

In the same way the tertiary alcohol XIII ($R = R' = H$; 250 mg.) gave, after chromatography over alumina, the 18,20-lactone XIV ($X = O$; 41 mg.).

Potassium *tert*-butoxide (2.4 g.) in benzene (90 ml.) was stirred with iodine (7.6 g.) for 5 min. before addition of 11 α -hydroxyprogesterone (XVII; 1.0 g.) in 1:1 benzene-tetrahydrofuran (10 ml.) under irradiation.³ Working up and further processing as in prior oxidations of 11 α -hydroxyprogesterone gave, on chromatography over alumina, the starting material (141 mg.) and 11 α -hydroxypregna-1,4-diene-3,20-dione (240 mg.).

Acknowledgment.—We thank Dr. M. M. Pechet for his interest and encouragement and Mrs. C. B. Pantuck and the Misses A. Scott and L. T. Gendron for their able assistance throughout the course of this work. Some preliminary experiments on the synthesis of 19-norsteroids were carried out by Dr. L. E. Geller. We thank Dr. H. R. Browning for his participation in the experiments indicated.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILL.]

Small-Ring, Spiroalkyl Cations. Solvolysis Studies on Some 1-Halospiroalkanes

BY JOHN A. LANDGREBE^{1,2} AND DOUGLAS E. APPELQUIST

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1-Chlorospirohexane and 1-chlorospiro[2.4]heptane were synthesized by the addition of chlorocarbene to methylenecyclobutane and methylenecyclopentane, respectively. The corresponding bromides were prepared from the same alkenes by the addition of dibromocarbene followed by treatment with zinc and glacial acetic acid. The ethanolysis rate constant (50% aqueous ethanol, 95°) of 1-chlorospirohexane was 1.24 times that of cyclohexyl chloride and at least 1000 times greater than that of cyclopropyl chloride. 1-Chlorospiro[2.4]heptane solvolyzed 1.98 times faster than cyclohexyl chloride. The implications of these rate measurements are discussed. The solvolysis rate of chlorospiropentane (50% aqueous ethanol, 200°) relative to cyclopropyl chloride was found to be 4-6.2. Tiglaldehyde was the only product isolated from the silver nitrate assisted hydrolysis (100°) of chlorospiropentane.

Introduction

Roberts and Chambers³ noted that in acetic acid containing 1% acetic anhydride, cyclopropyl tosylate solvolyzed 2×10^{-5} times as fast as cyclohexyl tosylate and produced allyl acetate as the sole product.

The very low solvolytic reactivity of cyclopropyl derivatives was first explained by Brown⁴ as a manifestation of excessive internal angle strain upon going to the assumed trigonal transition state.

Cromwell and Graff⁵ have explained the low solvolytic reactivity of cyclopropyl halides by a large increase in the double bond character (and hence, bond energy) caused by overlap of the halogen p-orbitals with the "bent bonds" of the cyclopropane ring.

Although the difficulty of forming the cyclopropyl cation suggests that the transition state for its formation does not resemble the completely opened resonance stabilized allylic cation, there is evidence that cyclopropyl derivatives may undergo an assisted type of solvolysis faster than one might predict on the basis of simple angle strain arguments. Schleyer⁶ has pointed out that although the bridging angle ($C_1-C_7-C_4$) of the norbornyl system is 98.3° as compared to the 60° internal angle of cyclopropane, the tosylate of the former solvolyzes about 100 times slower than that of the latter. The low reactivity in the norbornyl system has been attributed to angle strain alone, by comparison of its reactivity to corresponding adamantane derivatives.⁶ A partially opened cyclopropyl cation involving extensive charge delocalization was proposed for the transition state resulting from heterolytic reactions of cyclopropyl derivatives leading to carbonium ion intermediates.

DePuy⁷ has observed that *trans*-2-phenylcyclopropyl tosylate solvolyzed some 50 times faster than cyclopropyl tosylate at 100° (extrapolated rates), and Roberts and Snyder⁸ have also observed a solvolytic rate increase upon introduction of a *cis*- or *trans*-2-methyl group on cyclopropyl bromide. Both of these observations are consistent with some degree of charge delocalization and thus more direct substituent participation in the transition state.

In the present study, solvolysis rate measurements have been made on spiroethyl chloride and several previously unknown strained spiroalkyl halides. These rate constants, together with a knowledge of the products of solvolysis, provide further insight relative to carbonium ion formation on three-membered rings.

Results and Discussion

Synthesis.—The 1-halospiroalkanes were prepared by carbene reactions. Because of the successful reported additions of chlorocarbene to alkenes to form the corresponding chlorocyclopropanes,^{9,10} this method was applied to methylenecyclobutane (I). Chlorocarbene is normally generated by the addition of a simple alkyl lithium reagent, *e.g.*, *n*-butyllithium, to a cold solution of methylene chloride in the presence of the alkene. *n*-Propyllithium was chosen for convenience because the coupling product, *n*-hexane, can be readily separated from the product chloride II. 1-Chlorospirohexane (II) was isolated in 19.5% of the theoretical yield and showed no sign of unsaturation in the infrared spectrum.

The structure of the compound was readily confirmed from the nuclear magnetic resonance (n.m.r.) spectrum. A quartet at τ 7.15 (area 1) was assigned to the proton on the chlorine-bearing carbon atom; a broad, slightly split peak at 7.90 (area 6) was assigned

(1) Abstracted from the Ph.D. Thesis of John A. Landgrebe, University of Illinois, 1962.

(2) National Science Foundation Graduate Fellow, 1960-1962.

(3) J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, **73**, 5034 (1951).

(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).

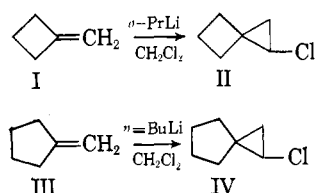
(7) C. H. DePuy, Abstracts, 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962, p. 1-O.

(8) J. D. Roberts and E. I. Snyder, private communication.

(9) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **81**, 4996 (1959).

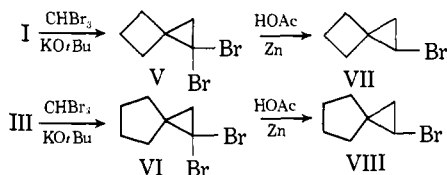
(10) G. L. Closs and L. E. Closs, *ibid.*, **82**, 5723 (1960).

to the cyclobutane protons; and two quartets at 9.00 and 9.37 (each area 1), respectively, were assigned to the two remaining nonequivalent cyclopropane protons.



