A Stabilized Cyclopropyl Cation. Synthesis and Solvolysis of 1-Chlorobicyclopropyl[1,2]

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Abstract: The silver ion assisted acetolysis of 1-chlorobicyclopropyl (**2**), prepared by vapor phase chlorination of the parent hydrocarbon, produced only unrearranged 1-acetoxybicyclopropyl (**8**) (42.6%) and a mixture of *trans*- and *cis*-enol acetates **9** and **10** (34.8 and 22.6%). Similarly, silver ion assisted hydrolysis of chloride **2** produced ethyl cyclopropyl ketone, presumably *via* the intermediate 1-bicyclopropanol (**13**). Both solvolyses represent unique examples of a cyclopropyl cation which does not undergo rearrangement in preference to a direct reaction with the nucleophilic solvent. Rate data for solvolyses in 50 vol % aqueous ethanol were measured: 1-chlorobicyclopropyl, 70°, 2.74×10^{-5} sec^{-1}; 95°, 1.58×10^{-4} sec^{-1}; $\Delta H^{\ddagger}$, 16.9 kcal/mole; $\Delta S^{\ddagger}$, −30.4 eu; 1-chloro-1-isopropylcyclopropane, 150°, 2.78×10^{-6} sec^{-1}.

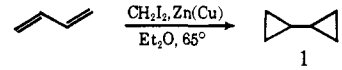
Although the low solvolytic reactivity of cyclopropyl derivatives has been variously ascribed to inductive, resonance, and steric factors,[3-5] more detailed consideration of the bond angle strain arguments by Schleyer[6] have implied a solvolysis transition state which involves a partially opened cyclopropane ring and extensive charge delocalization. This general viewpoint has been supported by observations of substantial rate enhancements (relative to the unsubstituted compounds) in the solvolyses of various 2-substituted cyclopropyl halides[7] and 2-alkyl-[8] and 2-arylcyclopropyl tosylates.[9]

In sharp contrast to the relatively low reactivities of cyclopropyl halides and tosylates are the unusually rapid solvolysis rates of cyclopropylcarbinyl derivatives, a phenomenon which has been the subject of considerable interest[10] and which has generally been rationalized by considerations of a highly delocalized carbonium ion like transition state.[11]

In the present study the unique structural features of the cyclopropyl and cyclopropylcarbinyl systems have been incorporated into a single reaction site in order to further our understanding of solvolytic behavior of various cyclopropyl derivatives.

Starting Materials

Although bicyclopropyl has been prepared by a variety of techniques in low over-all yield,[12] it was most conveniently synthesized in an average yield of 16% (based on 1,3-butadiene) and in high purity by a modification of the procedure of Wittig and Wingler[13] in which the Simmons–Smith reaction was carried out on 1,3-butadiene at 65° in an autoclave.[14]



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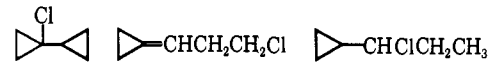
Bicyclopropyl was photochlorinated in the vapor phase. Because of the difficulty of being able to exactly reproduce various experimental conditions such as the chlorine to hydrocarbon ratio, the vapor temperature, and the light intensity and wavelength distribution of the sunlamps, the product distribution showed variations from run to run, but in general five monochloride products, a–e, were produced with an average distribution (three runs) of 5.7, 88.7, 1.0, 3.6, and 1.0%, respectively (order of increasing retention times on a β,β'-oxydipropionitrile vpc column). Analysis of the monochloride mixture by vpc before and after treatment with aqueous potassium permanganate clearly indicated that only chlorides d and e were unsaturated.

The major product b, obtained in an over-all yield of 30–44% based on bicyclopropyl consumed, was identified on the basis of its elemental analysis, nmr, infrared, and mass spectra (see Experimental Section) as 1-chlorobicyclopropyl (**2**). Similar spectral and analytical data were used to identify a collected sample of d as α-(2-chloroethyl)methylenecyclopropane (**3**).



2 3 4

In view of the known facility of the interconversion

(1) Taken from the M.S. and Ph.D. Dissertations of L. W. Becker, University of Kansas, 1967. Partial support of this work by a University of Kansas grant and a grant from the Socony Mobil Company is gratefully acknowledged.

(2) A preliminary account of this work has appeared: J. A. Landgrebe and L. W. Becker, *J. Am. Chem. Soc.*, **89**, 2502 (1967).

(3) J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5034 (1951), and references cited therein.

(4) H. C. Brown, R. S. Fletcher, and R. B. Johannesen, *ibid.*, **73**, 212 (1951).

(5) J. H. Cromwell and M. A. Graff, *J. Org. Chem.*, **17**, 414 (1952).

(6) P. von R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.*, **83**, 182 (1961).

(7) (a) J. A. Landgrebe and D. E. Applequist, *ibid.*, **86**, 1536 (1964); *cf.* ref 8 therein; (b) J. A. Landgrebe and L. W. Becker, *J. Org. Chem.*, in press.

(8) P. von R. Schleyer, G. W. Van Dine, U. Schöllkopf, and J. Paust, *J. Am. Chem. Soc.*, **88**, 2868 (1966).

(9) C. H. DePuy, L. G. Schnack, and J. W. Hausser, *ibid.*, **88**, 3343 (1966).

(10) (a) M. J. S. Dewar and A. P. Marchand, *Ann. Rev. Phys. Chem.*, **16**, 321 (1965); (b) N. C. Deno, *Progr. Phys. Org. Chem.*, **16**, 321 (1965); (c) R. Breslow *in* "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 4.

(11) P. von R. Schleyer and G. W. Van Dine, *J. Am. Chem. Soc.*, **88**, 2321 (1966), and references cited therein.

(12) (a) V. A. Slabey, *ibid.*, **74**, 4928 (1952); (b) M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 1689 (1962); (c) C. G. Overberger and G. W. Halek, *J. Org. Chem.*, **28**, 867 (1963).

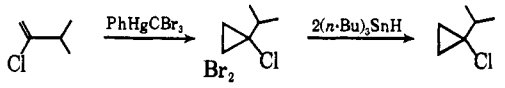
(13) G. Wittig and E. Wingler, *Chem. Ber.*, **97**, 2146 (1964).

