

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

Small-Ring, Spiroalkyl Cations. Solvolysis Studies on 4- and 5-Chlorospirohexane. The Vapor Phase Chlorination of Spirohexane and Spiro[2.4]heptane

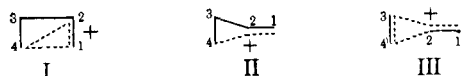
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RECEIVED OCTOBER 11, 1963

The vapor phase chlorination of spirohexane, which was prepared by treatment of methylenecyclobutane with methylene iodide and zinc-copper couple, produced the following typical distribution of monochlorinated products: 19.7% 5-chlorospirohexane, 27.6% 4-chlorospirohexane, 28% 1-chloro-1-ethylcyclobutane, and 22.3% 1-(2'-chloroethyl)cyclobutene. Evidence is presented that the 4-spirohexyl radical, a cyclopropylcarbinyl radical, has no unusual stability. The solvolysis of (1-methylcyclopropyl)carbinyl chloride took place 4.23 times faster than that of 4-chlorospirohexane (50% aqueous ethanol, 30°), but at least 100 times faster than that of cyclobutyl chloride. The ethanolsis rate (95°) of cyclobutyl chloride was 210 times faster than that of 5-chlorospirohexane. The implications of these rate measurements are discussed.

Introduction

The nature of the carbonium ions derived from cyclopropylcarbinyl and cyclobutyl derivatives has been the subject of much research and debate.³ The formation of similar or identical product mixtures from the two has suggested common intermediates, and the skeletal scrambling observed^{3a} has suggested that the intermediates are a rapidly equilibrating set of classical or nonclassical carbonium ions. The rate enhancements observed in solvolyses of both cyclobutyl and cyclopropylcarbinyl derivatives have found no serious explanation other than delocalization of the positive charge in the transition states.⁴ The principal remaining problem is to determine the detailed structures of the transition states and of the intermediates, some of which the transition states may be presumed to resemble closely. The possibilities are outlined most clearly by Winstein and Kosower^{3c} and include the unsymmetrical bicyclobutonium ion (I), the unsymmetrical homoallylic ion (II), and the symmetrical homoallylic ion (III). The most basic distinction between I and either II or III is that I has significant



1,4-bonding and hence appreciable charge at position 2, while in II and III the 1,4-bonding and charge at 2 may be considered too small to affect rates or products. A powerful argument for structure I is that cyclobutyl compounds are major products^{3a} and, according to the Hammond postulate,⁵ the product distributions will be a qualitative reflection of charge distribution in the intermediate or intermediates collectively. Direct experimental confirmation of the importance of 1,4-bonding in the transition state for cyclopropylcarbinyl solvolyses would still be desirable, especially in view of the fact that stable homoallylic cations without a large amount of 1,4-bonding are known in cases

where stereochemistry prevents it^{3c} or where substituents provide special stabilization for type II or III homoallylic cations.^{3b,6}

The present study was conceived as an attempt to demonstrate the presence or absence of 1,4-bonding in substituted cyclopropylcarbinyl systems of type IV by a systematic variation of n . If IV must have bicyclobutonium ion character (type I) for optimum



stabilization by the cyclopropane ring, then there should be a marked increase in stabilization of IV (relative to appropriate models) as n increases. If the cyclopropylcarbinyl stabilization of IV is purely hyperconjugative (types II and III), then there appears no *a priori* reason to expect a dependence upon n . It must be recognized, of course, that secondary cations like IV will in general have less bicyclobutonium character than the parent cyclopropylcarbinyl system,^{3b} so if such character is found in IV, it may be safely inferred for cyclopropylcarbinyl itself, whereas if it is absent in IV, no conclusion will be reached for the parent system.

A preliminary study⁷ has already shown that spiro-pentylamine reacts with aqueous nitrous acid to give (presumably through cation IVa) the two methylenecyclobutanols rather than typical cyclopropylcarbinyl-cyclobutyl-allylcarbinyl products, and it has been shown qualitatively⁷ and quantitatively⁸ that spiro-pentyl chloride has nearly the same solvolytic reactivity as cyclopropyl chloride. The present paper adds to the data a synthetic and kinetic study of the 4-spirohexyl cation IVb and a preliminary report on the 4-spiroheptyl cation IVc. The collective data on all of the systems IV are analyzed.

Results and Discussion

Synthesis.—Spirohexane (V) was prepared in 20–25% yield by treatment of methylenecyclobutane with methylene iodide and zinc-copper couple in diethyl ether (Simmons-Smith reaction⁹). Although use of diethyl ether prevents the convenient recovery of unreacted methylenecyclobutane because of the proximity

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

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

(3) Leading references are: (a) R. H. Mazur, W. N. White, D. A. Semenov, C. C. Lee, M. S. Silver, and J. D. Roberts, *J. Am. Chem. Soc.*, **81**, 4390 (1959); (b) M. S. Silver, M. C. Caserio, H. E. Rice, and J. D. Roberts, *ibid.*, **83**, 3671 (1961); (c) S. Winstein and E. M. Kosower, *ibid.*, **81**, 4399 (1959); (d) H. C. Brown, "The Transition State," Special Publication No. 16. The Chemical Society, London, 1962, p. 140.

(4) Brown^{3d} prefers the language that "the enhanced rates observed in the solvolysis of these compounds is primarily due to their strained condition," but no suggestion as to how the strain could be relieved without delocalization of the charge appears to have been published.

(5) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

(6) (a) H. Hart and J. M. Sandri, *ibid.*, **81**, 320 (1959); (b) N. C. Deno, H. G. Richey, Jr., J. S. Liu, J. D. Hodge, J. J. Houser, and M. J. Wisotsky, *ibid.*, **84**, 2016 (1962).

(7) D. E. Applequist and G. F. Fanta, *ibid.*, **82**, 6393 (1960).

(8) J. A. Landgrebe and D. E. Applequist, *ibid.*, **86**, 1536 (1964).