1-Chlorospiro[2.4]heptane (IV) was obtained in 25.7% yield by the addition of chlorocarbene to methylenecyclopentane (III).¹¹ The n.m.r. spectrum was virtually identical in its general appearance with that of chloride II. The quartets at 7.06 (area 1), 8.97 (area 1), and 9.03 (area 1) were assigned to the three protons on the cyclopropane ring, while the complex multiplet at *ca.* 8.3 (area 8) was assigned to the cyclopentane protons.

The simple monobromospiroalkanes were prepared by removal of one bromine atom from the corresponding *gem*-dibromides. The addition of dibromocarbene¹⁴ to the alkenes I and II produced 1,1-dibromospirohexane (V) and 1,1-dibromospiro[2.4]heptane (VI) in yields of 63.4 and 43.5%, respectively. Similar results have been obtained recently by others.¹⁵ Dibromide V gave a positive alcoholic silver nitrate test and a negative test with potassium permanganate in acetone. The n.m.r. spectrum showed a singlet at 8.4 (area 2), which was assigned to the cyclopropane protons, and a complex partially resolved multiplet



at *ca.* 7.8 (*ca.* area 6), which was assigned to the cyclobutane protons. The infrared spectrum showed no unsaturation. Dibromide VI gave a similar n.m.r. spectrum with a singlet at 8.44 (cyclopropane protons), which was located at the high field edge of a complex multiplet attributed to the cyclopentane protons.

Further evidence for structure V was obtained from its conversion to spirohexane by treatment with either hydrogen and Raney nickel or lithium in tetrahydrofuran and *t*-butyl alcohol.¹⁶ Dibromide V was also treated with magnesium in dry ether to yield a small amount of material, which by analogy with similar reactions studied by Doering,¹⁷ should be vinylidene-

(11) An interesting attempt was made to prepare chloride IV by the treatment of chloromethylenecyclopentane with methylene iodide and zinc-copper couple. Although this reagent has been successfully applied to numerous alkenes to make the corresponding cyclopropane compounds,¹² no previous application has been made to a vinyl chloride. The previously unknown chloromethylenecyclopentane was prepared in a manner analogous to a preparation of chloromethylenecyclohexane.¹⁸ The chloromethylenecyclopentane was treated with methylene iodide and zinc-copper couple, first in ether under reflux at atmospheric pressure and second in a sealed pressure vessel for 24 hr. at 65°. The starting material was recovered in each case.

(12) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959).

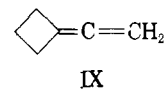
(13) D. Seyferth, S. O. Grim, and T. O. Read, *ibid.*, **83**, 1617 (1961).

(14) W. von E. Doering and A. K. Hoffmann, *ibid.*, **76**, 6162 (1954).

(15) E. Tunakubo, I. Moritani, S. Murahashi, and T. Tujii, *Tetrahedron Letters*, 539 (1962).

(16) These reductions are discussed with reference to the preparation of spirohexane in the next paper of this series: D. E. Applequist and J. A. Landgrebe, *J. Am. Chem. Soc.*, **86**, 1543 (1964).

cyclobutane (IX). The crude product gave a positive test with alcoholic mercuric chloride solution (indicative



of allenes¹⁷) and had an infrared spectrum with bands at 1980 and 1050 cm^{-1} , which have been assigned to the allene double bond system.¹⁸ A small amount of polymeric material was also formed.

1-Bromospirohexane (VII) and 1-bromospiro[2.4]heptane (VIII) were prepared in 31.1 and 56.7% yields, respectively, by treatment of the corresponding dibromides with zinc and glacial acetic acid. The infrared spectra of VII and VIII showed no unsaturation. The n.m.r. spectra were extremely similar to those of chlorides II and IV.

The n.m.r. spectra of all the 1-halospiroalkanes showed typical ABX spectra for the three protons on the cyclopropane ring. The spectrum of chloride IV, for example, consisted of an X quartet of equal signals at 171–182 c.p.s. (from tetramethylsilane at 60 Mc.) and an AB octet at 37–69 c.p.s. The spectrum was readily analyzed to yield the parameters $\nu_A = 42.4$, $\nu_B = 61.6$, $\nu_X = 176.5$, $|J_{AB}| = 6.0$, $|J_{AX}| = 4.2$, and $J_{BX} = 7.4$. The ratio $(\nu_A - \nu_B)/J_{AB}$ is too large to permit determination of the relative signs of $|J_{AX}|$ and $J_{BX}|$. The magnitudes of the coupling constants are in fair agreement with the analogous coupling constants in the cyclopropane systems recently studied by Graham and Rogers.¹⁹ Hydrogen A is almost certainly *cis* to chlorine and B is *trans*. The spectra of the other 1-halospiroalkanes resembled that of IV closely, except that the ABX system of chlorospiropentane was considerably downfield from the positions in the higher members of the series. In chlorospiropentane, $\nu_X = 196$, $\nu_B = 83$, $\nu_A = 68$.²⁰

Kinetics.—Solvolysis kinetics in 50% ethanol (volume) have been carried out on the various 1-halospiroalkyl compounds. The data are listed in Table I. A description of the kinetic procedure as well as sample raw data may be found in the Experimental section.

Note that 1-chlorospirohexane (II) and 1-chlorospiro[2.4]heptane (IV) both solvolyzed somewhat faster than cyclohexyl chloride, and considerably faster than chlorocyclopropane. Because of the inherent approximation introduced for the estimation of the chlorocyclopropane solvolysis rate at 95° (see Experimental), this value may be somewhat in error, but one can be confident from the comparison at 130°, that the introduction of a spirocyclobutane or spirocyclopentane ring to a cyclopropyl halide increased the ethanolysis rate by a factor of *ca.* 1000 or perhaps more in the case of the chloride. Bromides VII and VIII solvolyzed 48.8 and 52.8 times faster than the corresponding chlorides and thus followed the same relative rate pattern as one might have expected.²¹

(17) W. von E. Doering and P. M. LaFlamme, *Tetrahedron*, **2**, 75 (1958).

(18) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 57.

(19) J. D. Graham and M. T. Rogers, *J. Am. Chem. Soc.*, **84**, 2249 (1962).

(20) The spectrum had been described previously, but with an external calibration standard: D. E. Applequist, G. F. Fanta, and B. W. Henriksen, *ibid.*, **82**, 2368 (1960).

