans*-1,3-dibromocyclobutane have been published: K. B. Wiberg and D. E. Barth, *J. Amer. Chem. Soc.*, **91**, 5124 (1969).

(10) H. K. Hall, Jr., E. P. Blanchard, Jr., S. C. Cherkofsky, J. B. Sieja, and W. A. Sheppard, *ibid.*, **93**, 110 (1971).

(11) To the author's knowledge, this is the first report of the conversion of a cyanohydrin to an α-chloronitrile using the triphenylphosphine–carbon tetrachloride procedure. Phosphorus pentachloride gave only a 13% yield of the α-chloronitrile **27**.

(12) The author wishes to thank Dr. S. C. Cherkofsky for carrying out this reaction on the tetradeuterated species.[10]

(13) (a) A. J. Burn and J. I. G. Cadogan, *J. Chem. Soc.*, 5788 (1963); (b) I. M. Downie, J. B. Holmes, and J. B. Lee, *Chem. Ind. (London)*, 900 (1966); (c) J. B. Lee and T. J. Nolan, *Can. J. Chem.*, **44**, 1331 (1966); (d) J. B. Lee and I. M. Downie, *Tetrahedron*, **23**, 359 (1967); (e) J. B. Lee and T. J. Nolan, *ibid.*, **23**, 2789 (1967); (f) J. Hooz and S. S. H. Gilani, *Can. J. Chem.*, **46**, 86 (1968); (g) R. G. Weiss and E. I. Snyder, *Chem. Commun.*, 1358 (1968); (h) I. M. Downie, J. B. Lee, and M. F. S. Matough, *ibid*, 1350 (1968); (i) D. Brett, I. M. Downie, J. B. Lee, and M. F. S. Matough, *Chem. Ind. (London)*, 1017 (1969); (j) I. M. Downie, J. B. Lee, T. J. Nolan, and R. M. Allen, *Tetrahedron*, **25**, 2339 (1969).

(14) References 13d, f, g, and i report inversion of configuration. References 13e and j report retention of configuration, but a hemiacetal might be expected to be more prone to S_N1 cleavage than the other cases. The observed retention of configuration is probably due to steric control of an ionized intermediate.

Experimental Section

All melting and boiling points are uncorrected. The nmr spectra were recorded at 60 MHz unless otherwise noted.

3-Methoxycyclobutanone. A heavy-walled polymer tube containing 50 ml of methyl vinyl ether and 37 ml of ketene was heated at 100° for 4 hr. Distillation of the products at 1 mm into a cold (−78°) receiver gave 37 g of volatile material and 8.5 g of nonvolatile residue. Fractionation of the volatile material gave 8 g of diketene, bp 46° (25 mm), and 19 g of 3-methoxycyclobutanone, bp 62° (25 mm): n^{25}D 1.4266; ir (neat) 3.34, 3.43, 3.54, 5.59, 8.97 μ; nmr (neat) δ 4.18 (~p, 1 H, methine H), 3.28 (s, 3 H, OCH_3), 2.7–3.4 (m, 4 H, CH_2).

Anal. Calcd for $C_5H_8O_2$: C, 59.99; H, 8.06. Found: C, 58.96; H, 7.72.

3-Ethoxycyclobutanone (1). A stainless steel bomb containing 750 g (10.5 mol) of ethyl vinyl ether and 380 g (9.1 mol) of ketene was heated to 100° for 4 hr. Excess ethyl vinyl ether (350 g) was removed at 1 atm up to a pot temperature of 100°. The remaining material was distilled at ~1 mm into a cold (−78°) receiver up to a pot temperature of 100°. Fractionation of the volatile material gave 50 g of diketene, bp 38–40° (20 mm), 30 g of a mixture of diketene and **1**, and 260 g (25%) of **1**, bp 65° (20 mm): n^{25}D 1.4276; ir (neat) 3.34, 3.39, 3.46, 5.58, 8.93 μ; nmr (neat) δ 4.29 (~p, 1 H, methine H), 3.49 (q, 2 H, OCH_2), 2.6–3.5 (m, 4 H, ring CH_2), 1.17 (t, 3 H, CH_3).

Anal. Calcd for $C_6H_{10}O_2$: C, 63.16; H, 8.83. Found: C, 62.67, 63.03; H, 8.86, 8.90.

3-Benzyloxycyclobutanone. A stainless steel bomb containing 110 g of ketene (2.6 mol) and 112 g of benzyl vinyl ether (1.1 mol) was heated at 100° for 4 hr. Volatile material was collected in a cold (−78°) receiver at ~1 mm, leaving a residue of 11.5 g. Fractionation of the volatiles gave 33 g (20%) of 3-benzyloxycyclobutanone: bp 97–102° (0.25 mm); n^{25}D 1.5232; ir (neat) 3.28, 3.30, 3.43, 3.50, 5.58, 6.21, 6.29, 6.68, 9.05, 13.53, 14.35 μ; nmr (neat) of δ 7.27 (s, 5 H, Ar), 4.32 (s, 2 H, CH_2O), 4.09 (~p, 1 H, methine), 2.94 (broad doublet, 4 H, ring CH_2).

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.87. Found: C, 74.52; H, 6.93.

3-*tert*-Butoxycyclobutanone (18). A stainless steel bomb containing 110 g (2.6 mol) of ketene and 400 g (4.0 mol) of *tert*-butyl vinyl ether was heated at 100° for 4 hr. A mixture (27 g) of diketene and *tert*-butyl vinyl ether was removed at 25° (15 mm). The residue was distilled into a cold (−78°) receiver at ~40° (1 mm) up to a pot temperature of 120°. This gave 364 g of volatile material and 11 g of residue. The volatiles were fractionated and gave 44 g of *tert*-butyl vinyl ether, bp 30° (135 mm), 22 g of a mixture of diketene and 3-*tert*-butoxycyclobutanone, bp 30–74° (15 mm), and 260 g (70%) of 3-*tert*-butoxycyclobutanone, bp 74° (15 mm): n^{25}D 1.4319; ir (neat) 3.35, 5.57, 7.17, 7.30, 9.0 μ; nmr (neat) δ 4.43 (~p, 1 H, methine H) 2.9–3.2 (m, 4 H, CH_2), 1.20 (s, 9 H, *tert*-butyl). By using a 1700-ml bomb and correspondingly larger quantities of ketene and vinyl ether, 520 g of **18** can be obtained from one run.