(9) H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4236 (1959).

of their boiling points, attempts to use tetrahydrofuran or dioxane as the solvent failed to yield any detectable



amount of spirohexane. Hydrocarbon V gave a negative test with an acetone solution of potassium permanganate and showed no unsaturation in its infrared spectrum. The n.m.r. spectrum showed a sharp singlet at τ 9.64 (area 4), which was assigned to the cyclopropane protons, and a sharp singlet at 7.92 (area 6), which was assigned to the cyclobutane protons.

During the course of this work, the preparation of spirohexane from 1,1-bisiodomethylcyclobutane and zinc dust in the presence of a chelating agent was reported.¹⁰ Spirohexane was also prepared in this work by reduction of 1,1-dibromospirohexane⁸ with either lithium in tetrahydrofuran and *t*-butyl alcohol¹¹ or hydrogen and Raney nickel. The Simmons-Smith reaction remained the most convenient method for the preparation of pure spirohexane in the large quantities which were necessary for vapor phase chlorination studies.

Spiro[2.4]heptane (VI) was prepared in 66% yield by the hydrogenation of spiro[2.4]heptadiene-4,6 with a platinum oxide catalyst in diethyl ether.¹² Although the conditions of hydrogenation minimize cyclopropane ring cleavage, some ring opening to the *gem*-dimethyl compound was observed. The n.m.r. spectrum of the pure hydrocarbon VI showed a singlet at 9.63 (area 4), which was assigned to the cyclopropane protons, and a complex multiplet at *ca.* 8.4 (area 8), which was assigned to the cyclopentane protons.

The vapor phase chlorination of spirohexane was carried out in the same manner as that employed for spiro[2.4]heptane.¹³ Because the chlorine to hydrocarbon ratio as well as the temperature within the reaction chamber was difficult to control and not entirely reproducible, the ratio of various chlorination products sometimes differed in successive chlorinations.

In a chlorination which was terminated when the temperature of the boiling product mixture reached 129°, the main volatile fraction, b.p. 120–131° (about 10% yield), contained only one major component, which represented 65–70% of the fraction, and approximately six minor components, which were not fully resolved on the vapor phase chromatogram. A sample of the predominant peak, which was collected from a didecyl phthalate v.p.c. column, gave an approximate analysis for C_6H_9Cl and showed no sign of unsaturation in its infrared spectrum.

The n.m.r. spectrum showed a quintet at τ 5.52 (area 1), peak separation 7.8 c.p.s., which was assigned to a proton on a chlorine-bearing carbon atom.¹⁴ The spectrum also showed a doublet at 7.49 (area 4), peak separation 7.8 c.p.s., and a singlet at 9.53 (area 4). The structure 5-chlorospirohexane (VII) was assigned;

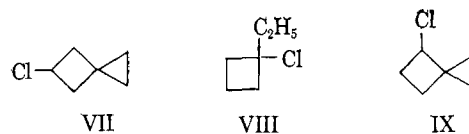
(10) D. E. McGreer, *Can. J. Chem.*, **38**, 1639 (1960).

(11) P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind. (London)*, 455 (1959).

(12) G. Chiurdoglu and B. Tursch, *Bull. soc. chim. Belges*, **66**, 600 (1957).

(13) D. E. Applequist, G. F. Fanta, and B. W. Henrikson, *J. Am. Chem. Soc.*, **82**, 2368 (1960).

(14) The proton on the chlorine-bearing carbon of cyclobutyl chloride occurs at 5.65 as a quintet with peak separations of 7.9 c.p.s.: D. F. O'Brien, Ph.D. Dissertation, University of Illinois, 1962.

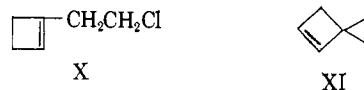


the singlet was attributed to the cyclopropane protons and the doublet to the cyclobutane protons. The quintet and doublet of VII are deceptively simple multiplets¹⁵ which represent a degenerate A_2B_2X spin system and closely resemble the corresponding peaks in the previously reported spectrum of 3-methylene-cyclobutanol⁷ except that in the latter the doublet is further split by the exocyclic methylene protons.

Another product, somewhat lower boiling, was formed in the chlorinations in highly variable amounts, 4–40%. It was assigned the structure 1-ethyl-1-chlorospirobutane (VIII) from its analysis, infrared spectrum (which showed no unsaturation), and n.m.r. spectrum, which showed the ethyl triplet at τ 9.01 (area 3, $J = 7.5$ c.p.s.), the ethyl quartet at 8.1, and a complex multiplet at 7–8 for the remaining cyclobutyl hydrogens. The presence of olefinic hydrogens, cyclopropane hydrogens, or hydrogens α to chlorine was clearly ruled out. Compound VIII is undoubtedly formed by addition of HCl to spirohexane.

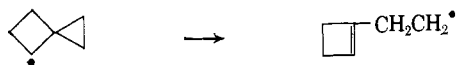
The apparent absence of 4-chlorospirohexane (IX) in the chlorination product was a surprise, but it was soon found that this result was critically dependent upon the conditions of the reaction. When the chlorinations were stopped at earlier stages, higher yields of monochlorides were obtained (43%) and the 5-chlorospirohexane fraction (collected by v.p.c.) was found to contain as high as 58% of 4-chlorospirohexane (IX) as judged by elemental analysis (which showed the compound to be an isomer), analysis of the n.m.r. spectra, and, subsequently, by kinetic analysis. The n.m.r. spectrum of IX was very similar to that of VII, but the proton on the chlorine-bearing carbon was a complex multiplet rather than a symmetrical quintet (but still at τ 5.5) and the ring methylenes were a more extended set of multiplets in the 7.3–7.9 region, partly obscured by the doublet of VII in the spectra examined. The cyclopropane peak at 9.53 had some fine structure on the low-field side, similar to that found in chlorospiro[2.4]heptane.¹³ The areas were in approximately the 1:4:4 ratio required. It was possible to isolate the pure 5-isomer (VII) from the mixture by solvolysis for a few days in 50% aqueous ethanol followed by re-isolation, but the 4-isomer was not isolated pure. The best yields were 9% of VII and 12% of IX.