(14) Hydrocarbon **1** was also prepared by the treatment of 2,3-bis(bromomethyl)-1,4-dibromobutane with zinc dust and disodium dihydrogen ethylenediaminetetraacetate, but the product was contaminated with an equal amount of 2,3-dimethyl-1,3-butadiene and the over-all yield from malonic ester was quite low (see Experimental Section).

of cyclopropylcarbinyl and allylcarbinyl radicals,[15] the presence of unsaturated chloride **3** is quite reasonable and completely analogous to the production of similar unsaturated products in the vapor phase chlorination of methylcyclopropane[16] and spirohexane.[17]

The isolated major component b from additional larger scale vapor phase chlorinations of **1**, although it appeared to be homogeneous on several vpc columns, gave rise to solvolysis products (*vide infra*) characteristic of those expected from the presence of both chloride **2** and 1-chloro-1-cyclopropylpropane (**4**), the expected product of hydrogen chloride attack on one ring of the bicyclopropyl.[17] The presence of chloride **4** was verified by suitable spectral and solvolysis product comparisons with a sample prepared by treatment of the corresponding alcohol with thionyl chloride and pyridine.

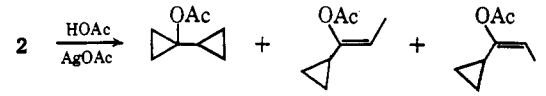
A suitable model system with which to compare the rate of solvolysis of chloride **2** is 1-chloro-1-isopropylcyclopropane (**7**) which was synthesized in 57.5% yield from 2-chloro-3-methyl-1-butene (**5**) as indicated below.



5 **6** **7**

Solvolysis Studies

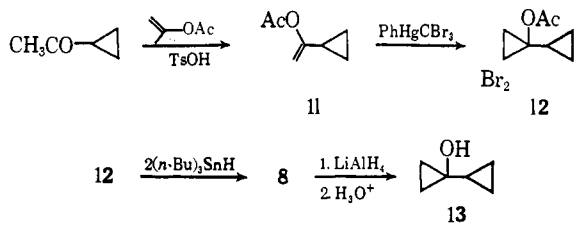
Products. The acetolysis of 1-chlorobicyclopropyl (**2**) carried out at 115° for 72 hr in the presence of silver acetate produced a mixture of 42.6% 1-acetoxybicyclopropyl (**8**) and 34.8 and 22.6%, respectively, of the *trans*- and *cis*-enol acetates **9** and **10** of ethyl cyclopropyl ketone.[18]



8 **9** **10**

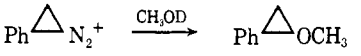
Acetate **8** was characterized by nmr, infrared, and vpc comparison with a sample prepared from methyl cyclopropyl ketone by the route indicated in Scheme I. The gross structure of enol acetates **9** and **10** was readily apparent from nmr and infrared spectral data

Scheme I



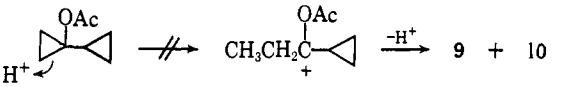
on collected samples (see Experimental Section), and the stereochemistry was assigned on the basis that the allylic methyl doublet of *cis* isomer **10** appeared 0.23 ppm upfield of that from **9**, consistent with the expected diamagnetic shielding effect of the cyclopropane ring.[19]

The isolation of a large fraction of unrearranged acetate **8** in the acetolysis of chloride **2** represents the first example in which the solvolysis of any simple cyclopropyl derivative did not result in the exclusive formation of products from ring opening to the allylic ion. Although reports have appeared that the nitrous acid deamination of apotricyclylamine,[20] 1-aminonortricyclene,[21] and 3-amino-1,2-cyclopropanoacenaphthene[22] resulted in unrearranged products, the results can be explained by considerations of orbital symmetry requirements during the electrocyclic transformation to the allylic structure[9,23] or by the assumption that the mechanism may have been free radical in nature[24] rather than involving a carbonium ion. More recently Kirmse and co-workers[25] have isolated very small amounts (*ca.* 0.3% yield) of 2-phenylcyclopropyl methyl ether from the decomposition of N-nitroso-N-2-phenylcyclopropylurea with excess sodium formate in methanol, a process which is believed to involve a cyclopropyl cation intermediate. Similarly, Turro and Hammond[26] have suggested that a 1-hydroxycyclopropyl cation may



be an intermediate in the observed facile addition of acetic acid or hydrogen chloride to the carbonyl group of cyclopropanone.[27]

The mode of formation of enol acetates **9** and **10** is not entirely clear.



Although one might imagine an acid-catalyzed opening of the acetate-substituted ring of **8** and subsequent loss of a proton to give **9** and **10**, treatment of **8** with acetic acid and silver acetate at 115° for 5 days resulted in the recovery of all of the starting compound. In addition, the acetolysis of **2** in the presence of sodium acetate produced **8**, **9**, and **10** in essentially the same proportions, 40.6, 36.2, and 23.2%, as in the presence of silver acetate, a result which suggests that there may be a common first step in the formation of **8**, **9**, and **10**, but further investigation is necessary to clarify this point.

The silver ion assisted hydrolysis of chloride **2** which contained chloride **4** as a major contaminant of the vapor phase chlorination gave five products in significant amounts.[29] The major product (50%) and,

(15) T. A. Halgren, M. E. H. Howden, M. E. Medof, and J. D. Roberts, *J. Am. Chem. Soc.*, **89**, 3051 (1967); (b) L. K. Montgomery and J. W. Matt, *ibid.*, **89**, 3050 (1967); (c) D. C. Neckers, *Tetrahedron Letters*, 1889 (1965); (d) E. S. Huyser and J. D. Taliaferro, *J. Org. Chem.*, **28**, 3443 (1963).

(16) H. C. Brown and M. Borkowski, *J. Am. Chem. Soc.*, **74**, 1894 (1952).

(17) D. E. Applequist and J. A. Landgrebe, *ibid.*, **86**, 1543 (1964).

(18) 1-Acetoxy-1-cyclopropylpropane and *trans*-3-hexenyl acetate were also present as acetolysis products of the contaminant chloride **4**.

(19) (a) K. Tori and K. Kitahonki, *J. Am. Chem. Soc.*, **87**, 386 (1965); (b) T. Norin and K. Forsen, *Tetrahedron Letters*, 2845 (1964); (c) D. J. Patel, M. E. Howden, and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 3218 (1963).

(20) L. Lipp and C. Padberg, *Chem. Ber.*, **54B**, 1316 (1921).