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.61, 67.47; H, 10.10, 9.94.

3-Ethoxycyclobutanol (2). To a slurry of 10 g (0.26 mol) of lithium aluminum hydride in 1 l. of ether was added at 0–10° over 1 hr a solution of 100 g (0.89 mol) of 3-ethoxycyclobutanone in 100 ml of ether. After addition was complete, the mixture was stirred at 25° for 1.5 hr and then cooled to 0°. In turn were added 10 ml of water, 10 ml of 15% sodium hydroxide solution, and 30 ml of water. The mixture warmed to 25° over 1 hr and was filtered. Solvent was evaporated, and the product was distilled to give 90 g (87%) of **2**: bp 50° (0.25 mm); n^{25}D 1.4393; ir (neat) 2.95, 3.35, 3.40, 3.47, 7.28, 9.0 μ; nmr (neat) δ 4.86 (s, 1 H, OH), 3.3–4.1 (m, 2 H, methines), 3.33 (q, 2 H, OCH_2), 1.5–2.9 (m, 4 H, ring CH_2), 1.12 (t, 3 H, CH_3). The general appearance of the methylene ring hydrogens in the nmr spectrum indicated a cis relationship of the oxygens. Glpc showed the product to be ~95% one isomer.

Anal. Calcd for $C_6H_{12}O_2$: C, 62.01; H, 10.40. Found: C, 62.15, 62.06; H, 10.52, 10.63.

1-Chloro-3-ethoxycyclobutane (3). To a cold (0°) solution of 66 g (0.57 mol) of *cis*-3-ethoxycyclobutanol and 50 ml (0.62 mol) of pyridine in 400 ml of ether was added over 1 hr a solution of 23 ml (0.32 mol) of thionyl chloride in 75 ml of ether. When the mixture had warmed to 25°, the pyridine hydrochloride was filtered off and the solvent was removed under reduced pressure, leaving 74 g of a mixture of sulfite ester and pyridine hydrochloride. This residue was cooled to 0° and 23 ml (0.32 mol) of thionyl chloride and 3 ml (0.037 mol) of pyridine were added. On heating the mixture to 80°, sulfur dioxide was evolved. The mixture was heated slowly to 100°, where it was maintained until evolution of gas subsided (~30 min). The mixture was cooled and poured into 500 ml of ice–water with stirring. This was then extracted with four 100-ml portions of ether; the extracts were washed with two 75-ml portions of 10% hydrochloric acid solution, water, and saturated sodium chloride solution. After removal of solvent at 1 atm, the dark residue was quickly distilled into a cold (−78°) receiver at 3 mm giving 56 g of almost pure product. Fractionation gave 53 g (70%) of pure 1-chloro-3-ethoxycyclobutane: bp 69° (50 mm); n^{25}D 1.4364; ir (neat) 3.55, 3.40, 3.47, 8.94 μ; nmr (neat) δ 4.33 (septet, splitting = 6 Hz, 2 methine H), 3.32 (q, J = 7 Hz, CH_2O), 2.45 (t, splitting = 6 Hz, four-ring CH_2), 1.12 (t, J = 7 Hz, CH_3). The simplicity of the nmr spectrum indicates that the compound is the trans isomer. Glpc showed it to be ~95% one isomer.

Anal. Calcd for $C_6H_{11}OCl$: C, 53.53; H, 8.24; Cl, 26.34. Found: C, 52.77; H, 8.23; Cl, 26.33.

Bicyclobutane (4). Sodium Procedure. To a dispersion of 2.5 g (0.11 mol) of sodium in 50 ml of refluxing dioxane was added over 5 min 3.5 g (0.026 mol) of *trans*-1-chloro-3-ethoxycyclobutane. The mixture was heated strongly until dioxane refluxed at the head of an air condenser, which was connected to a cold trap. The volatiles in the cold trap (~0.5 ml) proved to be bicyclobutane. The nmr spectrum revealed no cyclobutene.

Bicyclobutane (4). Magnesium Procedure. All glassware used in this operation had been washed with 10% sodium hydroxide solution. A 3-l., four-necked flask was equipped with a mechanical stirrer, thermometer, 250-ml addition funnel with a pressure-equalizing side arm, and a 15-in. Vigreux distillation column. A 1-l., two-necked receiver was attached to the distillation column. A Dry Ice trap and a source of positive nitrogen were attached to one neck of the receiver. The entire apparatus was heated and allowed to cool under nitrogen. Magnesium turnings (75 g, 3.12 mol), 1.8 l. of THF, and 0.2 g of iodine were added to the pot and then refluxed. After the color had disappeared, 279 g (2.1 mol) of *trans*-1-chloro-3-ethoxycyclobutane was added over about 3 hr. Initiation of the reaction was indicated by the reaction mixture becoming brown and cloudy in appearance. During the addition, the pot temperature was maintained at 65°, and the head temperature remained at 57–60°. After addition was complete, the pot was heated until the head temperature reached 65°. The receiver, which contained about 0.6 l. of distillate, was connected to a 15-in. spinning-band column with a closed take-off. A Dry Ice-cooled trap and a source of positive nitrogen were connected to the column outlet. The material in the pot was then heated until the head temperature reached 65°. The material in the cold trap was distilled at 25° under N_2 through two traps at ~20°, and finally into one at −78°. About 15 ml of THF remained as a residue. The volatile material weighed 85 g (1.57 mol, 75%). The last traces of THF were removed by distilling the product at 25° through two gas-scrubbing towers filled with slightly basic water. Water was then removed from the sample by distillation through a mixture of anhydrous barium oxide and potassium carbonate. Glpc of the final product showed it to contain one peak of 99.5–99.7 area %. The product was identified by its nmr spectrum,[15] which showed no trace of olefinic hydrogen absorption.