A fourth product was obtained in 10% yield and isolated by v.p.c. It was identified as 1-(2'-chloroethyl)cyclobutene (X) by its n.m.r. spectrum, which showed a singlet olefinic peak at τ 4.26 (area 1), a triplet chloromethylene signal at 6.47 (area 2, $J = 6$ c.p.s.), and a combined signal at 7.56 (area 6) for the allylic methylenes with two small shoulder peaks on either side and 12 c.p.s. apart. Compound X is an expected product from hydrogen abstraction at the 4-position of spirohexane if the resulting radical opens



(15) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 216 (1961).

in the manner observed in the vapor phase chlorination of methylcyclopropane.¹⁶ It may easily be seen that if formation of the 4-chloro compound IX is thus competitive with formation of X, then the sensitivity of yield of IX to reaction conditions such as temperature or partial pressure of chlorine would be expected.¹⁷



(Neither of these factors was accurately controllable with the apparatus used in this work.)

The structure of chloride VII was further confirmed by reaction with potassium *t*-butoxide or *t*-pentoxide to give in 52–58% yields an olefinic substance with the n.m.r. expected for 4-spirohexene (XI). The spectrum consisted of an AB multiplet at τ 4.15 (area 2) for the olefinic protons, a singlet at 7.42 (area 2) for the allylic methylene, and a singlet at 9.31 (area 4) for the cyclopropane methylenes. It has been reported that the vinyl protons in cyclobutene do not couple with the methylene protons.¹⁸

It is quite clear from the chlorination results that hydrogen abstraction at the cyclopropane ring position is very unfavorable relative to abstraction on the cyclobutane ring. The cyclobutane ring is of course statistically favored 6:4, but, in addition, cyclopropane C–H bonds are known to be quite difficult to break homolytically when compared with other simple aliphatic C–H bonds.¹⁹

Perhaps the most significant aspect of the observed chloride product distribution is that the product ratio of chlorides IX plus X, which arise from hydrogen abstraction at the 4-position of V, to chloride VII, which arises from abstraction at the 5-position of V, is *ca.* 2.5:1 or nearly statistical. An experimentally determined solvolysis rate for chloride IX (to be discussed) indicated considerable driving force from the cyclopropane ring and was best interpreted in terms of a transition state with some nonclassical character. However, the above product distribution for the vapor phase chlorination of spirohexane strongly suggests that there is little nonclassical character in the cyclopropylcarbinyl radical generated at the 4-position of V. The observation is in contrast with the unusually high reactivity noted in the decomposition of bicyclopropylacetyl peroxide,²⁰ in the chlorination of methylcyclopropanes,²¹ and in the decomposition of 2,2'-azobis-2-cyclopropylpropionitrile.²² The present results are not seriously out of line, however, if a major part of the unidentified (mainly high-boiling) products arose from initial abstraction at position 4, in which case the 4-position:5-position reactivity ratio could be as high as 7.1:1, or 3.5:1 with a statistical correction. It would be reasonable for X to give dichlorides and trichlorides before it escapes from the reaction zone, for example.¹³

(16) E. Renk, P. R. Shafer, W. H. Graham, R. H. Mazur, and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 1987 (1961).

(17) Another possibility not ruled out is that IX isomerizes to X by an ionic or radical mechanism in the refluxing reaction mixture.

(18) L. M. Jackman, unpublished work, in "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Inc., New York, N. Y., 1959, p. 86.

(19) A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 329 (1951).

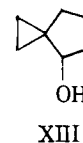
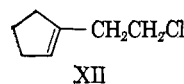
(20) H. Hart and R. A. Cipriani, *J. Am. Chem. Soc.*, **84**, 3697 (1962).

(21) C. Walling and P. S. Fredricks, *ibid.*, **84**, 3326 (1962).

(22) C. G. Overberger and M. B. Berenbaum, *ibid.*, **73**, 2618 (1951).

The vapor phase chlorination of spiro[2.4]heptane (VI) produced almost entirely monochlorinated products. Vapor phase chromatography on a variety of columns indicated that at least twelve components, many of which were not fully resolved, were present. Treatment of the product with aqueous potassium permanganate destroyed only the component which had the longest retention time (17.5% of the monochlorinated products). The collected peak gave the correct analysis for $C_7H_{11}Cl$ and exhibited infrared absorptions at 3040 (w), 2930 (s), 1645 (w), 1450 (m), 1425 (w), and 1300 (m) cm^{-1} in addition to absorption in the lower fingerprint region. In analogy with 1-(2'-chloroethyl)cyclobutene (X) formed in the chlorination of spirohexane, 1-(2'-chloroethyl)cyclopentene (XII) was assigned and was confirmed by the n.m.r. spectrum. The vinyl proton at 4.55 is slightly split into a triplet with $J \approx 1.5$ –2.0 c.p.s. The acyclic methylene groups appear as two triplets at 6.46 and 7.48 with $J = 7$ c.p.s., while the remaining methylene groups give additional multiplet structures at 7.71 and 8.1.

It was not convenient in this study to isolate or characterize any of the other monochlorides from VI, but a sample of the entire monochlorinated product mixture was subjected to ethanolysis (50% aqueous ethanol) for 24 hr. at room temperature and then recovered for v.p.c. analysis. All of the major groups of peaks except that for XII decreased in amount relative to XII (not expected to solvolyze under such mild conditions), but remained in about the same proportion to each other, indicating that no major component was unusually reactive or unreactive. Further study of this chlorination is of obvious interest for its own sake, but for the present purpose of finding a suitable source of cation IVc, attention was turned to the potentially more specific conversion of the spiroheptanol XIII to the corresponding chloride.