(21) H. Hart and R. H. Martin, *J. Am. Chem. Soc.*, **82**, 6362 (1960).

(22) R. Pettit, *ibid.*, **82**, 1972 (1960).

(23) S. J. Cristol, R. M. Sequeira, and C. H. DePuy, *ibid.*, **88**, 4007 (1966); R. B. Woodward and R. Hoffman, *ibid.*, **87**, 395 (1965).

(24) K. V. Scherer, Jr., and R. S. Lunt, III, *ibid.*, **88**, 2860 (1966).

(25) W. Kirmse and H. Schütte, *ibid.*, **89**, 1284 (1967).

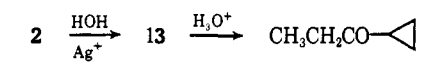
(26) N. J. Turro and W. B. Hammond, *ibid.*, **89**, 1028 (1967).

(27) It is interesting to note that the methanolyses of the various corresponding chlorides produced only allylic products in spite of the potential stabilization of an intermediate cyclopropyl cation by oxygen.[28]

(28) Professor D. Schöllkopf, private communication, 1967.

(29) Two additional products each representing $\leq 1\%$ of the total product mixture were also noted, one of which was tentatively identified from vpc data as 1-cyclopropyl-1-propanol.

based on the acetolysis results, perhaps the only product which arose from the hydrolysis of chloride **2**, was ethyl cyclopropyl ketone (**14**) identified by infrared spectral comparison of a collected sample with authentic material. The formation of ketone **14** undoubtedly occurs by way of the acid-catalyzed ring opening of an intermediate 1-bicyclopropanol (**13**), this reaction having been well established for a variety of 1-substituted cyclopropanols.[30] 1-Bicyclopropanol prepared by the lithium aluminum hydride reduction of acetate **8** (Scheme I), when subjected to solvolysis in 50 vol % aqueous ethanol (solvent for the kinetic study) which contained 0.2 *M* hydrochloric acid,[31] was converted entirely to ketone **14** at a rate qualitatively much faster than the rate of solvolysis of chloride **2**.



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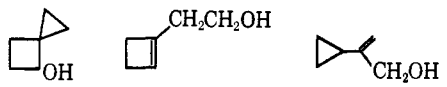
A second product (21.5%) was identified as *trans*-3-hexen-1-ol by comparison of the infrared spectrum of a collected sample with that from authentic material. The compound is an expected product of solvolysis of chloride **4**.

Although no positive identification of the remaining three products was made, it was noted that the two of these which were not completely resolved by vpc (total of 8.9% of the product mixture) and the third product (18.2%) had retention times which did correspond to those of several unidentified products of hydrolysis of a small sample of chloride **4** prepared from the corresponding alcohol (see Experimental Section). Of particular significance was the fact that the nmr spectrum of a small collected sample of the 18.2% fraction showed no olefinic or cyclopropyl hydrogens and is therefore not compatible with structures **15**, **16**, or **17** which might have been expected as additional solvolysis products of chloride **2**.



15 16 17

Kinetics. The rate data for the aqueous ethanolysis of chloride **2**[32] and several closely related model compounds appear in Table I.

Consistent with the fact that 1-chlorobicyclopropyl gives solvolysis products atypical of those expected from a cyclopropyl halide, the compound also solvolyzes at a rate considerably faster than that for cyclopropyl chlorides. A comparison of the aqueous ethanolysis rates at 150° for the isopropyl-substituted **7** with the cyclopropyl-substituted **2** indicates a 1355-fold rate difference. In view of the expected similarity in the inductive effects of the cyclopropyl and isopropyl groups,[33] the observed rate enhancement by cyclopropyl must be attributed to charge delocalization similar to that believed to be responsible for the unusually high solvolytic reactivity of the cyclopropylcarbinyl system.[11] However it should be noted that the solvolysis rate of **2** at 50° is slightly less than that for cyclopropylcarbinyl chloride at the same temperature, a fact which may reflect an increase in the energy of the transition state for the solvolysis of **2** because of ring strain introduced by one of the cyclopropyl groups. Although the detailed structure of the transition state cannot be accurately determined from the available information, it is clear from the isolation of unrearranged products that there is considerable positive charge density on the cyclopropyl carbon atom.

It should be pointed out for the purpose of comparison that the acetolysis rate enhancement observed upon introduction of a 1-phenyl substituent into cyclopropyl tosylate is *ca.* 13,000 at 108°, and no 1-phenylcyclopropyl acetate was found.[9,37]

Table I. Absolute and Relative Solvolysis Rate Data for Selected Alkyl Chlorides in 50 Vol % Aqueous Ethanol

Chloride	Temp, °C	k, sec^{-1}	Rel rate 150°	Rel rate 50°
Cyclopropyl	150	1.32×10^{-8} [a]	1.0	
1-Isopropylcyclopropyl (**7**)	150	2.78×10^{-6} [b]	211	
1-Bicyclopropyl (**2**)	50	5.72×10^{-6} [c]		0.0458
	70	2.74×10^{-5} [b]		
	95	1.58×10^{-4} [b]		
	150	3.77×10^{-3} [c]	286,000	
Cyclopropylcarbinyl	50	1.25×10^{-4} [d]		1.0
1-Cyclopropylethyl (**4**)	20	5.2×10^{-2} [e]		

[a] Estimated from tosylate[3] and chloride[7a] solvolysis data by assuming the same relative rates for cyclopropyl *vs.* cyclohexyl for the chlorides as for the tosylates. [b] This work; average deviation for two runs is ±0.4%. [c] Extrapolated value determined using $\Delta H^{\ddagger}$ 16.9 kcal/mole and $\Delta S^{\ddagger}$ −30.4 eu from data at 70 and 95°. [d] E. F. Cox, M. C. Caserio, M. S. Silver, and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 2719 (1961). [e] M. Nikoletić, S. Borčić, and D. E. Sunko, *Tetrahedron*, **23**, 649 (1967).

Experimental Section[38]

Tetraethyl 1,1,2,2-Ethanetetracarboxylate. The compound was prepared by the method of Bailey and Sorensen[39] in 51% yield from malonic ester. The average melting point was 75–76° (lit.[39] 75–76°).

2,3-Bis(hydroxymethyl)-1,4-butanediol. This tetraol was prepared in 58–65% yield by lithium aluminum hydride reduction

(30) C. H. DePuy, F. W. Breitbeil, and K. R. DeBruin, *J. Am. Chem. Soc.*, 88, 3347 (1966), and references cited therein.