1-Chloro-1-phenyl-3-ethoxycyclobutane (6). An ethereal solution of phenylmagnesium bromide (200 ml, 3 *M*, 0.6 mol, Arapahoe) was diluted with 100 ml of ether. To this solution was added at 0–10° over 1 hr a solution of 57 g (0.5 mol) of 3-ethoxycyclobutanone in 100 ml of ether. The mixture was stirred at 25° for 1 hr and acidified with 50% hydrochloric acid solution. The layers were separated and 100 ml of water was added to the aqueous layer, which was then extracted with three 60-ml portions of ether. The combined organic phase was washed with two 250-ml portions of water, 250 ml of aqueous sodium bicarbonate, and 100 ml of saturated sodium chloride solution, and dried over magnesium sulfate.

Removal of solvent gave 100 g of residue. An nmr spectrum ($CDCl_3$) of the crude material showed absorption at δ 6.7–7.7 (5.75 H, Ar), broad singlet at 4.28 (1 H, OH), complex multiplet at 2.0–3.8 (6.5 H, CH_2), and triplet at 1.07 (3 H, CH_3). This residue was shaken in a separatory funnel for 4 min with 300 ml of hexane and 300 ml of concentrated aqueous hydrochloric acid. The layers were separated, and the aqueous phase was extracted with two 50-ml portions of hexane. The combined organic phase was

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(15) R. Srinivasan, *J. Amer. Chem. Soc.*, **85**, 4045 (1963).

washed with two 300-ml portions of dilute salt solution, two 300-ml portions of cold 5% aqueous bicarbonate solution, and 100 ml of saturated sodium chloride solution. Removal of solvent under reduced pressure gave 82 g (77%) of product. Distillation from $CaCO_3$ in a molecular still, bp 68° (0.1 mm), gave a center cut of 31 g of **6**. Biphenyl is a troublesome by-product. An nmr spectrum (neat) showed δ 7.0–7.6 (m, 5.75 H, Ar), (∼p, 0.8 H, methine), 2.3–3.6 (m, 6.2 H, CH_2 and methine), 1.05 (t, 3 H, CH_3).

1-Phenylbicyclobutane (7) from 1-Chloro-1-phenyl-3-ethoxycyclobutane (6). A mixture of 25 g (1.04 g-atoms) of magnesium turnings, 0.5 ml of 1,2-dibromoethane, and 1 l. of dry THF was heated to reflux, and the mantle was removed. 1-Chloro-1-phenyl-3-ethoxycyclobutane (208 g, 0.987 mol) was added at a rate to maintain reflux (∼1 hr). The mixture was stirred overnight at 55°, but this was later found to be unnecessary. The mixture was cooled, and 1 g each of phenothiazine and phenyl-β-naphthylamine was added. The mixture was poured into 3 l. of water containing 225 ml of saturated sodium bicarbonate solution (helps break emulsions) and then extracted with five 200-ml portions of petroleum ether or pentane. The extracts were washed with water and saturated sodium chloride and dried over magnesium sulfate. Solvent was removed at reduced pressure and the residue was distilled in a molecular still to give 52 g (40%) of product, bp ∼24° (0.1 mm). Glpc showed the product to consist of about 13% phenylcyclobutane (**8**) and 85% 1-phenylbicyclobutane (**7**). An nmr spectrum of the crude product showed no olefinic absorption, but showed δ 7.1 (s, 5 H, Ar), 2.1 (d, J = 3 Hz further split into triplets ∼0.5 Hz, 2 H, exo H), 1.55 (seven lines from overlapping triplet of triplets, J = 3, 1.7 Hz, 1 H, methine), 0.95 (d, J = 1.7 Hz further split into triplets ∼0.5 Hz, 2 H, endo H); ir (neat) 3.25, 3.36, 3.45, 6.23, 6.58, 6.74, 6.92, 9.02, 9.32, 9.78, 11.93, 13.30, 14.50 μ.

Preparative glpc was carried out on the above sample on a 4-ft (Prepkro) column of 25% butanediol succinate on Gas Chrom R at 125° (injection port 125°) with a flow rate of 57.5 ml/min. The peak at 7.3 min was shown to be phenylcyclobutane by its ir spectrum ((neat) 3.29, 3.35, 3.47, 6.22, 6.70, 6.92, 13.40, 14.43 μ) and its nmr spectrum ((CCl_4) δ 7.11 (s, 5 H, Ar), 3.12–3.85 (m, 1 H, methine), 1.6–2.5 (m, 6 H, CH_2)). The peak at 12.9 min was shown to be 1-phenylcyclobutene by its ir spectrum ((neat) 3.32, 3.45, 3.57, 5.93, 6.26, 6.35, 6.73, 6.92, 7.53, 7.63, 7.74, 7.85, 8.05, 8.52, 9.33, 9.77, 10.74, 11.12, 11.46, 11.77, 12.80, 13.75, 14.55 μ) and its nmr spectrum ((CCl_4) δ 7.0–7.4 (m, 5 H, Ar), 6.14 (t, J = ∼1 Hz, 1 H, olefinic), 2.63–2.8 (m, 2 H, CH_2), 2.33–2.54 (m, 2 H, CH_2)). The peak at 15.35 min appears to be 2-phenyl-1,3-butadiene by its ir spectrum ((neat) 3.22, 3.28, 6.10, 6.21, 6.70, 6.91, 7.75, 8.61, 9.33, 9.98, 10.56, 11.13, 11.67, 13.28, 13.76, 14.53 μ) and its nmr spectrum ((CCl_4) δ 7.0–7.4 (m, 5 H, Ar), 6.05–6.75 (m, 3 H, vinyl), 4.9–5.4 (m, 2 H, $=CH_2$). Since neither of the latter two compounds was revealed by the nmr spectrum of the crude product, both must be produced in the gas chromatograph.