Alcohol XIII was prepared by lithium aluminum hydride reduction of the known ketone and was characterized by its satisfactory infrared and n.m.r. spectra (see Experimental) and by analysis of the alcohol and its *p*-nitrobenzoate. Attempts were made to convert XIII to the chloride by reactions with thionyl chloride, thionyl chloride and triethylamine in ether, or a mixture of *p*-toluenesulfonyl chloride and pyridine hydrochloride. All failed, giving only mixtures of two unsaturated chlorides in comparable amounts. One was identical with chloride XII described above and the other, an isomeric chloride, appeared from its infrared and n.m.r. spectra to be a ring-chlorinated methylenecyclohexane (XIV). The terminal methylene was indicated by strong bands at 165) and 900 cm^{-1} and

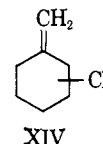
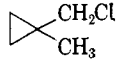



TABLE I
 SOLVOLYSIS RATES IN 50% AQUEOUS ETHANOL

| Compound | Temp. ±0.05° ^a | k, sec. ⁻¹ | Relative rates | | |
|---|------------------------------|---|------------------------|--------|--------|
| | | | 30° | 90° | 95° |
| Cyclohexyl chloride | 95.00 | (1.045 ± 0.008) × 10 ⁻⁵ | ... | ... | (1.00) |
| VII | 95.00 | (1.80 ± 0.05) × 10 ⁻⁶ | 4.9 × 10 ⁻⁶ | ... | 0.172 |
| | 120.00 | (2.04 ± 0.03) × 10 ⁻⁶ | | | |
| Cyclobutyl chloride | 50 | 4.7 × 10 ⁻⁶ ^b | | | |
| | 70 | 4.2 × 10 ⁻⁶ ^b | 2.8 × 10 ⁻³ | ... | 36.1 |
| | 95 | 3.78 × 10 ⁻⁴ ^c | | | |
| IX | 30.00 | (1.63 ± 0.01) × 10 ⁻⁴ ^d | (1.00) | ... | ... |
|  | 30 | 6.9 × 10 ⁻⁴ ^d | 4.23 | ... | ... |
| X | 95.00 | (3.55 ± 0.04) × 10 ⁻⁶ | ... | 1.38 | ... |
| | 120.00 | (2.65 ± 0.03) × 10 ⁻⁵ ^e | | | |
|  | 90 | 1.7 × 10 ⁻⁶ ^b | ... | (1.00) | ... |

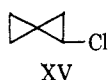
^a Errors estimated only for new data reported here. ^b Ref. 25. ^c Ref. 26. ^d Ref. 27. ^e Represents the average of more than one kinetic run. ^f Errors are least-squares probable errors.

by an n.m.r. singlet with area 2 in the vinyl region at τ 5.33. The n.m.r. also showed a multiplet of area 1 at 6.13, suggesting one hydrogen on the chlorine-bearing carbon, and a complex group of signals from 7.1 to 9.0 (total area 8). The chloride was reactive with silver nitrate (much more so than cholesteryl chloride), suggesting an allylic structure, but the infrared spectrum differs from that reported for 2-chloro-1-methylenecyclohexane.²³ The structure is therefore not specifically assigned at this time, but either the 2-chloro or 3-chloro isomer can be readily envisaged from rearrangements of the spiroheptyl cation IVc.

Thionyl chloride is known to give carbonium ion products from cyclopropylcarbinol, but rearrangement in this case is largely suppressed by tertiary amine in ether solvent.²⁴ Failure to obtain the chloro-spiroheptane in the present work is suggestive of a high stability for cation IVc, but further work must establish the relative stabilities of IVc and the smaller spirohexyl cation IVb.

Kinetics.—In Table I are given the solvolysis rates of VII, IX, and X and some selected literature data for comparison. The most significant features of these data are (1) that 5-chlorospirohexane (VII) is *slower* than cyclobutyl chloride by a factor of about 570 at 30° (based upon a rather lengthy extrapolation of the data for VII) or 210 at 95° (measured values); (2) that 4-chlorospirohexane (IX) is *faster* than cyclobutyl chloride by a factor of 360 at 30°; and (3) that the homoallylic chloride X shows no rate enhancement over homoallyl chloride itself, and hence probably has no π -type participation in the medium used.

These results are most interesting in comparison with the solvolysis of chlorospiropentane (XV), which has been found to go only about five times as fast as



(23) (a) R. T. Arnold and W. W. Lee, *J. Am. Chem. Soc.*, **75**, 5396 (1953); (b) W. W. Lee, Ph.D. Thesis, University of Minnesota, 1952.

(24) M. C. Caserio, W. H. Graham, and J. D. Roberts, *Tetrahedron*, **11**, 171 (1960).

(25) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951).

(26) J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5034 (1951).

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

cyclopropyl chloride in 50% aqueous ethanol at 200°.⁸ The conclusion which tempts one first is that participation by the α -cyclopropyl group in XV is much less favorable than that in IX, which would provide evidence for bicyclobutonium ion character in the transition states, as discussed in the Introduction above. Such a conclusion is probably unwarranted, however, because of certain pitfalls in the selection of cyclobutyl chloride and cyclopropyl chloride as models for the detection of rate enhancement in IX and XV. Specifically, both cyclobutyl³ and cyclopropyl^{8,28} cations are already stabilized by their own varieties of charge delocalization and hence structural modification. These modifications are almost certain to affect differently the ability of an additional α -cyclopropyl group, as in IX or XV, to participate. Thus the ideal model rates for comparison with IX and XV would be the rates of formation of hypothetical *classical* cyclobutyl and cyclopropyl cations from the chlorides.

Since the heat of hydrogenation of methylenecyclobutane is larger than that of methylenecyclopentane by 2.5 kcal./mole,²⁹ one can calculate that on the basis of strain alone, cyclobutyl chloride should give a classical, planar cationic transition state by solvolysis at a rate $1/31$ that of cyclopentyl chloride at 95°, or $1/85$ that of cyclobutyl chloride,³⁰ which is 2.7 times as fast as cyclopentyl chloride at 95°.

It is of interest that the rate of 5-chlorospirohexane (VII), being $1/210$ that of cyclobutyl, is very close to the theoretical rate for classical cyclobutyl. It is not unreasonable that the three-membered ring in VII should interfere with bicyclobutonium or homoallylic resonance, and the classical cyclobutyl cation therefore seems at present the best model for the transition state from VII. Product studies may shed some light on this matter.

Further support for the approximate magnitude of the rate for classical cyclobutyl is that 1-methylcyclopentyl chloride solvolyzes 476 times as fast as 1-methyl-

(28) P. von R. Schleyer and R. D. Nicholas, *ibid.*, **83**, 183 (1961).

(29) R. B. Turner in "Theoretical Organic Chemistry," papers presented to the Kekulé Symposium, Butterworths, London, 1959, p. 79.