(31) The acid concentration corresponds to *ca.* 50% reaction of chloride **2** under the experimental conditions employed for the kinetic study.

(32) It should be noted that the sample of **2** used in the kinetic study contained ≤5% contamination by chloride **4**. Because of the very rapid solvolysis of **4**, good first-order kinetics for **2** were obtained after the first few minutes.

(33) The measured σ_m values for the cyclopropyl group are −0.102[34] and −0.07[35] while that for the isopropyl group can be estimated as *ca.* −0.085.[36]

(34) Determined from the pK_a (5.90) of *m*-cyclopropylbenzoic acid in 50 vol % aqueous ethanol at 25.0° by Dr. Ronald H. Rynbrandt.

(35) J. Smejkal, J. Jones, and J. Furkas, *Collection Czech. Chem. Commun.*, **29**, 2950 (1964).

(36) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

(37) See data in Table I of ref 2.

(38) Melting points were determined on a Thomas-Hoover capillary melting point apparatus and corrected. Boiling points are uncorrected. Infrared spectra were taken on a Beckman IR-8 double-grating spectrophotometer with a 1601-cm^{-1} absorption (polystyrene *vs.* air) as standard. All nmr spectra were measured on a Varian A-60 spectrometer and chemical shifts are expressed in ppm relative to an internal tetramethylsilane standard (τ scale). Vapor phase chromatographic analyses were effected on a F & M Model 700 instrument with a thermal conductivity detector, or an Aerograph Model 600 instrument with a flame ionization detector. Elemental analyses were performed by Weiler and Strauss, Oxford, England, or by Huffmann Laboratory, Knoxville, Tenn.

(39) W. J. Bailey and W. R. Sorenson, *J. Am. Chem. Soc.*, 78, 2287 (1956).

of tetraethyl 1,1,2,2-ethanetetracarboxylate according to the procedure of Bailey and Sorenson[39] with the exception that the crude product was recrystallized from a 50 vol % ethanol–dioxane solution, mp 112–114° (lit.[39] 114°).

2,3-Bis(bromomethyl)-1,4-dibromobutane. Phosphorus Tribromide Method. Phosphorus tribromide (145 g, 0.52 mole) was slowly (4 hr) added to 2,3-bis(hydroxymethyl)-1,4-butanediol (37.5 g, 0.25 mole) which was gradually heated to 90° in an oil bath. After the addition was complete the reaction mixture was maintained at 170° for 15 hr. Higher temperatures caused charring. The hot orange-red solution was poured into ice water (100 ml) and stirred until a red precipitate appeared, which was then filtered, washed several times with boiling water (100-ml portions), and washed with cold absolute ethanol. Recrystallization from acetone or carbon tetrachloride gave 54.0 g (0.1344 mole, 53.7% yield) of the tetrabromide, mp 94–95°. The infrared spectrum (CCl_4) showed absorptions at 3010–2850 and 1460–1420 cm^{-1} in addition to peaks at lower frequency. The nmr spectrum showed a complex absorption at 5.7–6.6 (8 H) and a broad absorption at *ca.* 7.4–7.9 (2 H).

Anal. Calcd for $C_6H_{10}Br_4$: C, 17.93; H, 2.51. Found: C, 18.20; H, 2.59.

2,3-Bis(bromomethyl)-1,4-dibromobutane. Tosylate Displacement Method. Freshly distilled pyridine (350 ml) and 2,3-bis(hydroxymethyl)-1,4-butanediol (10.0 g, 0.0667 mole) were stirred in a flask equipped with a drying tube and cooled to −10° with an ice–salt bath. *p*-Toluenesulfonyl chloride (80.0 g, 0.408 mole) was added to the diol solution in *ca.* five equal portions over a period of 1 hr while the temperature was maintained at −5 to −10°. Pyridinium hydrochloride began to separate after *ca.* 30 min and caused the mixture to become viscous. After 9 hr the reaction mixture was poured into ice water (500 ml), and the resulting flocculent off-white precipitate was filtered, washed with 100-ml portions of absolute ethanol and ether, and dried to give 41.5 g (0.0572 mole, 85.8% yield) of the tetratosylate of the starting tetraol, mp 149–150°.

Anhydrous lithium bromide (100 g, 1.15 moles) was added to a solution of the tosylate in 300 ml of anhydrous acetone and was maintained at reflux for 7 hr. The cooled solution was diluted with water, 1000 ml, and the resulting white precipitate was filtered to give 19.0 g (0.0473 mole, 82.7% yield) of the tetrabromide, mp 94–96°, in an over-all yield of 70.9% based on the tetraol.

Zinc Ring Closure of 2,3-Bis(bromomethyl)-1,4-dibromobutane. The general method of Applequist[40] was followed. Disodium dihydrogen ethylenediaminetetraacetate dihydrate (107.0 g, 0.288 mole), sodium hydroxide (25.9 g, 0.647 mole) dissolved in water (64 ml), 95% ethanol (184 ml), and sodium iodide (2.58 g, 0.0172 mole) were placed into a 500-ml, three-necked Morton flask equipped with a high-speed stirrer (Nester and Faust), a solids-addition apparatus, and a 12-in. Vigreux distilling head arranged for distillation into a Dry Ice trap. The mixture was heated to *ca.* 75° and zinc dust (26.4 g, 0.41 g-atom) was slowly added. A slow stream of nitrogen was passed through the system to carry volatile products to the cold trap while 2,3-bis(bromomethyl)-1,4-dibromobutane (40.2 g, 0.10 mole) was added slowly (*ca.* 1 hr) to the stirred mixture at reflux. The reaction mixture was maintained at reflux for 0.5 hr after addition was completed.

The aqueous ethanolic condensate in the cold trap was mixed with ether, washed with two 150-ml portions of saturated sodium chloride solution, and dried over magnesium sulfate and calcium hydride. Two products were formed and shown by vpc analysis (20% β,β′-oxydipropionitrile on Chromosorb P, 12 ft, 35°) to be in a *ca.* 1:1 ratio. The nmr spectrum of the mixture showed a singlet at 8.03 (3 H), an unresolved doublet at 4.73 (2 H), and a complex absorption at 8.6–10.2. The latter absorption was identical with a nmr spectrum of pure bicyclopropyl. A portion of the mixture gave a positive test for unsaturation (potassium permanganate in acetone). A comparison of the vpc retention times for a known mixture of bicyclopropyl and 2,3-dimethyl-1,3-butadiene was identical with the product mixture. Confirmation of the olefin identity was made by mixing the product (*ca.* 1.5 ml) with maleic anhydride (200 mg, 0.0024 mole). After *ca.* 12 hr, a solid product was filtered, washed with petroleum ether, and dried to give a quantitative yield of the correct Diels–Alder adduct, mp 77.5° (lit.[41] mp 78°). The total amount of bicyclopropyl and 2,3-dimethyl-1,3-butadiene formed (6.32 g, 0.077 mole, 1:1 ratio) corresponded to a 38.5% yield of each based on the tetrabromide.