1-Hydroxy-1-phenyl-3-*tert*-butoxycyclobutane (19). To a solution of 335 ml (3 *M*, 1 mol) of phenylmagnesium bromide in 300 ml of ether was added over 1 hr at 0–5° a solution of 142 g (1 mol) of 3-*tert*-butoxycyclobutanone in 100 ml of ether. The mixture was stirred at 25° for 1 hr, treated with 150 ml of ammonium chloride solution, and filtered. Removal of solvent gave a solid (231 g) which was recrystallized from hexane to give 141 g (64%) of 1-hydroxy-1-phenyl-3-*tert*-butoxycyclobutane: mp 66–68° (74–75°); ir (KBr) 3.05, 3.37, 6.23, 6.30, 6.67, 7.22, 7.33, 9.59, 13.22, 14.31 μ; nmr (CCl_4) δ 7.1–7.6 (m, 5 H, Ar), 3.80 (∼p 1 H, methine), 3.20 (s, 1 H, OH), 2.1–3.0 (m, 4 H, CH_2), 1.12 (s, 9 H, $C(CH_3)_3$).

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.57; H, 9.00.

1,3-Dibromo-1-phenylcyclobutane (20). 1-Hydroxy-1-phenyl-3-*tert*-butoxycyclobutane (413 g, 1.88 mol) was added over 0.5 hr to 1100 g (4.05 mol) of phosphorus tribromide at 25°. The mixture was heated to 100° and 1 ml of boron trifluoride etherate was added. The solution was heated for an additional 0.5 hr, cooled, and poured onto ∼3 l. of ice. This was extracted with one 500-ml and three 200-ml portions of ether, which were then washed with three 200-ml portions of water and 100 ml of saturated salt solution and dried. Removal of solvent under reduced pressure gave a semisolid. The solids were filtered off and about 400 ml of ether was added to the filtrate. Cooling the filtrate to −78° with stirring gave further crops of dibromide. Recrystallization of the solid from petroleum ether gave 80 g (14%) of 1,3-dibromo-1-phenylcyclobutane: mp 61.5–65°; ir (KBr) 3.27, 3.32, 6.20, 6.29, 6.67, 13.05, 14.38 μ; nmr (CCl_4) δ 7.25 (s, 5 H, Ar), 4.95 (∼p, 1 H, methine), 2.8–3.7 (m, 4 H, CH_2).

Anal. Calcd for $C_{10}H_{10}Br_2$: C, 41.41; H, 3.48; Br, 55.11. Found: C, 41.40; H, 3.60; Br, 48.60. At the time of bromine analysis, the sample had deteriorated considerably.

1-Phenylbicyclobutane (7) from 1,3-Dibromo-1-phenylcyclobutane (20). All equipment had been washed with 10% sodium hydroxide solution prior to use. To a mixture of 1.2 g (0.05 mol) of magnesium turnings in 200 ml of dry THF at 0° was added all at once 14.5 g (0.05 mol) of 1,3-dibromo-1-phenylcyclobutane. The mixture was stirred for 22 hr at 15–20° and then poured into 1 l. of water containing 100 ml of saturated sodium bicarbonate solution. This was extracted with four 100-ml portions of pentane, which were then washed with water and saturated salt solution. Solvent was removed under reduced pressure. Glpc showed only a small quantity (<1%) of phenylcyclobutane. An nmr spectrum showed small amounts of 1-phenylcyclobutene. Distillation at room temperature (0.1 μ) gave 3.9 g (60%) of 1-phenylbicyclobutane contaminated with about 5% 1-phenylcyclobutene.

1,3-Diiodo-1-phenylcyclobutane. To a solution of 22 g of 1-phenylbicyclobutane (containing about 15% phenylcyclobutane) in 50 ml of carbon tetrachloride was added a solution of iodine in carbon tetrachloride until a pink color persisted. Solvent was removed to give a semisolid which was recrystallized from petroleum ether to give pale-yellow crystals: dec pt 100°; ir 3.27, 3.30, 3.42, 6.27, 6.34, 6.70, 13.16, 14.35 μ; nmr ($CDCl_3$) δ 7.55 (s, 5 H, Ar), 4.8–5.4 (m, 1 H, methine), 2.75–3.8 (m, 4 H, CH_2).

Anal. Calcd for $C_{10}H_{10}I_2$: C, 31.28; H, 2.63; I, 66.10. Found: C, 31.77; H, 2.60; I, 65.87.

1,2-Dibromo-1-phenylcyclobutane. Bromine was added to a carbon tetrachloride solution of a mixture of 85% 1-phenylcyclobutene and 15% phenylcyclobutane until a pink color persisted. The product was distilled, bp 60° (2 μ). The nmr spectrum ((CCl_4) δ 7.05–7.37 (m, 5 H, Ar), 4.86–5.13 and 4.17–4.57 (m, 1 H, methines), 1.8–3.75 (m, 4 H, CH_2)) is consistent with a mixture of *cis*- and *trans*-1,2-dibromo-1-phenylcyclobutane. Similar treatment of an 85% 1-phenylbicyclobutane–15% phenylcyclobutane mixture gave an identical nmr spectrum.

1-Phenylbicyclo[1.1.0]butane Dimer (21). The crude material obtained by heating 1-phenylbicyclobutane with or without benzoyl peroxide was triturated with hot methanol to remove polymer, which was filtered off. The methanol was removed and the residue was dissolved in ether and cooled with stirring to −78°. The solid was filtered off and recrystallized from methanol to give white needles: mp 86–88°; ir, 3.30, 3.43, 3.50, 6.23, 6.34, 6.71, 13.40, 14.44 μ; nmr ($CDCl_3$, 220 MHz), δ 7.40–7.08 (m, 10 H, Ar), 6.45 (d, J = 1 Hz, 1 H, vinyl H), 3.55 (∼p, splitting = 8 Hz, 1 H, benzylic H), 3.0–3.1 (m, 1 H, tertiary allylic H), 2.40 (doublet of doublets, J = 13 Hz, 4.5 Hz, 1 H, allylic methylene H), 2.52–2.12 (m, 6 H, all other H); uv max (isooctane) 292 (ε 642), 258 (ε 22,000), 219 (ε 20,400), 213 mμ (ε 26,300). The mass spectrum shows a parent peak at *m/e* 260 (10.7% of base peak) and 156 (98.2% of base peak) resulting from loss of styrene.