(30) This estimated rate for classical cyclobutyl cation formation neglects concurrent changes in ΔS^\ddagger with ΔH^\ddagger . If an isokinetic relationship with a typical isokinetic temperature³¹ is assumed, a smaller ratio of cyclobutyl to classical cyclobutyl would be estimated.



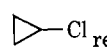
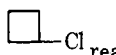
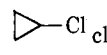
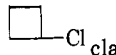
(31) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 337.

cyclobutyl chloride in 80% ethanol at 35°. ³² or 195 times as fast at 95° (extrapolated). In this case, the charge delocalization which occurs in bare cyclobutyl cation is replaced by the superior stabilization of ring strain from the methyl group, and hence the full effect of ring strain is reflected in the 4-ring-5-ring rate ratio. ²⁷

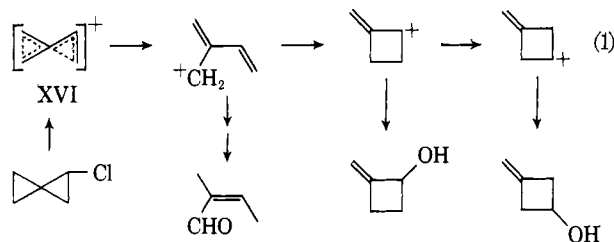
An estimate of the free energy of the classical cyclopropyl cation can be made in the same manner. The extra strain energy in 2-methyl-1-methylenecyclopropane over that in cyclopropane is about 11.1 kcal./mole. ³³ If one can then assume that the classical cyclopropyl cation has 11.1 kcal. of extra strain, then the cyclopentyl/cyclopropyl solvolysis ratio may be calculated as 4×10^6 at 95°, assuming $\Delta\Delta F^\ddagger = \Delta\Delta H^\ddagger$. Data are unfortunately not available for comparison from ethanolysis of chlorides, but an extrapolated rate ratio for the tosylates in acetic acid at 95° is 5.6×10^5 . ²⁶ If we can use this number as an approximation for the chlorides, then cyclopropyl chloride would seem to solvolyze ten times as fast as the hypothetical classical chloride.

The magnitudes of the above crude estimates are summarized in Table II. No one figure in the table has exact numerical significance, it must be emphasized, but the important point is that by making the best estimates possible with the data at hand, only weak evidence for more cyclopropylcarbinyl participation in IX than in XV can be adduced, and if there is such an effect, it is unlikely to amount to more than two or three orders of magnitude in rate.

TABLE II
ESTIMATED MAGNITUDES OF RELATIVE SOLVOLYSIS RATES AT 95°

| | |
|---|---|
|  10^2 |  10^4 |
|  10 (real) |  10^2 (real) |
|  1 (classical) |  1 (classical) |

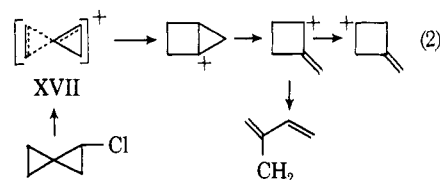
The question of whether spiro[3.3]heptan-2-yl chloride (XV) solvolyzes like the 1-halospiranes reported in the accompanying paper⁸ or like a cyclopropylcarbinyl type now assumes paramount importance. In the first case, products could be derived from a conventional near-allylic transition state XVI as shown in reaction 1. In the second case, a homoallylic cationic transition state XVII would also serve to give the same observed



products (reaction 2). Experiments are underway to distinguish these and other possibilities. If reaction 1

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

(33) R. Turner, private communication reported by J. P. Chesick, *ibid.*, **85**, 27 (1963).



should be the correct mechanism, then the rate enhancement (Table II) observed in solvolysis of XV cannot be cited as evidence for primarily homoallylic character in the cations IV, and the above experiments can be reinterpreted in favor of some bicyclobutonium character.

It is also clearly necessary to obtain quantitative data on the spiroheptyl cation IVc, since a comparison of IVb and IVc will have less ambiguity than the IVa-IVb comparison reported here and should yield the same kind of information. The fact that IX, a secondary chloride, is slower than 1-methylcyclopropylcarbinyl chloride (Table I), even though by a factor of only 4, suggests that a strain effect may still be retarding IX and provides special incentive to examine IVc.

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-Elmer Model 21B double-beam recording spectrometer with sodium chloride optics.

Spirohexane (V).—Zinc-copper couple was prepared by the method of Shank and Shechter.³⁴ Anhydrous diethyl ether (165 ml.) and zinc-copper couple (16.3 g., 0.25 g.-atom of zinc) were mixed, followed by 0.15 g. of iodine, and 53.6 g. (0.20 mole) of diiodomethane (Eastman, reagent grade, colorless). The mixture was stirred under reflux for 30 min. Methylenechlorobutane (27.2 g., 0.4 mole) was then allowed to drop into the stirred reaction mixture so as to maintain spontaneous refluxing. After the addition was complete (ca. 30 min.), the solution was maintained under reflux for an additional 20 hr.

The reaction mixture was then filtered through Super-Cel on a Büchner funnel with gentle suction, and the Super-Cel pad was subsequently washed with ether. The combined ether washings were extracted with 5% aqueous hydrochloric acid, saturated sodium bicarbonate solution, and saturated sodium chloride solution. The ether layer was dried over anhydrous magnesium sulfate, filtered, and carefully distilled through a 3-ft. wire spiral column. Diethyl ether and 5.11 g. (0.0752 mole) of unreacted methylenecyclobutane were obtained. The remaining liquid was distilled on a Holzman column to yield 6 g. (22.5%) of spirohexane, b.p. 68–70°, n_D^{20} 1.4193 (lit.¹⁰ b.p. 70°, n_D^{20} 1.4245). Vapor phase chromatography on didecyl phthalate indicated 97% purity and a negative test was obtained with an acetone solution of potassium permanganate. The infrared spectrum confirmed the lack of unsaturation. An n.m.r. spectrum showed singlets at 9.64 and 7.92 in an area ratio of 2:3, respectively. Subsequent reactions gave yields of 25.6 and 21.3%.