Bicyclopropyl (1) from 1,3-Butadiene. The zinc–copper couple was prepared by the method of Shank and Shechter[42] from zinc dust (33.0 g, 0.5 g-atom).

Methylene iodide (300.0 g, 1.12 moles) and 400 ml of anhydrous ethyl ether were added to a 1-l. stainless steel autoclave (Parr pressure reaction vessel) equipped with an overhead stirrer. The vessel was sealed and the ether solution cooled to 5°, at which time nitrogen gas was passed into the system; the bomb was opened and 126 g (1.93 g-atoms) of freshly made zinc–copper couple was added, followed by the rapid addition of 1,3-butadiene (30 g, 0.56 mole), which had been condensed in a test tube, and iodine (1.0 g, 0.0039 mole).

The bomb was sealed, heated to 50°, and rapidly stirred. At this point, heating was discontinued since the reaction became very exothermic and caused the temperature to rise to *ca.* 130° during the next hour. After the temperature had dropped to 65°, it was maintained at this point for 24 hr. The bomb was then cooled to room temperature and vented; the solution was filtered through a Super-Cel pad to remove the excess zinc. The pad was washed twice with 100-ml portions of ether, and the combined etherate solution was then transferred to a 2-l. separatory funnel and washed successively with three 300-ml portions of 5% aqueous hydrochloric acid, three 300-ml portions of saturated sodium bicarbonate solution, and three 300-ml portions of saturated sodium chloride solution. The slightly yellow ether solution was then dried over anhydrous magnesium sulfate. The ether was removed by careful distillation on a 2-ft, wire-spiral column until the head temperature started to drop, at which time the column was heated to *ca.* 70°, and the pot temperature increased very slowly until a fraction was collected between 70 and 74° (mostly at 74°.)

The bicyclopropyl fraction (7.3 g, 0.089 mole, 16% yield based on 1,3-butadiene) exhibited a vpc purity of 99% (Carbowax 20M, 10 ft, 90°). The nmr and infrared spectra were consistent with the structure.

Vapor Phase Chlorination of Bicyclopropyl. Bicyclopropyl of high purity was fractionated from calcium hydride, bp 73–74°. The chlorination utilized a 50-ml flask with a thermometer well and a chlorination apparatus similar to that used by Roberts and Mazur.[43] Two 275-w GE sunlamps were placed *ca.* 5 cm from the glass coil.

Bicyclopropyl (10.0 g, 0.122 mole) was heated in the boiler until the refluxing liquid reached the Dry Ice condenser. Chlorine gas (first passed through concentrated sulfuric acid) was added at a rate of *ca.* 0.0025 mole/min, and the sunlamps were turned on. The bicyclopropyl in the boiler turned only a light brown during the chlorination. When the temperature reached 121° (*ca.* 6 hr), the reaction was stopped, and the liquid product was distilled on a 1-ft wire-spiral column to yield 1.3 g of crude recovered bicyclopropyl, bp 70–76°, and 6.1 g of monochlorinated material, bp 115–121°, while 4.0 g of higher boiling residue remained in the flask. Vpc of the monochloride fraction (20% β,β′-oxydipropionitrile on Chromosorb P, 12 ft) showed five components (Table II). Treatment of the monochloride mixture with a solution of bromine in methylene chloride followed by vpc analysis indicated that chlorides a, b, and c were saturated while d and e were clearly unsaturated.

Table II. Monochloride Product Distribution

Compd[a]	Composition, % Run 1	Run 2	Run 3[b]
a	6.8	8.8	1.5
b	89.2	80.4	96.5
c	1.0	1.0	1.0
d	2.0	8.8	0.0
e	1.0	1.0	1.0

[a] Listed in order of increasing retention times on β,β′-oxydipropionitrile. [b] Greater chlorine flow rate than in the previous runs.

(40) D. E. Applequist, G. F. Fanta, and B. W. Henrikson, *J. Org. Chem.*, 23 1715 (1958).
(41) E. H. Farmer and F. L. Warren, *J. Chem. Soc.*, 897 (1929).
(42) R. S. Shank and H. Shechter, *J. Org. Chem.*, 24, 1825 (1959).
(43) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, 73, 2509 (1951).

The predominant peak of run 1 was collected. The nmr spectrum showed a multiplet at 8.23–8.70 (1 H, $-\overset{\frown}{C}HC\overset{\frown}{C}$) and a complex absorption at 8.70–9.85 (8 H). The infrared spectrum showed, among others, absorptions at 3100 (sharp) and 1020 cm^{-1}, but no unsaturation was indicated. Chloride **2** gave a positive alcoholic silver nitrate test and was assigned the structure 1-chlorobicyclopropyl. The average yield of this component was 30–44% based on the amount of bicyclopropyl consumed. The mass spectrum showed significant peaks for *m/e* 118, 116 (M^+), 86, 85, 84, 83, 82, 81, 80, 49, 48, 47, 44, 40, 35, 32, and 28.

Anal. Calcd for C_6H_9Cl: C, 61.81; H, 7.78; Cl, 30.41. Found: C, 61.57; H, 8.02; Cl, 30.01.

Chloride d (run 2) was collected by semimicro preparative vpc from a Carbowax 20M column. The nmr spectrum showed a symmetrical multiplet at 4.05 (1 H, $=CH$) a triplet at 6.35 (2 H, J = 7 cps, CH_2Cl), a quartet at 7.30 (2 H, J = 7 cps, $=CCH_2$) broadened by fine structure, and a narrow multiplet at 8.92 (4 H, $\overset{\frown}{C}H_2\overset{\frown}{C}H_2$). The infrared spectrum (CCl_4) showed absorptions at 3080, 2970–2830, 1440, 1430, and 1410 cm^{-1} as well as other absorptions at lower frequency but no absorption in the 1600–1700-cm^{-1} region. The compound gave a positive test with potassium permanganate in acetone and a negative test with alcoholic silver nitrate. The structure α-(2-chloroethyl)methylenecyclopropane (**3**) was assigned.