Anal. Calcd for $C_{20}H_{20}$: C, 92.24; H, 7.74. Found: C, 92.22; H, 7.75.

1-Hydroxy-1-vinyl-3-ethoxycyclobutane (9). Magnesium turnings (14.5 g, 0.604 mol) were activated by heating to 50° with 1 ml of 1,2-dibromoethane in 500 ml of THF. While the temperature was held at 25–35°, 80 g (0.75 mol) of vinyl bromide was bubbled into the THF over 2 hr. After the magnesium had reacted, the solution was cooled to 0–10° and a solution of 57 g (0.5 mol) of 3-ethoxycyclobutanone in 60 ml of THF was added over 1 hr. The mixture was stirred at 25° for 1 hr, cooled, and acidified with 50% aqueous hydrochloric acid. The layers were separated and 200 ml of water was added to the lower water layer. The water was extracted with five 100-ml portions of ether, which were then combined with the original THF layer. The organic phase was washed with 100 ml of saturated sodium bicarbonate solution and 100 ml of saturated sodium chloride solution and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was distilled giving 50 g (70%) of 1-hydroxy-1-vinyl-3-ethoxycyclobutane: bp 46° (0.3 mm); $n^{25}D$ 1.4574; ir, 2.95, 3.23, 3.34, 3.39, 3.47, 6.07, 7.27, 9.0, 10.06, 10.89 μ; nmr (neat) δ 4.80–6.22 (m, 3 H, vinyl), 4.55 (s, 1 H, OH) 3.15–3.80 (m, 3 H, CH_2O, >CHO), 1.9–2.7 (m, 4 H, CH_2), 1.12 (t, 3 H, CH_3). The nmr spectrum reveals only one vinyl and one ethoxy group, suggesting only one isomer. Steric arguments favor the isomer with cis oxygen functions.

1-Chloro-1-vinyl-3-ethoxycyclobutane (10) and 1-(2-Chloroethylidene)-3-ethoxycyclobutane (11). A mixture of 100 ml of pentane, 25 g (0.176 mol) of 1-hydroxy-1-vinyl-3-ethoxycyclobutane, and 75 ml of 12 *N* aqueous hydrochloric acid was shaken in a separatory funnel for 5 min, and the layers were separated. The aqueous phase was extracted with 25 ml of pentane and the combined organic phase was washed with four 150-ml portions of ice water and 100 ml of saturated salt solution, and then dried over magnesium sulfate. Removal of the solvent and distillation of the residue gave 3.7 g (13%) of 1-chloro-1-vinyl-3-ethoxycyclobutane (**10**) (bp 43° (2.7 mm); $n^{25}\text{D}$ 1.4532) and 9.3 g (33%) of 1-(2-chloroethylidene)-3-ethoxycyclobutane (**11**) (bp 66° (2.7 mm); $n^{25}\text{D}$ 1.4743): first product (**10**) ir 3.23, 3.35, 3.40, 3.46, 6.08, 7.27, 8.86, 10.12, 10.81 μ; nmr (neat) δ 4.9–6.4 (m, 3 H, vinyl), 4.32 (~p, splitting 7 Hz, 0.85 H, >CHO), 3.15–3.9 (m indicating two OCH_2 quartets, one >CHO pentuplet, 2.3 H), 2.15–3.05 (m, 4 H, CH_2), 1.11 (t, 3 H, CH_3). *Anal.* Calcd for $C_8H_{13}OCl$: C, 59.82; H, 8.16; Cl, 22.08. Found: C, 59.78; H, 8.36; Cl, 22.29. Second product (**11**): ir (neat) 3.35, 3.46, 5.87, 7.27, 8.89 μ; nmr (neat) δ 5.2–5.7 (m, 1 H, olefinic H), 3.75–4.2 (m, 3 H, CH_2Cl, >CHO), 3.35 (q, J = 7 Hz, CH_2O), 2.3–3.3 (m, 4 H, CH_2), 1.13 (t, J = 7 Hz, 3 H, CH_3). *Anal.* Found: C, 59.52; H, 8.30; Cl, 21.92.

1-Vinylbicyclobutane (12). All glassware used in this preparation had been washed with 10% sodium hydroxide solution. A high dilution apparatus[8] was used to reduce the side product resulting from a coupling reaction. To a magnetically stirred mixture of 30 g (1.25 mol) of magnesium turnings in ~1.4 l. of refluxing ether was added 161 g (1 mol) of 1-(2-chloroethylidene)-3-ethoxy cyclobutane (1-chloro-1-vinyl-3-ethoxycyclobutane can also be used) over 26 hr. During the addition, 15 drops of ether were returned to the pot for each drop of chloro ether added. The volatiles were removed under reduced pressure up to a pot temperrature of 40° on a rotary evaporator and collected in a cold (−78°) receiver. The residual material was volatilized into a liquid nitrogen trap using the full vacuum of an oil pump. A small amount of phenyl-β-naphthylamine was added to each of the volatile fractions, and the ether was separately distilled from each through a 15-in. spinning-band column until the ratio of ether to **12** was about 4:1. Both residues were combined and further concentrated at 1 atm up to a pot temperature of 60°. Further fractionation at reduced pressure gave 14.9 g (18%) of pure 1-vinylbicyclobutane: bp 41° (280 mm); $n^{25}\text{D}$ 1.4549; ir 3.24, 3.34, 3.43, 3.48, 6.12, 10.22, 11.42 μ; uv $\lambda_{\text{max}}^{\text{isooctane}}$ 221 mμ (14,000); nmr (neat) δ 4.7–6.3, (m, 3 H, vinyl), 1.81 (m, 2 H, exo CH), 1.23 (m, 1 H, methine), 0.85, (m 2 H, endo CH). A considerable forerun containing ether and **12** was obtained.

Anal. Calcd for C_6H_8: C, 89.94; H, 10.07. Found: C, 90.03, 90.21; H, 9.82, 10.00.