(21) It is noteworthy that preliminary studies by P. S. Skell (ref. 22) on the reaction of silver perchlorate with *gem*-dihalocyclopropanes indicated no electronic substituent effects on the reaction rates.

(22) P. S. Skell and S. R. Sandler, *J. Am. Chem. Soc.*, **80**, 2024 (1958).

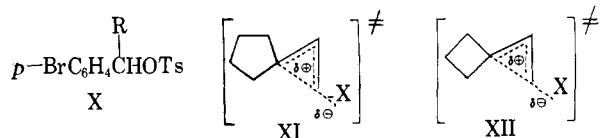
TABLE I

RELATIVE AND ABSOLUTE ETHANOLYSIS RATES OF THE 1-HALOSPIROALKANES (50% AQUEOUS ETHANOL BY VOLUME)				
Compound	Temp., ±0.05°	k, sec. ⁻¹	Relative rates—	
			95°	130°
Cyclopropyl chloride	95.00	2.5×10^{-10} ^a	2.4×10^{-3}	..
Cyclohexyl chloride	95.00	$(1.045 \pm 0.008) \times 10^{-5}$	1.00	..
II	120.00	$(1.077 \pm 0.009) \times 10^{-4}$
	95.00	$(1.299 \pm 0.005) \times 10^{-6}$ ^c	1.24	..
	120.00	$(1.669 \pm 0.004) \times 10^{-4}$ ^c
IV	95.00	$(2.07 \pm 0.01) \times 10^{-5}$	1.98	..
	120.00	$(2.310 \pm 0.007) \times 10^{-4}$
Cyclopropyl bromide	130.00	2.6×10^{-9} ^b	..	1
VII	70.00	$(4.34 \pm 0.04) \times 10^{-3}$
	95.00	$(6.36 \pm 0.03) \times 10^{-4}$	60.8	..
	130.00	2.35×10^{-3} ^d	..	904
VIII	95.00	$(1.091 \pm 0.003) \times 10^{-3}$	104.0	..

^a Calculated from tosylate solvolysis data³ by assuming the same relative rates of cyclopropyl and cyclohexyl for chlorides as for tosylates. ^b J. D. Roberts, ref. 28. ^c This value represents the average of more than one kinetic run. Individual runs are tabulated in ref. 1. ^d Extrapolated value.

Because of the very large solvolysis rate enhancement exhibited by halides II, IV, VII, and VIII when compared to the corresponding cyclopropyl halides, direct participation of the spiroalkyl group in the stabilization of the transition state is indicated. Nevertheless, it is still of interest to consider the stabilization effect that one would expect if the spiroalkyl group were to act in a purely inductive manner through the cyclopropane ring to stabilize a cation generated on one of the adjacent cyclopropane ring carbon atoms.

Streitwieser²³ has successfully correlated solvolysis reactions which involve the formation of secondary carbonium ions with Taft's σ^* -values. Consider tosylate X in which a comparison can be made between R = methyl, the standard compound, and R = cyclopentyl. By the use of $\rho^* = -3.49$ ²³ and Taft's σ^* -value for the cyclopentyl group, -0.20 ,²⁴ one finds that a first approximation to the inductive rate enhancement for the cyclopentyl group is 4.99, but this factor must now be corrected for the increased inductive transmission ability of a cyclopropyl C-C bond as



compared to the simple aliphatic C-C bond of model X. The necessary correction factor can be obtained by a comparison of the acidities of certain carboxylic acids (Table II). One needs the difference in pK between cyclopropanecarboxylic acid and *trans*-2-methylcyclopropanecarboxylic acid, 0.16, as well as the pK difference between propionic and butyric acids, 0.04, which was calculated (because of the anomalous acidity of butyric acid) from the pK difference between acetic and propionic acids, 0.12, by a reduction of this factor by three.²⁵ The rate enhancement due entirely to an inductive effect of the spirocyclopentane ring is then $4.99 \times 4.00 \cong 20$, considerably smaller than that which was observed.

(23) A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **78**, 4935 (1956).

(24) R. W. Taft, Jr., in M. S. Newman's "Steric Effects in Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1956, p. 619.

(25) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 217.

TABLE II

TABULATION OF SELECTED ACIDITIES

Compound	pK	ΔpK	Ref.
Cyclopropanecarboxylic acid	6.24		^a
<i>trans</i> -2-Methylcyclopropanecarboxylic acid	6.40	0.16	^a
Acetic acid	4.76		^b
Propionic acid	4.88	0.12	^b

^a This work. The measurement was made in 50% (volume) aqueous methanol by determination of the pH at half-neutralization. ^b J. F. J. Dippy, *Chem. Rev.*, **25**, 151 (1939).

The introduction of two methyl groups at the 3-position of allyl chloride is known to enhance the solvolysis rate (50% aqueous ethanol at 0°) by a factor of 250,000.²⁶ The methyl groups participated directly in the stabilization of the allylic carbonium ion. The enhancement factor for the solvolysis of chloride II compared to chlorocyclopropane (95°) was at best *ca.* 80,000 and may be somewhat smaller than this figure, depending upon the accuracy of the solvolysis rate of cyclopropyl chloride at 95° (see Experimental). The transition state for the ethanolysis of halides II, IV, VII, and VIII is probably best represented by a partially opened cyclopropane ring, XI and XII, which would allow the spirocyclobutyl or spirocyclopentyl group to interact with the developing positive charge. The cyclopropane ring would then open completely to form an intermediate tertiary allylic carbonium ion, which would react with solvent to form products. Some confirmation of this hypothesis is found in the preliminary product study described below.

That the solvolysis rate for spiroheptyl chloride (IV) is only 1.6 times that of spirohexyl chloride (II) is puzzling in comparison with the value of about 500 which has been observed for the ratio of solvolysis rates of 1-methylcyclopentyl and 1-methylcyclobutyl chlorides,²⁷ and which is explained by the greater increase in angle strain in forming a transition state from the cyclobutyl compound than is obtained from the cyclopentyl compound. However, the above explanation would be reasonable if we consider that the hybridization change at the spiro carbon atom of II and IV, upon going to a solvolysis transition state such as XI and XII, would undoubtedly not be as great as the hybridization change experienced during the solvolysis of 1-methylcyclopentyl or 1-methylcyclobutyl chloride. The transition states of the latter compounds are probably nearly fully developed tertiary carbonium ions.²⁷ There has been little or no evidence for the intervention of nonclassical character in the solvolysis of 1-methylcyclobutyl chloride.^{27,28} Such participation is therefore quite unlikely in the solvolyses of II, IV, VII, or VIII.