Anal. Calcd for C_6H_9Cl: C, 61.81; H, 7.78; Cl, 30.41. Found: C, 61.83; H, 7.58; Cl, 30.65.

No attempt was made to identify the other minor constituents of the monochloride fraction nor any of the polychlorides.

2-Chloro-3-methyl-1-butene (5). Isopropyl methyl ketone (86.0 g, 1.0 mole) was added rapidly to phosphorus pentachloride (250 g, 1.19 moles), and the mixture was stirred and maintained at reflux for 1 hr. Water (750 ml) was added carefully to the cold mixture (ice bath), and the organic layer was separated, dried, and fractionated to give a monochloride mixture (22.5 g, 0.211 mole), bp 77–84°, which exhibited two peaks on a QF-1 vpc column (68°), with the compound of shorter retention time in predominance (63.6%). The pot residue contained more of the isomer with longer retention time and a higher boiling material, possibly 2,2-dichloro-3-methylbutane.

The monochloride fraction (49.5 g) from two runs was fractionally distilled through a 2-ft Widmer column to give pure 2-chloro-3-methyl-1-butene (27.0 g, 0.258 mole, 12.9%), bp 77–77.5°. The nmr spectrum showed a multiplet at 4.73–5.00 (2 H), a heptet at 7.45 (1 H, J = 7 cps), and a doublet at 8.86 (6 H, J = 7 cps). The infrared spectrum showed significant absorptions at 2990 (w), 1640, 1460, 1200, 1125, 1085, 1040, 880, and 660 cm^{-1}.

Anal. Calcd for C_5H_9Cl: C, 57.42; H, 8.67. Found: C, 57.70; H, 8.57.

The higher boiling isomer from the above distillation was identified as 2-chloro-3-methyl-2-butene.

1,1-Dibromo-2-chloro-2-isopropylcyclopropane (6). A mixture of 2-chloro-3-methyl-1-butene (5.0 g, 0.0478 mole) and phenyl(tribromomethyl)mercury (22.0 g, 0.0415 mole) in dry benzene (50 ml) was maintained at reflux under a nitrogen atmosphere for 2 hr, cooled, and filtered. The filtrate was concentrated and distilled to give the desired product (8.0 g, 0.029 mole, 71.1%) as a slightly yellow oil, bp 48–49° (0.55–0.60 mm). Vpc (QF-1, 188°) showed <1% impurity. The nmr spectrum (100 MHz) showed an AB quartet at 8.04–8.29 (J = 9 cps) superimposed on a multiplet (3 H) and a pair of doublets centered at 8.83 and 8.87 (6 H, J = 4 cps). The infrared spectrum showed significant absorptions at 2975, 2950, 1455, 1420, 1385, 1370, 1345, 1190, 1052, and 950 cm^{-1}.

Anal. Calcd for $C_6H_9Br_2Cl$: C, 26.07; H, 3.28; Br, 57.82; Cl, 12.83. Found: C, 25.96; H, 3.19; Br, 57.64; Cl, 12.86.

1-Chloro-1-iospropylcyclopropane (7). 1,1-Dibromo-2-chloro-2-isopropylcyclopropane (13.0 g, 0.047 mole) was reduced with tri-*n*-butyltin hydride (29.1 g, 0.10 mole) for 90 hr to give 4.5 g (0.038 mole, 80.9%) of clear product, bp 103.5–104°. Vpc (Carbowax 1540, 80°) indicated <1% impurity. The nmr spectrum showed multiplets at 8.67–9.12 (9 H) and 9.23–9.55 (2 H). The infrared spectrum showed significant absorptions at 3030, 2975, 2880, 1420 (w), 1382, 1363, 1200, 1052, 1018, 932, and 795 cm^{-1}.

Anal. Calcd for $C_6H_{11}Cl$: C, 60.75; H, 9.35. Found: C, 60.46; H, 9.20.

α-Acetoxyvinylcyclopropane (11). Methyl cyclopropyl ketone (16.8 g, 0.2 mole), isopropenyl acetate (40.0 g, 0.4 mole), and *p*-toluenesulfonic acid (1 g) were allowed to react according to the general method of Hagemeier and Hull.[44] After the theoretical amount of acetone had been removed, the mixture was cooled and extracted with 10% aqueous sodium bicarbonate solution (100 ml). The organic layer was extracted into ether (50 ml) and dried over magnesium sulfate. Distillation gave 15.0 g of a mixture of unchanged ketone and isopropenyl acetate, bp 50–78° (54 mm), and the desired enol acetate (6.0 g, 0.0471 mole, 23.6% conversion), bp 78–83° (54 mm), which contained ≤5% impurity by vpc (Carbowax 1540, 122°).

The nmr spectrum showed a multiplet at 5.30–5.45 (2 H), a singlet at 7.95 (3 H), a multiplet at 8.35–8.77 (1 H), and a multiplet at 9.13–9.55 (4 H). The infrared spectrum showed important absorptions at 3100, 3030, 1760, 1660, 1365, 1225, 1195, 1090, 1060, 1015, 960, and 930 cm^{-1}.

Anal. Calcd for $C_7H_8O_2$: C, 66.64; H, 7.99. Found: C, 66.58; H, 8.02.

1-Acetoxybicyclopropyl (8). α-Acetoxyvinylcyclopropane (5.0 g, 0.0396 mole) in benzene (40 ml) was treated with phenyl(tribromomethyl)mercury (22.0 g, 0.0416 mole) for 2 hr at reflux and the product was obtained in the usual manner as a thick oil. The nmr spectrum showed a singlet at 7.94 superimposed on a multiplet at 7.8–8.25 (4 H), a narrow multiplet at 8.37 (2 H), and a multiplet at 9.0–10.0 (4 H). The infrared spectrum showed prominent absorptions at 3100, 3030, 1760, 1365, 1225, 1195, 1177, 1095, 1050, 1030, 1018, and 680 cm^{-1}.