2,2,4,4-Tetramethyl-3-ethoxycyclobutanone (13). To a mixture of 41 g (1.71 mol) of sodium hydride (washed free of mineral oil with pentane), 243 g (1.71 mol) of methyl iodide, and 400 ml of dry THF was added at 10–20° under nitrogen over 2.7 hr, 33.7 g (0.295 mol) of 3-ethoxycyclobutanone. About 28 l. of hydrogen was liberated. The mixture was stirred overnight at 25° and filtered. Solvent was removed and the residue was distilled to give 28 g (56%) of **13**: bp 51° (6 mm); $n^{25}\text{D}$, 1.4230; ir (neat) 3.38, 3.49, 5.63, 7.25, 7.34, 8.92 μ; nmr (neat) δ 3.52 (q, 2 H, CH_2O), 3.55 (s, 1 H, methine), 1.21 (t, 3 H, CH_3CH_2), 1.11 (s, 6 H, CH_3), 1.15 (s, 6 H, CH_3). *Anal.* Calcd for $C_{10}H_{18}O_2$: C, 70.74; H, 10.47. Found: C, 70.56; H, 10.66.

1-Halo-1-phenyl-2,2,4,4-tetramethyl-3-ethoxycyclobutane (15). To an ethereal solution of 60 ml (3 *M*, 0.18 mol, Arapahoe) of phenylmagnesium bromide in 100 ml of ether at 0–5° was added over 0.5 hr a solution of 20.4 g (0.12 mol) of 2,2,4,4-tetramethyl-3-ethoxycyclobutanone in 20 ml of ether. The mixture was stirred for 2 hr at 25°, and 25 ml of saturated ammonium chloride solution was added. The solids were filtered off and washed with ether, and the solvent was removed from the filtrate to give 27 g (91%) of 1-hydroxy-1-phenyl-2,2,4,4-tetramethyl-3-ethoxycyclobutane. The infrared spectrum showed OH absorption at 2.9 μ and no carbonyl absorption. The nmr spectrum (neat) showed a broad singlet at δ 7–7.3 (5 H, Ar), multiplet at 3.1–3.6 (3.4 H, OCH_2 and methine H), two singlets at 2.0 and 2.32 (1 H, OH), and a multiplet at 0.9–1.4 (15 H, CH_3's). This material was not purified but was dissolved in petroleum ether and shaken in a separatory funnel for 3 min with 150 ml of 48% aqueous hydrobromic acid. The layers were separated and the ether layer was washed with water, sodium bicarbonate solution, and saturated salt solution, and then dried over magnesium sulfate. Removal of solvent gave 26.3 g of residue, which still showed the presence of hydroxyl absorption in its infrared spectrum. Therefore, the same procedure was used again, but 12 *N* aqueous hydrochloric acid was substituted for the hydrobromic acid. Work-up as before gave a residue which showed no hydroxyl absorption in its infrared spectrum. The residue was distilled in a molecular still to give ~1 g of biphenyl, bp 45–80° (0.05 mm), and 24.5 g (84%) of a liquid, bp 80° (0.05 mm). The nmr spectrum (CCl_4) showed a broad singlet at δ 7.1–7.3 (5.5 H, Ar), quartet at 3.42 (2 H, OCH_2), two singlets at 3.56 and 3.6 (1 H, methines), two singlets at 1.52 and 1.63 (6 H, CH_3), triplet at 1.22, and a broad singlet at 1.24 (9 H, CH_3's). The spectra are consistent with the proposed structure (**15**), but the sample probably contained some biphenyl. No further purification was attempted.

1-Phenyl-2,2,4,4-tetramethylbicyclobutane (16). To a mixture of 2 g (0.083 mol) of magnesium turnings and 200 μl of 1,2-dibromoethane in 60 ml of refluxing THF was added over 0.5 hr 19.4 g (0.073 mol) of 1-halo-1-phenyl-2,2,4,4-tetramethyl-3-ethoxycyclobutane. The mixture was refluxed for 5 hr, cooled, and poured into 600 ml of water containing 200 ml of saturated sodium bicarbonate solution. This was extracted with four portions of petroleum ether which were then dried. Removal of solvent and distillation of the residue in a molecular still gave 5.5 g (40%) of product. Redistillation of this material through a 6-in. spinning-band column gave **16**: bp 34–36° (0.1 mm); $n^{25}\text{D}$ 1.5189; ir (neat), 3.28, 3.39, 3.45, 6.24, 6.66, 7.24, 7.30, 13.47, 14.32 μ; nmr (neat) δ 7.15 (s, 5 H, Ar), 1.48 (s, 1 H, methine), 1.40 (s, 6 H, *exo*-CH_3's), 0.85 (s, 6 H, *endo*-CH_3's). The spectrum also showed absorption due to impurities at δ 1.1, 1.7, and 7.12. Mass spectrum: parent peak at m/e 186, 55% of base peak.

3-*tert*-Butoxycyclobutanol (22). To a slurry of 1.5 g (0.04 mol) of lithium aluminum hydride in 100 ml of ether at 0° was added over 20 min 20 g (0.14 mol) of 3-*tert*-butoxycyclobutanone in 15 ml of ether. The mixture was stirred at 25° for 1 hr and was then cooled to 0°. In turn were added 1.5 ml of water, 1.5 ml of 15% aqueous sodium hydroxide solution, and 7.5 ml of water. The mixture was stirred at 25° for 1 hr and was then filtered and dried. Solvent was removed to give 18.1 g (90%) of 3-*tert*-butoxycyclobutanol: bp 50° (0.15 mm); ir 3.00, 3.35, 3.40, 7.21, 7.35, 9.5 μ; nmr (neat) δ 4.86 (s, 1 H, OH), 3.3–4.2 (m, 2 H, methines), 1.6–2.2, and 2.3–2.8 (m, 4 H, CH_2), 1.12 (s, 9 H, CH_3). The nmr spectrum indicated this isomer has the cis configuration. Glpc showed it to be about 95% of one isomer.

Anal. Calcd for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 67.42; H, 11.03.