The activation parameters for the 1-halospiroalkanes have been listed in Table III. The rate difference between chloride II and bromide VII can be almost entirely attributed to a difference in activation enthalpy, while the rather small rate increase of chloride IV compared to chloride II is primarily an entropy effect.

The solvolysis rate of chlorospiropentane (XIII) in 50% aqueous ethanol by volume at 200° has been

(26) C. A. Vernon, *J. Chem. Soc.*, 423 (1954).

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


(28) E. F. Cox, M. C. Caserio, M. S. Silver, and J. D. Roberts, *ibid.*, **83**, 2719 (1961).

TABLE III
ACTIVATION PARAMETERS FOR THE 1-HALOSPIROALKANES

Compound	ΔH^\ddagger , kcal./mole	ΔS^\ddagger , e.u.
Cyclohexyl chloride	26.9 ± 0.2	-13.0 ± 0.5
II	$24.3 \pm .1$	$-20.3 \pm .2$
IV	$25.9 \pm .1$	$-16.8 \pm .3$
VII	$20.0 \pm .2$	$-21.6 \pm .4$

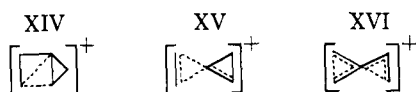
measured and compared with the ethanolysis rate of chlorocyclopropane (Table IV).

TABLE IV
ETHANOLYSIS RATE OF CHLOROSPIROPENTANE IN 50% AQUEOUS ETHANOL BY VOLUME

Compound	Temp., °C.	k , sec. ⁻¹ × 10 ⁶	$k_{rel.}$ (200°)
 XIII	200	7.1 ± 1.5	4-6.2
Cyclopropyl chloride	200	1.4 ^a	1.00

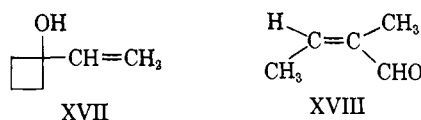
^a Reference 3.

The ethanolysis rate of chloride XIII, contrary to previous qualitative observations,²⁹ was at least 4 to 6.2 times greater than that of chlorocyclopropane. In view of the arguments which have been made for delocalized character in the solvolysis transition state of chlorocyclopropane,⁶ it is almost necessary to propose some kind of delocalization for chlorospiropentane also. It is not possible at present to say whether a transition state of the bicyclobutonium ion type (XIV), a homoallylic type (XV), or a modified version (XVI) of the conventional (see above) cyclopropyl type is responsible for the rate enhancement here. Structure XVI is shown in a general form with delocalization into the left-hand ring, but the actual extent of such delocalization could be small. The problem is of greatest interest when spiropentyl is compared with related cyclopropylcarbinyl types, discussed in the accompanying paper.¹⁶



Solvolysis Products.—Only a preliminary survey of solvolysis products can be reported at this time, but the products obtained are in agreement with the mechanistic paths up to the transition states as suggested by the above kinetic studies.

The solvolysis of 1-bromospirohexane (VII) in aqueous acetone at 95° gave primarily a nonvolatile oil, presumably polymeric, and a few volatile components separable by gas chromatography. The principal volatile component (14% yield) was identified as 1-vinylcyclobutanol (XVII) from its analysis and spectra.



The n.m.r. spectrum showed a complex multiplet at *ca.* 7.8 (area 6), which was assigned to the cyclobutane protons, a singlet hydroxyl proton at 6.12 (area 1), a quartet of peaks at 3.96 (area 1), which was assigned to the vinyl proton nearest to the hydroxyl group, and three partially resolved multiplets at 4.72, 4.97,

(29) D. E. Applequist and G. F. Fanta, *J. Am. Chem. Soc.*, **82**, 6393 (1960).

and 5.16, respectively (total area 2), which were assigned to the terminal vinyl protons. The ABC spectrum exhibited by the vinyl group is similar to that which has been observed for methyl vinyl thioether.³⁰ The infrared spectrum contained bands expected for a hydroxyl group (3350 cm.⁻¹) and for a vinyl group attached to an oxygen-bearing carbon (1645, 1000, 925 cm.⁻¹).³¹ Only end absorption was observed in the ultraviolet spectrum. None of the minor volatile products were identified, but it was shown by a control reaction that they were not formed by self-condensation of acetone under the reaction conditions.

A silver ion assisted hydrolysis of bromide VII was carried out to confirm the above results. A 97.3% yield of silver bromide was obtained together with a 61.9% yield (based upon the weight of silver bromide) of vinyl alcohol XVII. It was especially significant that the vinyl alcohol product represented 94% of the ether-extractable material from the hydrolysis.

Pure 1-bromospiro[2.4]heptane (VIII) was also subjected to aqueous acetone solvolysis for ten half-lives at 95°. Only a small amount of distillable product was formed, which consisted of mesityl oxide (63.1%) and five unidentified minor products (37.9%). The major part of the product was a glassy solid which was fractionated on neutral alumina into three red polymer-like substances, each of which gave a very broad n.m.r. signal. The infrared spectrum showed only saturated hydrocarbon bands plus a broad band at 1700 cm.⁻¹.

It was uncertain whether the expected product, 1-vinylcyclopentanol, was unstable to the solvolysis conditions, or whether an initially formed cation dehydrated to form a reactive diene which then polymerized.

Spiropentyl chloride reacted with aqueous silver nitrate in a sealed tube at 100° with a half-life of about 4-5 days, as judged by the amounts of silver chloride precipitated. The only product extractable into ether was tiglaldehyde (XVIII) in amounts accounting for 35% of the observed silver chloride. The aldehyde was identified by the identity of its infrared and n.m.r. spectra with those of an authentic sample. By contrast, the deamination of spiropentylamine²⁹ has been shown to give only 2- and 3-methylenecyclobutanols as ether-extractable products. The conditions of the latter reaction were much milder than those employed here, however, so the possibility exists that the methylenecyclobutanols were formed as primary products and isomerized to tiglaldehyde under the reaction conditions. Samples of the methylenecyclobutanols were unfortunately not available in this preliminary study to check their stability. In any case, the product does not serve to distinguish the plausible transition states XIV-XVI described above and further discussed in the accompanying paper.¹⁶

Experimental

All melting and boiling points are uncorrected. All n.m.r. spectra were measured with either a Varian 60 Mc. high resolution spectrometer (Model V-4300-2, serial 343 with super stabilizer) or a Varian A-60. Chemical shifts are expressed in parts per million relative to an internal tetramethylsilane standard, which is given an arbitrary position of 10 (τ scale). All infrared spectra, unless otherwise specified, were obtained with a Perkin-

(30) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962.