Anal. Calcd. for C_6H_{10} : C, 87.81; H, 12.19. Found: C, 87.87; H, 12.47.

Spirohexane was prepared also by reduction of 1,1-dibromospirohexane⁸ with lithium in tetrahydrofuran and *t*-butyl alcohol (14% yield) or with Raney nickel (W-1) and hydrogen in *n*-butyl alcohol (about 34% yield), but in neither case was it convenient to prepare V on a practical scale.¹

Vapor Phase Chlorination of Spirohexane.—Spirohexane (94.0 g., 1.145 moles) was chlorinated in an apparatus like that described by Roberts and Mazur,²⁵ using three 250-watt sunlamps. The reaction was carried out in three batches followed by fractional distillation of the product on a 12-in. wire spiral column

(34) R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1825 (1959).

to yield 15.8 g. (0.192 mole) of spirohexane, b.p. 70°; 48.2 g. of monochlorinated product, b.p. 60–75° (100 mm.); and 24.6 g. of presumed dichloride mixture, b.p. 65–75° (20 mm.). The monochloride mixture was refractionated to give 41.9 g., b.p. 55–65° (79 mm.). Vapor chromatography of this material on a 10-ft. Carbowax-20M column at 100° showed three major peaks which were, in order of increasing retention time, VIII (28.8%), VII, IX mixture (47.3%), and X (22.3%). Spectra of these materials are described in the Discussion.

Anal. Calcd. for $C_6H_{11}Cl$ (VIII): C, 60.80; H, 9.35. Found: C, 60.97; H, 9.62. Calcd. for C_6H_9Cl (VII, IX, or X): C, 61.80; H, 7.78. Found (VII, IX mixture): C, 61.67; H, 7.80. Found (X): C, 61.80; H, 7.78.

Typical runs were stopped when the temperature of the refluxing liquid reached 80° and yielded 24–28% yields of the VII–IX mixture. In one run, the mixture was allowed to reach 129° and gave less than 10% of VII with only slight contamination by IX, as judged by the n.m.r. spectrum (see Discussion).

Anal. Calcd. for C_6H_9Cl : C, 61.80; H, 7.80. Found (VII): C, 62.36; H, 7.98.

4-Spirohexene (XI).—Potassium (1.1 g., 0.281 g.-atom) was dissolved in a slight excess of *t*-amyl alcohol (nitrogen atmosphere) followed by removal of the excess alcohol by heating at 140° (30 mm.). 5-Chlorospirohexane (1 g., 0.00429 mole) was added and the resulting slurry heated for several hours on a steam bath. The flask was then attached to a Hickman distillation unit³⁵ and heated to ca. 100° to yield 0.2 g. (0.0025 mole) of crude 4-spirohexene (58%). A v.p.c. analysis on didecyl phthalate indicated 83% purity. One tenacious impurity was spirohexane (identified by n.m.r.), possibly present in the starting material. The n.m.r. spectrum described in the Discussion was obtained on a spirohexane–spirohexene mixture.

Spiro[2.4]heptadiene-4,6.—The method described by Wilcox³⁶ was used, with 2.0 moles of Fisher sodium amide, 1.0 mole of freshly distilled cyclopentadiene, and 1.0 mole of ethylene dibromide. The product (65.0 g., 0.705 mole) was isolated by distillation, b.p. 113–118° (lit.³⁶ b.p. 113° (737 mm.)), and was slightly discolored. The crude yield was 70.5% of the theoretical amount. Vapor phase chromatography on diisodecyl phthalate at 100° indicated 5.2% of ethylene dibromide impurity. The product was vacuum distilled, b.p. 52° (85 mm.), but still remained slightly discolored. An n.m.r. spectrum was fully consistent with the structure.

Spiro[2.4]heptane (VI).—Hydrogenation of spiro[2.4]heptadiene-4,6 (1 atm.) using platinum oxide in diethyl ether¹² produced spiro[2.4]heptane in 66% (based upon v.p.c. purity) of the theoretical amount. The product was distilled, b.p. 92–100°, through a 3-ft. wire spiral column from calcium hydride and magnesium; the latter removed some of the ethylene dibromide carried over from the diene preparation. A vapor-phase chromatogram on diisodecyl phthalate at 90° indicated 88% purity with only one major impurity. An n.m.r. spectrum of this material showed, in addition to the signals for spiroheptane at 8.4 and 9.63 (see Discussion), a small amount of ethylene dibromide (singlet at 6.38) and two other impurity peaks at 9.03 and 9.13, the former probably due to the methyl groups in 1,1-dimethylcyclopentane, an expected by-product. A sample of the major constituent collected on a preparative Carbowax-20M v.p.c. column showed only the spiroheptane peaks in the n.m.r. spectrum.

Vapor Phase Chlorination of Spiro[2.4]heptane (VI).—The same apparatus and method were used as for the vapor phase chlorination of spirohexane. A total of 47.0 g. (0.49 mole) of spiro[2.4]heptane was treated in two equal batches. The apparatus was allowed to equilibrate at reflux followed by the introduction of a slow stream of chlorine. Two 250-watt G.E. sunlamps were left on until the temperature of the boiling liquid reached 145° (ca. 8 hr.). Distillation yielded 8.45 g. (0.0647 mole) of recovered spiro[2.4]heptane, b.p. 50° (120 mm.), and 35.0 g. of the monochlorinated products, b.p. 80–90° (110–120 mm.). Very little higher boiling residue was formed.

Vapor phase chromatographic information was obtained on Carbowax-20M, tricresyl phosphate, diisodecyl phthalate, and polar UCON. The Carbowax-20M spectrum (10 ft., 0.25 in. in diameter, 100°) is tabulated in order of increasing retention times.

| Vapor phase chromatogram | |
|--------------------------|--------------|
| Peak no. | Rel. area, % |
| 1, 2 | 6.5 |
| 3, 4 | 10.7 |
| 5, 6, 7, 8 | 30.9 |
| 9 | 31.0 |
| 10, 11 | 3.4 |
| 12 | 17.5 |

A 1-g. sample of the monochlorinated mixture was dissolved in ether and shaken with several portions of concentrated aqueous potassium permanganate solution. Each extraction was followed by addition of saturated aqueous sodium bisulfite solution to destroy the manganese dioxide, and by a water wash. After the organic layer had been dried over anhydrous potassium carbonate, the ether was removed on a rotary evaporator and the residue was subjected to vapor phase chromatographic analysis on a 10-ft. Carbowax-20M column. The spectrum was identical in all respects with that of the starting material except for peak 12, which had been almost totally destroyed.