3-*tert*-Butoxycyclobutanol (22). A mixture of 454 g of 3-*tert*-butoxycyclobutanone and 25 g of Raney nickel in water (Grace No. 28) was hydrogenated at 2000 psi and 100° until hydrogen ceased to be absorbed (~4 hr). The catalyst was filtered off and the product was distilled to give 388 g (84%) of 3-*tert*-butoxycyclobutanol, bp 47° (0.05 mm). In subsequent runs, difficulties were encountered in obtaining complete hydrogenation. However, one run at 150° and 2200 psi H_2 gave complete hydrogenation. The yield of product was only 69%, because of the formation of an unidentified lower boiling material. Glpc and nmr showed the product to be ~90% of the cis isomer.

1,3-Dichlorocyclobutane (23). A 2-l. four-necked flask was equipped with a mechanical stirrer, thermometer, 500-ml addition funnel, and a long condenser connected in series to a cold (0°) trap, Nujol bubbler, Drierite tower, and gas scrubber. To the pot was added 250 ml (3.52 mol) of thionyl chloride, which was then heated to 70°. To this was added over 2.5 hr, 182 g (1.26 mol) of 3-*tert*-butoxycyclobutanol (~95% cis) containing 15 ml of dimethylformamide. The temperature of the mixture was increased to 105° and held there until sulfur dioxide was no longer evolved (~1 hr). A glpc analysis showed 1-chloro-3-*tert*-butoxycyclobutane to be present, and therefore another 100 ml of thionyl chloride was added and heating at 105° was continued for another hr. (Considerable thionyl chloride is swept into the cold trap by the evolved gases.) The contents of the flask were then cooled and rapidly distilled under reduced pressure into a cold (−78°) receiver. The yellow distillate was washed with water and sodium bicarbonate solution, dried, and distilled to give 135 g (86%) of **23**: bp 47° (30 mm); ir (neat) 3.32, 3.37, 3.49 μ; nmr (neat) δ 4.35–3.75 (m, 2 H, methine), 3.35–2.25 (m, 4 H, CH_2). The nmr spectrum indicates this to be the cis isomer. A weak pentuplet at δ 4.66 indicates the presence of small amounts of the trans isomer. Glpc showed this sample to be about 95% of one isomer.

Anal. Calcd for $C_4H_6Cl_2$: C, 38.42; H, 4.84; Cl, 56.73. Found: C, 38.64, 39.02; H, 5.21, 5.17; Cl, 56.88.

1,1-Dichloro-3-*tert*-butoxycyclobutane. To 108 g (0.52 mol) of phosphorus pentachloride in 200 ml of carbon tetrachloride was added at 0° over 1.75 hr a solution of 71 g (0.5 mol) of 3-*tert*-butoxycyclobutanone in 100 ml of carbon tetrachloride. The mixture was stirred at 0–5° for an additional 1.5 hr, and was then poured into 500 ml of ice water. Stirring was continued until the exotherm caused by the hydrolysis of phosphorus compounds ceased. The water layer was extracted with three 40-ml portions of carbon tetrachloride, and the combined organic phase was washed with two 350-ml portions of water, 100 ml of saturated sodium bicarbonate solution, 350 ml of water, and 200 ml of saturated salt solution. The solvent was distilled and the residue was quickly distilled into a cold (−78°) receiver under full vacuum. Distillation of the volatiles gave 35 g (50%) of 1,1-dichloro-3-*tert*-butoxycyclobutane: bp 26–28° (0.1 mm); $n^{25}\text{D}$ 1.4500; ir, 3.33, 3.46, 7.18, 7.28, 7.33 μ; nmr (CCl_4) δ 4.24 (~p, 1 H, methine) 2.6–3.4 (m, 4 H, CH_2), 1.12 (s, 9 H, CH_3). Pure product is stable indefinitely at room temperature, but impure material deteriorates on standing.

Anal. Calcd for $C_8H_{14}OCl_2$: C, 48.75; H, 7.16; Cl, 35.98. Found: C, 48.55; H, 7.19; Cl, 36.33.

1,1,3-Trichlorocyclobutane. To 33 g (0.159 mol) of phosphorus pentachloride was added all at once 30 g (0.152 mol) of 1,1-dichloro-3-*tert*-butoxycyclobutane. The temperature of the mixture rose to 35°. After 300 μl of boron trifluoride etherate was added, the temperature of the mixture was raised to 55°. Addition of another 100 μl of boron trifluoride etherate caused the temperature of the mixture to rise to 89° immediately, accompanied by refluxing and foaming. When the temperature of the mixture began to drop, it was refluxed (~90°) for 0.5 hr and then cooled. The mixture was poured into 300 ml of ice water, which was then extracted with one 100-ml portion and three 50-ml portions of ether. The ether was washed with three 100-ml portions of water, 100 ml of dilute sodium bicarbonate solution, and 100 ml of saturated salt solution, and was dried over magnesium sulfate. Solvent was removed, and the residue was distilled to give 7.2 g of starting material and 12 g (64%) of 1,1,3-trichlorocyclobutane: bp 86° (120 mm); $n^{25}\text{D}$ 1.4798; ir 3.32, 3.38 μ; nmr (neat) δ 4.48 (~p, 1 H, methine), 2.9–3.8 (m, 4 H, CH_2).

Anal. Calcd for $C_4H_5Cl_3$: C, 30.12; H, 3.16; Cl, 66.69. Found: C, 30.32; H, 3.33; Cl, 66.37.

1,3-Dichlorocyclobutane from Reduction of 1,1,3-Trichlorocyclobutane. To 30 g (0.189 mol) of 1,1,3-trichlorocyclobutane at 100–125° was added tributyltin hydride until starting material was no longer present. Volatiles were collected in a cold (−78°) trap at reduced pressure and then redistilled to give several fractions containing varying ratios of *cis*- and *trans*-1,3-dichlorocyclobutane. The cut richest in the trans isomer showed: bp 76–78° (150 mm); nmr (neat) δ 4.65 (p, splitting = 6 Hz, 2 H, methine), 2.76 (t, splitting = 6 Hz, 4 H, CH_2). The cut richest in the cis isomer showed the same nmr spectrum as that exhibited by the 1,3-dichlorocyclobutane prepared from 3-*tert*-butoxycyclobutanol and thionyl chloride.