(31) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 49.

Elmer Model 21B double-beam recording spectrometer with sodium chloride optics. The ultraviolet spectra were obtained on a Cary Model 14B double-beam recording spectrometer.

Chlorospiropentane (XIII) was prepared as previously described.²⁰

1-Chlorospirohexane (II).—A 1.5 *N* solution of *n*-propyllithium (0.28 mole) in pentane was added over 3 hr. to a stirred mixture of 22.1 g. (0.26 mole) of methylene chloride and 16.3 g. (0.24 mole) of methylenecyclobutane³² at -40° . The cooling bath was removed near the end of the addition period, and it was noted that most of the lithium chloride precipitate formed as the flask warmed. The liquid phase was washed with saturated sodium chloride solution and dried over potassium carbonate. Low boiling pentane, methylenecyclobutane, *n*-propyl bromide, and *n*-hexane were removed by distillation, and the residue (4.7 g.) of crude II was distilled with a Hickman distillation unit,³³ b.p. 57° (87 mm.), to give a colorless liquid whose vapor phase chromatogram on diisodecyl phthalate suggested 91.8% purity. The infrared and n.m.r. spectra (described above) and elemental analysis were taken on the collected major peak in the chromatogram.

Anal. Calcd. for C_6H_9Cl : C, 61.80; H, 7.78. Found: C, 61.82; H, 8.05.

1,1-Dibromospirohexane (V).—Potassium *t*-butoxide was prepared by the method of Doering¹⁴ from 18.1 g. (0.463 g.-atom) of potassium. Dry cyclohexane (300 ml.) was added to the powdered potassium *t*-butoxide, and the contents of the flask were cooled and stirred in an ice bath. After 31.5 g. (0.463 mole) of methylenecyclobutane was added, 117 g. (0.463 mole) of bromoform, which had been freshly passed through a 20-cm. column of activated alumina to remove the residual moisture and free bromine, was added over a period of 6 hr. and stirred at room temperature for an additional 30 min. Water was rapidly added to the contents of the flask, which were then extracted twice more with small portions of water. The aqueous extracts were combined and extracted with cyclohexane. The organic layer was dried over magnesium sulfate and carefully distilled to recover 10.7 g. (0.107 mole) of methylenecyclobutane. The cyclohexane was then flash distilled. The remaining liquid was vacuum distilled (Holzman column) to yield some bromoform and 54.2 g. (63.5%) of V, b.p. 74° (12 mm.), n_D^{25} 1.5375 (lit.¹⁵ b.p. $60-61^{\circ}$ (5.5 mm.), n_D^{20} 1.5411). The product gave a precipitate with alcoholic silver nitrate and no reaction with potassium permanganate in acetone. An n.m.r. spectrum at 60 Mc. showed a singlet at 8.4 with area 2 and a group of partially resolved peaks at ca. 7.8 with ca. area 6.

Anal. Calcd. for $C_6H_8Br_2$: C, 30.04; H, 3.33. Found: C, 30.03; H, 3.41.

1-Bromospirohexane (VII).—1,1-Dibromospirohexane (54 g., 0.225 mole) and 550 ml. of glacial acetic acid were stirred at 50° in a water bath while 145 g. (2.22 g.-atoms) of zinc dust was slowly added. Addition was complete in 1.7 hr. The slurry was heated for an additional 48 hr. After filtration, the acid solution was poured into 1 l. of distilled water, which was then extracted with diethyl ether. The extracts were combined and extracted with aqueous potassium hydroxide until the aqueous layer remained basic. After an additional water wash, the ether solution was dried over magnesium sulfate, filtered, and flash distilled. The residue was distilled from calcium hydride (Holzman column), b.p. $64-72^{\circ}$ (58-60 mm.), to yield 16.8 g. (31.1%) of crude VII. A vapor phase chromatogram on didecyl phthalate indicated 80.5% purity. Several impurities were present with lower retention times.

An n.m.r. spectrum of the large v.p.c. peak (20 mg./ml. in carbon tetrachloride) at 60 Mc. showed a quartet at 7.19 (area 1), a singlet with a slight split at 7.87 (area 6), a quartet at 8.85 (area 1), and a quartet at 9.27 (area 1). The infrared spectrum was consistent with the structure and showed no unsaturation.

Anal. Calcd. for C_6H_9Br : C, 44.75; H, 5.62. Found: C, 44.96; H, 5.83.

Reaction of 1,1-Dibromospirohexane (V) with Magnesium.—Magnesium (0.7 g., 0.0288 g.-atom) was added to a warm flask. Anhydrous ether (30 ml.) was placed in the flask with a syringe and 4.8 g. (0.02 mole) of 1,1-dibromospirohexane was slowly added. Addition was stopped after the first few drops had entered the flask, and a piece of magnesium was mashed under the

surface of the ether to start the reaction. The addition was adjusted so as to maintain the solution at reflux. After 3 hr., the addition was complete and a layer of magnesium bromide etherate had separated. Water was slowly added to the externally cooled solution. The aqueous layer was washed with ether. The combined ether layers were dried over magnesium sulfate and were distilled through a Holzman column to leave approximately 1 ml. of yellow liquid residue which was transferred to a small distillation apparatus and additional ether was removed. A large drop of material was collected, b.p. ca. 94° . A portion of the drop gave a positive test with alcoholic mercuric chloride solution; a white precipitate is indicative of allenes.¹⁶ An infrared spectrum taken with an Infracord (sodium chloride optics) showed bands at 1980 and 1050 cm^{-1} , indicative of the allene double bond system. The remainder of the drop was subjected to vapor chromatography on didecyl phthalate and showed one major component with two minor impurities (10%). The reaction was not repeated. A small amount of polymeric material was also formed in the reaction.

1-Chlorospiro[2.4]heptane (IV).—Methylenecyclopentane (8.15 g., 0.0993 mole) and methylene chloride (13.6 g., 0.16 mole) were cooled to -35° with a Dry Ice-isopropyl alcohol bath. A pentane solution of *n*-butyllithium (190 ml., 1.15 *N*, 0.218 mole) was pumped into the dropping funnel with nitrogen pressure and slowly added to the stirred contents of the flask.