Peak 12 was collected for infrared and n.m.r. analysis. An infrared spectrum (carbon tetrachloride) showed absorption at 3040 (w), 2930 (s), 2830 (s), 1645 (w), 1450 (m), 1425 (w), and 1300 (m) cm^{-1} , with several additional weak absorptions throughout the fingerprint region. The n.m.r. spectrum is described in the Discussion.

Anal. Calcd. for $C_7H_{11}Cl$: C, 64.38; H, 8.49. Found: C, 64.58; H, 8.56.

Spiro[2.4]heptane-4-one.—2-(2'-Bromoethyl)cyclopentanone was treated with aqueous potassium hydroxide according to the procedure of Mayer and Schubert³⁷ and was converted to 28.0 g. (97.3%) of spiro[2.4]heptan-4-one, b.p. 50–52° (11 mm.), n_D^{20} 1.466 (lit.³⁷ b.p. 54–55° (14 mm.), $n_D^{17.5}$ 1.4688). An n.m.r. spectrum of the material confirmed its structure. Two groups of peaks extending from 8.84 to 9.37 comprised a symmetrical multiplet (area 4) which bore a striking resemblance to the A_2B_2 multiplets of 2-ethylaminoethanol³⁸ and bromoethylphthalimide.³⁸ This multiplet was assigned to the cyclopropane protons. A second multiplet extending from 7.65 to 8.09 (area 6) was assigned to the remaining three methylene groups.

Spiro[2.4]heptane-4-ol (XIII).—Spiro[2.4]heptane-4-one (28.0 g., 0.255 mole) was dissolved in 30 ml. of dry ether and slowly dropped into a stirred mixture of 5 g. (0.132 mole) of lithium aluminum hydride and 50 ml. of anhydrous ether.

When the addition was complete, the excess lithium aluminum hydride was destroyed by careful addition of water. The aqueous layer was then extracted with ether, the ether was removed on a rotary evaporator, and the residue was vacuum distilled, b.p. 68–69° (13–14 mm.), to yield 20.45 g. (71%) of spiro[2.4]heptan-4-ol, n_D^{25} 1.4730. A vapor phase chromatogram indicated a purity of 89%; the impurities comprised several broad peaks.

An infrared spectrum on a collected sample showed absorptions at 3625 (w), 3400 (broad), 3090 (w), 2960 (s), 2870 (sh), as well as below 1475 cm^{-1} . An n.m.r. spectrum showed absorption at 6.5 (area 1), a singlet at 7.58 (area 1; shifted upfield 0.1 p.p.m. by a trace of HCl), a complex multiplet at ca. 8.2 (area 6), and an unsymmetrical multiplet extending from 9.16–9.69 (area 4).

Anal. Calcd. for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.95; H, 10.93.

The *p*-nitrobenzoate ester was prepared, m.p. 78.0–78.5°.

Anal. Calcd. for $C_{14}H_{15}NO_4$: C, 64.35; H, 5.79; N, 5.37. Found: C, 64.54; H, 5.87; N, 5.51.

Treatment of Spiro[2.4]heptane-4-ol with Thionyl Chloride.—Spiro[2.4]heptane-4-ol (5.62 g., 0.05 mole) and a few drops of pyridine were cooled in an ice bath while 5.95 g. (0.05 mole) of thionyl chloride was slowly added, and the contents of the flask were shaken occasionally. The resulting mixture was maintained at reflux for 45 min. followed by distillation of the product, b.p. 73–77° (58 mm.), to yield 5.26 g. of liquid, 92% of which consisted of two components (Carbowax-20M v.p.c. column) in the ratio of 1 to 1.19 (order of increasing retention times), each of which gave the correct analysis of $C_7H_{11}Cl$. Together they represented a 74.5% yield.

The components were collected for n.m.r. and infrared analysis. The compound with the longest retention time was shown to

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

(36) C. F. Wilcox, Jr., and R. R. Craig, *J. Am. Chem. Soc.*, **83**, 3866 (1961).

(37) R. Mayer and H. Schubert, *Chem. Ber.*, **91**, 768 (1958).

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

be identical with 1-(2'-chloroethyl)cyclopentene (identity of infrared and n.m.r. spectra), which was obtained as a product of the vapor phase chlorination of spiro[2.4]heptane.

Anal. Calcd. for $C_7H_{11}Cl$: C, 64.37; H, 8.49. Found: C, 64.08; H, 8.46.

The infrared spectrum of the second compound showed, among other absorptions, bands at 3100 (m), 1650 (s), 900 (s), and 872 (s) cm^{-1} . The n.m.r. spectrum showed a singlet at 5.33 (area 2), a multiplet at 6.13 (area 1), and a complex group of peaks extending from 7.1 to 9.0 (total area 8).

A solution of the compound in a 70% dioxane-30% water mixture gave an instantaneous heavy precipitate of silver chloride upon treatment with a dioxane-water silver nitrate solution under conditions where cyclohexyl chloride and cholesteryl chloride were completely unreactive. Cholesteryl chloride did not react even after heating the solution to 50°.

On the basis of the above information (see Discussion), the compound was assigned the structure of a chloro-1-methylenecyclohexane.

Anal. Calcd. for $C_7H_{11}Cl$: C, 64.37; H, 8.49. Found: C, 64.06; H, 8.52.

Treatment of Spiro[2.4]heptane-4-ol with Thionyl Chloride and Triethylamine in Ether.—Triethylamine (3.72 g., 5.14 ml., 0.0365 mole) and spiro[2.4]heptane-4-ol (4.1 g., 0.0365 mole) were dissolved in 53 ml. of ether and cooled in an ice-salt bath. Thionyl chloride (4.34 g., 2.62 ml., 0.0365 mole) was added slowly (ca. 30 min.) so that the temperature remained below 6°.