The crude dibromide was reduced with tri-*n*-butyltin hydride (35.0 g, 0.12 mole) for 72 hr.[45] The product (2.78 g, 0.0199 mole, 50.2%) was obtained as a colorless liquid, bp 60–80° (0.7–1.5 mm). The nmr spectrum showed a singlet at 8.10 (3 H), a multiplet at 8.2–8.65 (1 H), and a complex multiplet at 9.0–10.0 (8 H). An infrared spectrum showed prominent absorptions at 3100, 3040, 1750, 1370, 1320, 1250, 1190, 1170, 1105, 1028, and 1020 cm^{-1}. Vpc (tris(cyanoethoxy)propane, 150°) indicated ≤5% impurity. The analysis on a collected sample is given below.

Anal. Calcd for $C_5H_{10}O_2$: C, 68.54; H, 8.63. Found: C, 68.73; H, 8.62.

1-Hydroxybicyclopropyl (13). 1-Acetoxybicyclopropyl (0.692 g, 0.00493 mole) in ether (10 ml) was reduced with lithium aluminum hydride (0.50 g, 0.0132 mole) in ether (25 ml) in the usual manner. The product (0.484 g, 0.00493 mole, 100%) was shown by vpc (Carbowax 1540, 130°) to contain ≤2% impurity and to have a retention time indistinguishable from that of ethyl cyclopropyl ketone.

The nmr spectrum showed a singlet at 6.25 (1 H) and a complex multiplet at 8.17–10.0 (9 H). The infrared spectrum showed prominent absorptions at 3620, 3350, 3100, 2975, 2940, 1455, 1395, 1210, 1095, 1045, 1020, and 1018 cm^{-1}.

1-Cyclopropyl-1-propanol. Ethyl cyclopropyl ketone (9.8 g, 0.10 mole), bp 75–78° (50 mm) (lit.[46] 48–51° (35 mm)), prepared from cyclopropanecarbonyl chloride and diethylcadmium, was reduced with lithium aluminum hydride (1.9 g, 0.05 mole) in the usual manner. The product (8.2 g, 0.082 mole, 82%), bp 75–77° (49 mm), gave an nmr spectrum which showed a broad multiplet at 6.35–6.85 (1 H), a multiplet at 6.95–7.45 (1 H), approximately a quintet at 8.1–8.7 (2 H), and a triplet at 9.05 superimposed on a complex multiplet extending from *ca.* 9.0 to 9.85 (8 H). The infrared spectrum showed prominent absorptions at 3625, 3450, 3100, 3030, 2950, 1460, 1400, 1020, and 980 cm^{-1}. Vpc (Carbowax 1540, 150°) indicated ≤1% impurity.

Anal. Calcd for $C_6H_{12}O$: C, 71.95; H, 12.08. Found: C, 72.13; H, 11.82.

1-Acetoxy-1-cyclopropylpropane. Cyclopropylethylcarbinol (1.0 g, 0.010 mole) was esterified with acetyl chloride (0.785 g, 0.010 mole) in the presence of pyridine (0.79 g, 0.010 mole) and ether (35 ml). The nmr spectrum showed a multiplet at 5.7–6.08 (1 H), a sharp singlet at 8.02 (3 H), approximately a quartet at 8.17–8.6 (2 H), and a broad triplet at 9.1 superimposed on a multiplet extending to 9.85 (8 H). The infrared spectrum showed prominent absorptions at 3100, 3030, 2990, 1735, 1370, 1245, 1085, and 1020 cm^{-1}.

1-Chlorocyclopropylpropane (4). 1-Cyclopropyl-1-propanol (6.0 g, 0.05 mole) and pyridine (3.95 g, 0.05 mole) in ether (50 ml) were treated with thionyl chloride (5.95 g, 0.05 mole) in ether (25 ml) while the mixture was stirred and maintained at ≤0°. After 1 hr at 25°, the solution was filtered to remove pyridinium hydrochloride

(44) H. J. Hagemeier and D. C. Hull, *Ind. Eng. Chem.*, **41**, 2920 (1949).

(45) D. Seyferth, H. Yamazaki, and D. L. Alleston, *J. Org. Chem.*, **28**, 703 (1963).

(46) H. Hart and O. E. Curtis, Jr., *J. Am. Chem. Soc.*, **79**, 931 (1957).

and distilled to give 3.8 g (0.032 mole, 64%) of product, bp 125–126°. Vpc (QF-1, 100°) indicated the presence of a 10% impurity.

The nmr spectrum showed a multiplet at 6.3–7.0 (1 H), a quintet at 8.1 (2 H, J = 7 cps), and a triplet at 8.9 (J = 7 cps) superimposed on a multiplet extending up to 9.7 (8 H).

trans-**3-Hexenyl Acetate.** *trans*-3-Hexen-1-ol (2.0 g, 0.02 mole, K and K Laboratories Inc., containing 40% of an isomeric *trans* alcohol) was converted to the acetate in the usual manner with acetyl chloride (1.58 g, 0.02 mole). The desired acetate was isolated by preparative vpc (tris(cyanoethoxy)propane, 105°) as a 55% component of the mixture. The nmr spectrum (100 MHz) showed a multiplet at 4.55–4.78 (2 H), a triplet at 5.9–6.2 (2 H, collapsed to a singlet when part of the 7.55–8.38 multiplet was irradiated), a multiplet at 7.55–8.38 (4 H, changed to a doublet superimposed on a multiplet when the triplet at 5.9–6.2 was irradiated), a singlet at 8.06 (3 H), and a triplet at 8.85–9.21 (3 H, collapsed to a singlet when part of the multiplet at 7.55–8.38 was irradiated). The infrared spectrum showed prominent absorptions at 2980, 1745, 1460, 1385, 1368, 1235, 1032, and 968 cm^{-1}.

Silver-Assisted Acetolysis of 1-Chloro-1-cyclopropylpropane. 1-Chloro-1-cyclopropylpropane (0.500 g, 0.00422 mole), silver acetate (1.70 g, 0.01 mole), and anhydrous acetic acid (5 ml) in a sealed ampoule were heated at 115° for 2 days. The mixture was cooled, poured into 10% aqueous sodium carbonate (50 ml), and extracted with ether. Evaporation of the dry extracts gave a yellow oil which showed two major products (86.2%) by vpc (tris(cyanoethoxy)propane, 105°). The two products, 46.9 and 53.1%, respectively, in order of increasing retention times, were collected and shown by infrared and nmr comparison with authentic samples to be 1-acetoxy-1-cyclopropylpropane and *trans*-3-hexenyl acetate.