When the addition was complete (2.5 hr.), the solution was allowed to warm to room temperature, and water (50 ml.) was added. The organic layer was washed with saturated aqueous sodium chloride and dried over anhydrous sodium carbonate. The pentane was removed on a 3-ft. wire spiral column. The unreacted starting material and *n*-butyl chloride (from the *n*-butyllithium preparation) were removed on a 12-in. Holzman column. The remaining liquid was vacuum distilled on a Hickman unit and yielded *n*-octane, b.p. 45° (70 mm.) (coupling product from the *n*-butyllithium), and the final product, 2.54 g. (19.6%), b.p. $71-73^{\circ}$ (60 mm.). The infrared spectrum showed no unsaturation. The n.m.r. spectrum was virtually identical with that of 1-chlorospirohexane with the exception of the cyclopentane multiplet which occurred in the region 8.2-8.5.

Anal. Calcd. for $C_7H_{11}Cl$: C, 64.37; H, 8.49. Found: C, 64.67; H, 8.62.

1,1-Dibromospiro[2.4]heptane (VI).—Potassium *t*-butoxide was prepared by the method of Doering¹⁴ from 7.81 g. (0.20 g.-atom) of potassium. Dry cyclohexane (100 ml.) was added to the powdered base, and the contents of the flask were then cooled in an ice bath followed by the introduction of 16.58 g. (0.202 mole) of methylenecyclobutane. Bromoform (17.5 ml., 50.0 g., 0.20 mole), which had been passed through a short column of aluminum oxide to remove the residual bromine and moisture, was slowly added (2.75 hr.).

Water (80 ml.) was added and the organic phase was extracted with two additional portions of water, which were combined and extracted with several portions of cyclohexane. The cyclohexane extracts were dried over potassium carbonate and concentrated on a rotary evaporator. Bromoform, b.p. 48° (20 mm.), was removed by distillation through a 12-in. Holzman column followed by distillation of the product, b.p. $64-69^{\circ}$ (1.5 mm.) (lit.¹⁵ b.p. $75-76^{\circ}$ (6 mm.)). 1,1-Dibromospiro[2.4]heptane (22.3 g., 0.0870 mole) was obtained in 43.5% of the theoretical yield. Repeated distillation and an attempted purification by preparative vapor phase chromatography always resulted in some decomposition. Although a satisfactory analytical sample was not obtained, the compound did give an n.m.r. spectrum which showed a singlet at 8.44 (cyclopropane protons) with a complex multiplet at slightly lower field extending down to 7.44 (cyclopentane protons), analogous to the n.m.r. spectrum of 1,1-dibromospirohexane. The infrared spectrum showed no unsaturation.

Anal. Calcd. for $C_7H_{10}Br_2$: C, 33.10; H, 3.97. Found: C, 34.22; H, 4.06.

1-Bromospiro[2.4]heptane (VIII).—To a stirred solution of 8.87 g. (0.0349 mole) of 1,1-dibromospiro[2.4]heptane in 90 ml. of glacial acetic acid at 50° was added 22.9 g. (0.35 g.-atom) of zinc dust over 2 hr. The resulting slurry was stirred for an additional 48 hr. The slurry was filtered into water followed by extraction with ether. The ether layer was then extracted with 25-ml. portions of dilute aqueous potassium hydroxide until all of the acetic acid had been removed. The ether was removed on a rotary evaporator after the solution had been dried with potassium carbonate. The residue was distilled on a Hickman distillation unit, b.p. 76° (29 mm.), and yielded 3.47 g. (57%) of 1-

(32) J. D. Roberts and C. W. Sauer, *J. Am. Chem. Soc.*, **71**, 3925 (1949).

(33) K. B. Wiberg, "Laboratory Techniques in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p. 65.

bromospiro[2.4]heptane. Although vapor phase chromatography on silicone grease indicated only 4% impurity, the sample could not be obtained analytically pure; however, an excellent n.m.r. spectrum (virtually identical with 1-chlorospiro[2.4]heptane) was obtained and showed quartets at 9.30, 8.97, and 7.06 indicative of an ABX type spectrum and a complex multiplet at 8.3 for the cyclopentane protons. The infrared spectrum was in agreement with the structural assignment.

Anal. Calcd. for $C_7H_{11}Br$: C, 48.01; H, 6.34; Br, 45.65. Found: C, 48.59; H, 6.47; Br, 44.90.

Chloromethylenecyclopentane.—A procedure similar to that used in the preparation of chloromethylenecyclohexane was followed.¹³ Dry ether (500 ml.), 27.2 g. (0.321 mole) of methylene chloride (distilled from calcium hydride), and 74.2 g. (0.285 mole) of triphenylphosphine, which had been recrystallized from hot 95% ethanol and dried in a vacuum oven at 50° for 24 hr., were mixed and cooled to -33° in a Dry Ice-isopropyl alcohol bath. *n*-Butyllithium (190 ml., 1.5 *N*, 0.285 mole) was added by means of a Hershberg funnel. After the addition (2.25 hr.) the Hershberg funnel was replaced with a 24/40 joint fitted with a rubber septum, and 23.9 ml. (22.7 g., 0.27 mole) of cyclopentanone (distilled from calcium hydride and stored over Linde 5-A Molecular Sieves) was introduced with a syringe to the orange-yellow slurry. The bath was then removed and the ether slurry was maintained under reflux and stirred (argon atmosphere) for 13 hr. The solvent was distilled, followed by the addition of tetrahydrofuran (250 ml., purified by passage through Linde 5-A Molecular Sieves), and distillation from calcium hydride. The solution was maintained at reflux for 8 hr., and then washed with water, which was extracted with pentane. When the pentane had been removed, a colorless distillate (2.64 g.) was obtained at *ca.* 40° (43 mm.), which was shown by vapor phase chromatography to consist of 89.3% of a major product, 7.25% of cyclopentanone, and 3.45% of unidentified impurities. The yield of product based upon *n*-butyllithium was 7.1% of the theoretical amount. An infrared spectrum of the chloromethylenecyclopentane showed among other bands, a weak absorption of 3050 cm^{-1} and a medium absorption at 1647 cm^{-1} . The n.m.r. spectrum showed a quintuplet at 4.16 (area 1), a multiplet at 7.76 (area 4), and a multiplet at 8.26 (area 4).

Anal. Calcd. for C_5H_8Cl : C, 61.80; H, 7.78. Found: C, 61.96; H, 8.08.