The ether solution was flash distilled and the yellow liquid residue was then vacuum distilled, b.p. 70-72° (50 mm.), to yield 2.503 g. (53%) of alkyl chlorides. A vapor phase chromatogram on Carbowax-20M showed chloro-1-methylenecyclohexane and 1-(2'-chloroethyl)cyclopentene in a ratio of 1 to 1.09. The identities of the components were established by means of retention time comparison with samples from the previous reaction (under identical conditions), as well as with a mixed chromatogram.

Treatment of Spiro[2.4]heptane-4-ol with *p*-Toluenesulfonyl Chloride and Pyridine Hydrochloride.—Spiro[2.4]heptane-4-ol (4.5 g., 0.04 mole), pyridine (4.02 ml., 0.05 mole), pyridine hydrochloride (4.63 g., 0.04 mole), and *p*-toluenesulfonyl chloride (7.62 g., 0.04 mole) were mixed in that order. When the exothermic reaction subsided, the mixture was heated on a steam bath for 7 hr. Dry hydrogen chloride was then bubbled through the mixture to ensure that all of the pyridine had been converted to the hydrochloride salt, and the two-phase liquid was allowed to cool. The upper phase was decanted from the solid lower phase and distilled, b.p. 76-78° (55 mm.), to yield 2.38 g. (45.5%) of alkyl chlorides.

A vapor phase chromatogram on Carbowax-20M revealed a mixture of chloro-1-methylenecyclohexane and 1-(2'-chloroethyl)cyclopentene in a ratio of 1 to 2.27. Four closely spaced impurity peaks with shorter retention times were also present. The identities of the two compounds were confirmed by a comparison of the infrared spectra of collected samples with those for the compounds from the thionyl chloride reaction in which the original identifications were made.

Kinetic Procedure.—All kinetic runs carried out at 95 or 120° were accomplished by use of the ampoule procedure which has been described in the previous paper.⁸

Near Room Temperature Kinetic Procedure.—A constant temperature bath similar to that previously described was used, except that water was used as the bath liquid and glass wool and aluminum foil provided the insulation. A black 100-watt light bulb provided the only heat source for the 30° temperature and this together with a 50-ft. coil of 0.25-in. copper tubing through which tap water circulated was utilized for the 15° temperature. The tap water temperature was 13-14°.

Approximately 44 ml. of the ethanol-water solution was placed in a 50-ml. volumetric flask and allowed to equilibrate for several hours in the bath. A sample of the alkyl chloride was then quickly added to the alcohol solution (clock started) and the flask was shaken vigorously for a few moments followed by reimmersion in the bath. At appropriate time intervals a 5-ml. aliquot was taken from the flask and delivered into 20 ml. of cold acetone. The last aliquot was taken after at least ten half-lives had elapsed.

All of the acetone solutions were stored at -20° and titrated as a group using brom phenol blue indicator and standardized methanolic sodium methoxide.

The raw data from a typical kinetic run for the solvolysis of 4-chlorospirohexane (IX) at $30.00 \pm 0.05^\circ$ has been indicated below. Although a mixture of 4- and 5-chlorospirohexane was used, ethanolsis carried out at lower temperatures reflected only the solvolysis rate of the faster 4-chloride. A mixture of the 4- and 5-chloroalkanes was subjected to ethanolsis at room temperature (50% aqueous ethanol) for 9 days, followed by isolation of the starting material by continuous ether extraction. Alcohols were destroyed by the addition of calcium hydride and the resulting liquid gave, on a vapor phase chromatogram (Carbowax-20M at 100°), predominantly one peak, which corresponded to the retention time of the original chloride mixture. However, an n.m.r. spectrum showed that only 5-chlorospirohexane was present.

| Time elapsed, min. | Titrated (HCl) | -ln (HCl) | Time elapsed, min. | Titrated (HCl) | -ln (HCl) |
|--------------------|----------------|-----------|--------------------|----------------|-----------|
| ∞ | 0.01482 | 4.212 | 45 | 0.00578 | 4.706 |
| 15 | 0.00252 | 4.398 | 60 | .00697 | 4.847 |
| 25 | .00379 | 4.507 | 75 | .00798 | 4.985 |
| 35 | .00482 | 4.605 | 90 | .00884 | 5.120 |

$$\text{Rate constant} = (1.598 \pm 0.014) \times 10^{-4} \text{ sec.}^{-1}$$

Quantitative Analysis of the 4- and 5-Chlorospirohexane Mixture.—The relative amounts of 4- and 5-chlorospirohexane present in the vapor phase chlorination products of spirohexane was determined both by an examination of the nuclear magnetic resonance spectrum and kinetic solvolysis data. The sample of the mixture was collected on an 8-ft. Carbowax-20M chromatography column.

The kinetic data at 95 and 120° were extrapolated back by the least-squares technique to determine the initial concentration of the slower solvolyzing 5-chlorospirohexane, and this value was then compared to the total initial concentration of alkyl chloride from the infinity titer.

The n.m.r. spectrum of VII showed a doublet at 7.48 for the cyclobutane CH_2 groups, whereas that of IX showed a 2-proton multiplet at 7.82 for one of the cyclobutanemethylenes, the other being buried under the 7.48 peak. It was therefore simple to calculate the composition of a mixture by integration of these two peaks.

The results are

| | 5-Chlorospirohexane, % |
|----------------------------------|------------------------|
| N.m.r. spectrum A-60 integrator | 42.3 |
| N.m.r. spectrum HR 60 planimeter | 43.0 |
| Ethanolsis data at 95° | 39.9 |
| Ethanolsis data at 120° | 41.6 |
| Average | 41.7 |

Acknowledgment.—The authors wish to acknowledge the aid of the following staff members: Mr. Josef Nemeth and associates who performed the microanalyses, Messrs. P. McMahon and D. Johnson and associates who determined some of the infrared spectra, and Messrs. O. W. Norton and D. Johnson and their associates who determined the n.m.r. spectra. This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said fund. We are also indebted to Dr. S. G. Smith for his helpful suggestions with regard to many of the details of the kinetic procedure.