3-Chlorocyclobutane-1-carbonitrile (24). A mixture of 133 g (1.07 mol) of 1,3-dichlorocyclobutane, 21 g (0.428 mol) of sodium cyanide, and 133 ml of dimethyl sulfoxide was heated at 95° for 48 hr. The mixture was cooled, diluted with 900 ml of water, and extracted with one 300-ml portion and three 100-ml portions of ether. The ether was washed with three 200-ml portions of water and 100 ml of saturated salt solution and dried. Solvent was removed, and the residue was distilled to give 93.7 g (0.75 mol) of 1,3-dichlorocyclobutane, bp 70–72° (81 mm), and 18.6 g (0.16 mol) of 3-chlorocyclobutane-1-carbonitrile, bp 79–83° (15 mm) (50% based on recovered starting material). This material was compared with authentic material.[10]

3-*tert*-Butoxycyclobutanone Cyanohydrin (26). To 6.1 g (0.226 mol) of liquid hydrogen cyanide (**caution**: all work with hydrogen cyanide should be carried out in an efficient hood) at −10° was added all at once, 32.1 g (0.226 mol) of 3-*tert*-butoxy cyclobutanone. The solution was allowed to warm to 25°, and 110 μl of triethylamine was added. The temperature quickly rose to 60° and a cooling bath was applied. The temperature reached 68° and then started to fall. The cooling bath was removed and the solution was stirred overnight. An infrared spectrum of the viscous material showed strong hydroxyl absorption, and only weak carbonyl absorption. An nmr spectrum (neat) showed δ 4.72 (s, 1 H, OH), 4.06 (~p, 1 H, methine), 2.7–3.3 (m, 2 H, CH_2), 2.0–2.6 (m, 2 H, CH_2), 1.7 (s, 9 H, CH_3). A small spike at δ 1.22 may indicate a small amount of another isomer. The nmr spectrum and the results of following experiments suggest that the major isomer is the compound with cis oxygen functions.

1-Chloro-3-*tert*-butoxycyclobutane-1-carbonitrile (27). A solution of 115 g (0.441 mol) of triphenylphosphine and 62 g (0.367 mol) of 3-*tert*-butoxycyclobutanone cyanohydrin in 375 ml of carbon tetrachloride was heated under nitrogen to 70°, and then the heat source was removed. The solution reached 78° over the next 20 min, and was then cooled because of vigorous refluxing. When the temperature of the solution dropped steadily, heat was applied, and a temperature of 75–80° was maintained for 2 hr. The mixture was cooled, and solvent was removed under reduced pressure until a wet, brown solid remained. About 500 ml of ether was added to the residue, and the triphenylphosphine oxide was filtered off. The ether was removed under reduced pressure and the residue was distilled into a cold (−78°) trap under reduced pressure. Distillation of the volatile material gave 47.1 g (69%) of **27**: bp 45° (0.25 mm); $n^{25}\text{D}$ 1.4468; ir 3.40, 4.49, 7.0, 8–9 μ; nmr (neat) δ 4.54 (~p, 1 H, methine), 2.7–2.95 (two broad lines, 4 H, CH_2), 1.12 (s, 9 H, CH_3). The nmr spectrum indicates that the isomer formed has the oxygen and chlorine in a trans relationship.

Anal. Calcd for $C_9H_{14}NClO$: C, 57.59; H, 7.52; N, 7.46; Cl, 18.89. Found: C, 57.77; H, 7.80; N, 7.82, 7.66; Cl, 19.15.

1,3-Dichlorocyclobutane-1-carbonitrile (28). To 53 g (0.255 mol) of phosphorus pentachloride was added all at once, 39.5 g (0.211 mol) of 1-chloro-3-*tert*-butoxycyclobutane-1-carbonitrile followed by 200 μl of boron trifluoride etherate. The mixture was heated to 40°, where an exothermic reaction took place with the rapid evolution of gas. The heat source was removed and the reaction proceeded until a temperature of 90° was reached. When the initial reaction had subsided, 100 μl of boron trifluoride etherate was added and the solution was heated at 77° for 2.5 hr. Glpc analysis showed the presence of starting material, and therefore 4 g of phosphorus pentachloride was added. The addition caused considerable evolution of gas, but glpc showed that starting material was still present. Therefore, 8 g of phosphorus pentachloride and and 100 μl of boron trifluoride etherate were added, and heating was continued for 0.5 hr. No starting material remained at the end of this time. The mixture was cooled and poured with stirring into 300 ml of ice water. (**Caution!** There was a delayed exothermic reaction which should be observed before proceeding further.) The water was extracted with four portions of ether, which were then extracted twice with water, once with sodium bicarbonate solution, once with water, and once with saturated sodium chloride solution. The solution was dried and the solvent was removed under reduced pressure. Distillation of the reside gave 18.7 g (59%) of **28**, bp 67° (10 mm). The product crystallized on standing. An nmr spectrum (neat) showed δ 4.45 (~p, 1 H, methine), 3.35–3.80 (m, 2 H, CH_2), 2.7–3.25 (m, 2 H, CH_2). This spectrum indicates that the compound has the chlorines in a cis relationship. The nmr and ir spectra were identical with those of authentic material.[10]

Bicyclobutane-1-carbonitrile (25). To 15 ml of THF and 0.25 g (0.0104 mol) of magnesium turnings was added several drops of 1,2-dibromoethane. The mixture was heated to reflux to activate the magnesium and then cooled to 25°. To this mixture was added all at once, 1.5 g (0.01 mol) of 1,3-dichlorocyclobutane-1-carbonitrile. The reaction started in about 10 min and maintained itself at 30–32°. After 96 hr the mixture was poured into water and extracted with ether. Removal of solvent gave a liquid which proved to be a mixture of THF and **25** (nmr and glpc of authentic material[10]). During the work-up, extensive polymerization occurred.