Attempted Preparation of 1-Chlorospiro[2.4]heptane (IV) from Chloromethylenecyclopentane.—The zinc-copper couple was prepared as described in the synthesis of spirohexane¹⁶ and was used immediately after preparation. A mixture of anhydrous ether (10 ml.), 0.015 g. (0.0006 g.-atom) of iodine, 1.63 g. (0.025 g.-atom of zinc) of zinc-copper couple, and 5.36 g. (0.02 mole) of methylene iodide (Eastman; slightly colored) was stirred at reflux for 30 min. Freshly distilled chloromethylenecyclopentane (1.42 g., 0.0122 mole) in 5-ml. of dry ether was added slowly and the solution was maintained at reflux overnight.

After filtration of the reaction mixture through a pad of Super-Cel (dry), the combined ether washings were extracted with 5% aqueous hydrochloric acid, saturated aqueous sodium bicarbonate solution, and saturated aqueous sodium chloride solution. The ether extracts were dried over calcium hydride. When the solvent had been removed, the liquid residue was distilled under vacuum from a glass wool pad in a Hickman distillation unit and yielded 1.07 g. of distillate, b.p. 69° (65 mm.). An infrared spectrum was identical with that of the starting material (75.4% recovery). There was no indication of any product.

A similar reaction in a sealed vessel at 65° for 24 hr. gave essentially the same result.

Silver Ion Assisted Hydrolysis of Spiropentyl Chloride.—In a typical run, 1.16 g. (0.0113 mole) of spiropentyl chloride, 2.39 g. (0.0141 mole) of silver nitrate, and about 25 ml. of water were heated together at about 100° for 6 days in a sealed tube. When the cooled tube was opened, effervescence was noted. The mixture was filtered, and the precipitate was washed, dried, and weighed (0.864 g.) to determine total silver and silver chloride, then washed thoroughly with ammonium hydroxide, dried, and weighed (0.123 g.) to determine silver metal. By difference, the yield of silver chloride was 0.741 g. (56%).

The filtrate of the reaction mixture was extracted with ether, and the extract concentrated by fractional distillation. The residue (0.86 g.) was found by gas chromatography on Carbowax 20M to contain only solvent, unreacted spiropentyl chloride (identified by its n.m.r. spectrum) and tigraldehyde, which amounted to 16% of the liquid residue and which was identified

by the identity of its infrared and n.m.r. spectra with those of an authentic sample. The 2,4-dinitrophenylhydrazone melted at 213–216° (lit.³⁴ m.p. 215.5–217.5°).

Hydrolysis of 1-Bromospirohexane (VII).—1-Bromospirohexane (b.p. 60–63° (50 mm.), 8.512 g., 84.2% pure by v.p.c., 0.0445 mole) was dissolved in 135 ml. of 70% (volume) acetone in water. The impurities had been determined by vapor phase chromatography on an 8-ft. diisodecyl phthalate column at 150° to consist of two small overlapping peaks with somewhat shorter retention times, 0.605 and 0.714 times that of the major component. Three aliquots of the solution were sealed in tubes and placed in an oil bath at 95° for various time intervals. An approximate rate constant was determined by a simple acid titration of an accurate aliquot taken from each ampoule and a comparison with the initial alkyl halide concentration (corrected for the v.p.c. purity given above). The half-life was found to be 2.03 hr. The remainder of the material (0.0391 mole) was placed in two large ampoules and solvolyzed for 19 hr. at 95°.

The contents of the ampoules were poured into 400 ml. of saturated aqueous sodium bisulfite and 75 ml. of ether followed by extraction of the ether layer with two additional portions of sodium bisulfite solution. The aqueous layers were then combined and extracted with several portions of ether. The ether extracts were dried over anhydrous magnesium sulfate and distilled on a 3-ft. wire spiral column; 4.57 g. of liquid residue remained. In the final distillation (12-in. Holzman column), the bath temperature was allowed to reach 120° for a short time, but no distillate was observed. The liquid was vacuum distilled and yielded 0.147 g. at 35–55° (73 mm.), 0.896 g. at 55–58° (73 mm.), and 0.486 g. at 74–75° (0.5 mm.) of pale yellow liquid as well as an undistillable dark residue. Vapor phase chromatograms of the first two fractions were obtained on an 8-ft. polar UCON column at 130°. The relative areas of the peaks from the 55–58° fraction, in order of increasing retention time, were 38.5, 5.6, 5.2, and 50.7. The first peak was a mixture, never fully resolved. The second was mesityl oxide, as identified by its infrared and n.m.r.³⁵ spectra. The fourth peak was identified as 1-vinylcyclobutanol as described under Results and Discussion.

Anal. Calcd. for $C_6H_{10}O$: C, 73.43; H, 10.28. Found: C, 73.29; H, 10.43.

A control reaction was run to determine if any of these minor components or polymeric products could be attributed to the acetone. A mixture of 70% (volume) acetone in water which contained 0.36 *M* hydrobromic acid, the maximum concentration formed during the solvolysis reaction, was heated for 19 hr. at 95° followed by the same work-up procedure. Only 0.77 g. of mesityl oxide was obtained (the reaction was carried out on a 100-ml. scale), b.p. 64–66° (75–100 mm.). Two very minor components were observed when the material was subjected to vapor phase chromatography on a polar UCON column, but these did not correspond to any of the previously obtained unidentified products. Although there was a slight residue, no other distillable products were formed.

Silver Ion Assisted Hydrolysis of 1-Bromospirohexane (VII).—1-Bromospirohexane (3.0 g., 0.0186 mole), silver nitrate (3.95 g., 0.0233 mole), and 30 ml. of water in a sealed tube, protected from the light, were heated for 18.5 days at 50 ± 5°.

The silver bromide suspension (3.395 g., 0.0181 mole), which accounted for 97.3% of the starting compound, was filtered and washed with ether. The aqueous portion of the filtrate was extracted with several portions of ether, which were dried over anhydrous magnesium sulfate and distilled on a 3-ft. wire spiral column. The residue (brown) appeared to be 88% one component on a 10 ft. Carbowax-20M column. A collected sample had an infrared spectrum identical with that of a sample of 1-vinylcyclobutanol. The n.m.r. spectra of the two samples were also identical in every respect. The yield of 1.25 g. (0.112 mole based upon the v.p.c. purity) represents 61.9% of the collected silver bromide. If one neglects the area of the solvent (ether) peak in the vapor phase chromatogram, 1-vinylcyclobutanol represented 94% of the ether extractable material from the hydrolysis.