Silver-Assisted Acetolysis of 1-Chlorobicyclopropyl. A mixture of 1-chlorobicyclopropyl and 1-chloro-1-cyclopropylpropane (0.5 g) in approximately equal amounts[47] was heated at 115° for 72 hr in a sealed ampoule with silver acetate (1.70 g, 0.010 mole) and glacial acetic acid (5 ml) followed by neutralization with 10% aqueous sodium carbonate solution, filtration, and ether extraction. The dry extracts were evaporated to a dark oil which was shown by vpc (tris(cyanoethoxy)propane, 105°) to consist of five compounds, f–j in order of increasing retention time.

Compounds f and g present in equal amounts comprised 51.6% of the product mixture and were identified by infrared, nmr, and vpc comparison of the pure collected samples with authentically prepared material, as 1-acetoxy-1-cyclopropylpropane and *trans*-3-hexenyl acetate, products from the solvolysis of 1-chloro-1-cyclopropylpropane. The remaining three products are derived from 1-chlorobicyclopropyl. A collected sample of h was shown to be 1-acetoxybicyclopropyl (42.6% of the product derived from **2**) by spectral comparison with an authentic sample.

Components i and j (34.8 and 22.6% of the products derived from **2**) were the two isomeric enol acetates **9** and **10** of ethyl cyclopropyl ketone. Compound i (methyl *trans* to cyclopropyl) gave an nmr spectrum which showed a multiplet at 3.05–3.20 (1 H, C=CH), a singlet at 7.97 (3 H, CH_3CO), a doublet at 8.45 (3 H, J = 1.5 cps, CH_3), a multiplet at 8.05–9.05 (1 H), and a multiplet at 9.25–9.68 (4 H). Irradiation (100 MHz, *p*-dioxane lock signal) of the doublet at 8.45 or the multiplet at 3.05–3.20 caused the other group to collapse to a singlet. The infrared spectrum showed significant absorptions at 3030, 1750, 1680, and 1020 cm^{-1}.

The nmr spectrum of j (methyl *cis* to cyclopropyl) showed a multiplet at 3.05–3.20 (1 H, C=CH) a singlet at 7.93 (3 H, CH_3CO), a multiplet at 8.00–8.42 (1 H), a doublet at 8.68 (3 H, J = 1.5 cps, CH_3), and a multiplet at 9.16–9.55 (4 H). The decoupling results were the same as for i. The infrared spectrum showed significant absorptions at 3030, 1750, 1675, and 1020 cm^{-1}.

Treatment of 1-acetoxybicyclopropyl with silver acetate in acetic acid at 115° for 1 week resulted only in the recovery of starting material. Vpc (tris(cyanoethoxy)propane, 105°) showed that neither of the enol acetates **9** and **10** had been formed.

Acetolysis of 1-chlorobicyclopropyl was carried out in the presence of excess sodium acetate in glacial acetic acid for 3 days at 115°. After work-up, 1-acetoxy-1-cyclopropylpropane and *trans*-3-hexenyl acetate were formed in addition to 40.6, 36.2, and 23.2% of acetates **8**, **9**, and **10**.

Silver-Assisted Hydrolysis of 1-Chlorobicyclopropyl. A mixture of 1-chlorobicyclopropyl and 1-chloro-1-cyclopropylpropane[47] (0.46 g) was heated at 65° for 24 hr in a sealed ampoule with silver nitrate (1.70 g, 0.01 mole) in water (5 ml). After filtration and extraction with ether, the extract was dried and evaporated to an oil, the vpc of which (silver nitrate, 85°) showed seven components, k–q in order of increasing retention time. Peaks k and l (8.9% total) were not identified. Peak m was shown to be ethyl cyclopropyl ketone (**14**) by nmr, infrared, and vpc comparison with an authentic sample. Peak n (<1%) was tentatively identified as 1-cyclopropyl-1-propanol on the basis of vpc retention time comparison with an authentic sample. Component o (18.2%) gave an nmr spectrum (dilute solution) which showed a multiplet at 6.00–6.85 (1 H) and a multiplet at 7.25–9.40 (11 H). The same spectrum at 100 MHz clearly showed a quartet at 9.05 (J = 7 cps). The infrared spectrum showed prominent absorptions at 3350, 2970, 1460, and 1075 cm^{-1}. Although no structural assignment was made it was noted that a small amount of a product of identical retention time was formed during the hydrolysis of a sample of 1-chloro-1-cyclopropylpropane. Compound p was identified as *trans*-3-hexen-1-ol by nmr and infrared spectral comparison with an authentic sample (K and K Laboratories). Component q (<1%) was not isolated.

Solvolysis of the mixture of **2** and **4** in 50 vol % aqueous ethanol, *i.e.*, the conditions of the rate determination for **2**, with or without sodium carbonate present produced a mixture of alcohols qualitatively identical with that observed from the silver-assisted hydrolysis.

Treatment of 1-hydroxybicyclopropyl with hydrochloric acid as a 0.1 M solution in 50 vol % aqueous ethanol at 95° for 30 min gave only ketone **14**.

Silver-Assisted Hydrolysis of 1-Chloro-1-cyclopropylpropane. Chloride **4** (0.1185 g, 0.001 mole, 90% pure) was treated with excess aqueous silver nitrate solution at 65° for 24 hr. After work-up, vpc (silver nitrate, 90°) of the dried ether extracts from the reaction mixture showed a group of products which had counterparts among the products found from the previously described silver-assisted hydrolysis of the mixture of **2** and **4** with the one exception of the ethyl cyclopropyl ketone peak which was not a product of hydrolysis of **4**.

Kinetic procedure is described elsewhere.[7b] Data from a typical run for the solvolysis of 1-chlorobicyclopropyl in 50 vol % aqueous ethanol at 95 ± 0.05° are shown in Table III.

Table III

Time elapsed, min	Titrated (HCl)	−ln (RCl)	Time elapsed, min	Titrated (HCl)	−ln (RCl)
∞	0.03923		40	0.01415	3.6864
10	0.005627	3.3939	50	0.01672	3.8062
20	0.009000	3.4996	60	0.01800	3.8500
30	0.011900	3.6000			

$k = (1.565 \pm 0.006)10^{-4}$ sec^{-1}

(47) The hydrogen chloride cleavage product **4** appeared as a shoulder of the peak for 1-chlorobicyclopropyl when the mixture was subjected to vpc analysis on a QF-1 or β,β'-oxidipropionitrile at 100°. The two compounds account for ≥90% of the material subjected to solvolysis for purposes of product identification.