Hydrolysis of 1-Bromospiro[2.4]heptane (VIII).—1-Bromospiro[2.4]heptane (6.531 g., *ca.* 95% pure by v.p.c. on Carbowax 20M, 0.0373 mole) was dissolved in 100 ml. of 70% (vol.) acetone in water and placed into three tubes which were subsequently sealed and placed in an oil bath at 95° for 12 hr. (about ten half-lives).

(34) J. D. Roberts and C. Green, *J. Am. Chem. Soc.*, **68**, 214 (1946).

(35) G. V. D. Tiers, Central Research Dept., Minnesota Mining and Mfg. Co., Project 737602 (1958).

The contents of the tubes were poured into 300 ml. of saturated aqueous sodium bisulfite solution together with 70 ml. of diethyl ether. Several extractions were carried out with sodium bisulfite solution followed by extraction of the combined aqueous layers with ether. The other layers were dried for 24 hr. over magnesium sulfate and distilled on a 12-in. wire spiral column. The residue was vacuum distilled to yield 0.703 g. of a colorless liquid, b.p. 34–58° (69 mm.), and approximately 3.3 g. of a glassy red-brown residue. A vapor phase chromatogram of the low boiling liquid on Carbowax-20M indicated a predominance of mesityl oxide (retention time comparison with a previous chromatogram) with at least six additional minor components.

The red glass was dissolved in carbon tetrachloride and chromatographed on neutral alumina. Cyclohexane eluted a red band representing over 50% of the material (band A). Similarly, benzene and chloroform each eluted a dark red band (bands B and C), while some residue remained on the column. Infrared spectra on all three samples showed a broad band at *ca.* 3400 cm^{-1} , strong C–H stretching bands at 2920 and 2860 cm^{-1} , a broad band at *ca.* 1700 cm^{-1} (slight in B), methylene C–H deformation at 1465 cm^{-1} , and C–CH₃ absorption at 1380 cm^{-1} . An n.m.r. spectrum of sample A showed a sloping line which terminated as a broad absorption at *ca.* 9.00. The spectrum of sample B was superimposable in every way with A, except for a sharp singlet at 8.47. Neither n.m.r. spectrum showed absorption in the vinyl region. The broad absorptions confirmed the polymeric nature of the substances.

Ethanolysis Procedure.—All kinetic experiments utilized Pyrex baths which contained approximately 8 gal. of oil (Cities Service, D.C. 915), a Lightnin Model L continuous duty stirrer, a hydrogen jacketed microthermoregulator, and a 500 to 750 watt continuous heat source which was connected to a Variac. Fine heating was controlled by means of a 100-watt light bulb attached through a zero-current relay to the thermoregulator. The entire bath assembly was packed in Vermiculite and had an aluminum foil covered lid to minimize radiation and convection heat losses near the surface of the oil. Temperatures were checked with thermometers calibrated by the National Bureau of Standards.

After dissolving the appropriate amount of alkyl halide in an ethanol-water solvent (50% by volume at 15.56° or 42.47% by weight of ethanol), the solution was distributed among 16 ampoules each containing approximately 5.5 ml., and these were then carefully sealed and placed in the bath so that only the thin necks protruded above the surface of the oil. The time was taken first when the ampoule was placed in the bath and again at the instant it was quenched in the cold water. After quenching the ampoules with cold water, the necks were scored and snapped off, followed by removal of an exact aliquot (*ca.* 5 ml.) with an automatic delivery pipet calibrated with the same ethanol-water solution. The acid solution was titrated to a phenolphthalein end point with approximately 0.1 *N* sodium methoxide in methanol solution which had been standardized against potassium hydrogen phthalate. A 5-ml. microburet was used which could be read directly to 0.01 ml. Infinity titers were taken after ten half-lives.

Rate constants were determined by the method of least squares.^{36, 37}

The data for a typical kinetic run are indicated below for the ethanolysis of 1-bromospirohexane at $95.00 \pm 0.05^\circ$. The compound was distilled, b.p. 64–72° (58–60 min.), immediately

prior to the kinetic run. A vapor phase chromatogram on didecyl phthalate as well as a comparison of the initial weight concentration with the infinity titer indicated *ca.* 90–95% purity. Excellent first-order kinetics were found up to 89% reaction.

Suitable controls were run to confirm^{38, 39} that there is no significant reaction of HBr or HCl with ethanol under the conditions of the kinetic runs.

Time elapsed min.	Titred (HBr)	–ln (RBr)	Time elapsed min.	Titred (HBr)	–ln (HBr)
∞	0.04120	3.190	30	0.02745	4.288
10	.01222	3.542	35	.03020	4.512
15	.01730	3.735	40	.03210	4.700
20	.02190	3.950	55	.03610	5.281
25	.02470	4.106	60	.03695	5.463

Rate const. $(6.363 \pm 0.031) \times 10^{-4} \text{ sec}^{-1}$

Ethanolysis of Chlorospiropentane (XIII).—The compound was collected in high purity by preparative vapor phase chromatography on an 8-ft. Carbowax-20M column. The kinetics were done using heavy walled sealed ampoules, which were placed in a small silicone oil bath.

Although there are large inherent errors caused by the use of so small a bath and thick glass ampoules, the kinetic value obtained by averaging individual rate constants from each ampoule (below) is of utility for a crude comparison with the ethanolysis rate of cyclopropyl chloride at 200°.³ Two solutions which correspond to the two initial concentrations, (RCI)₀, were used in the determination of the rate constant.

Elapsed time, hr.	—50% aqueous ethanol (vol.) at 200°—				
	(HCl)	(RCI)	(RCI) ₀ ^a	$\frac{\ln [(RCI)_0 / (RCI)]}{(RCI)}$	$k, \text{ sec}^{-1} \times 10^{5b}$
2.0	0.0203	0.0224	0.0427	0.65	9.0
3.0	.0248	.0179	.0427	.87	8.1
4.0	.0262	.0165	.0427	.95	6.6
4.5	.0229	.0115	.0344	1.10	6.8
6.0	.0248	.0096	.0344	1.27	5.9
8.0	.0283	.0061	.0344	1.73	6.0

^a Initial concentration of alkyl halide/(infinity titer). ^b $k = (1/t) \ln [(RCI)_0 / (RCI)]$. $k_{av} = (7.1 \pm 0.5) \times 10^{-5} \text{ sec}^{-1}$.

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(36) L. P. Hammett, "Introduction to the Study of Physical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1952, p. 410.

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(39) S. P. Walvekar, N. L. Phalnikar, and B. V. Bhide, *J. Indian Chem. Soc.*, **19**, 409 (1942).