1965

# The acid and base catalyzed ring opening of 1-arylcyclopropanols

Robert Allen Klein
*Iowa State University*

# THE ACID AND BASE CATALYZED RING OPENING OF 1-ARYLCYCLOPROPANOLS

by

Robert Allen Klein

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1965

# TABLE OF CONTENTS

# INTRODUCTION

Cyclopropanol was first synthesized in the 1940's. It undergoes isomerization to propionaldehyde in either acid or base. The 1-substituted cyclopropanols also undergo rearrangement in acid or base to the corresponding ketones.

In general, the cyclopropanols can be considered analogous to the enol forms of either aldehydes or ketones. The cyclopropane ring itself can be considered as somewhat analogous to a double bond. We undertook these studies of 1-arylcyclopropanols to better determine what type of mechanism or mechanisms might be operative in the acid and base catalyzed ring opening of cyclopropanols. In order to accomplish this objective it was necessary to undertake the synthesis of a number of 1-arylcyclopropanols.

The following pages describe first the background of cyclopropane compounds in general, and finally, information obtained from studies carried out on the 1-arylcyclopropanols.

# HISTORICAL

Since Freund's[1] original synthesis in 1882, chemists have been intrigued by the chemical behavior of cyclopropane and its derivatives. It is the intent of this review to discuss a few methods of synthesis of cyclopropanes, considering only methods which are useful for the preparation of cyclopropanols, or which have been tried in the past and have not been effective in attaining cyclopropanols. Secondly, it is of interest to review some of the behavior of cyclopropanes which provide such a source of interest for the chemist.

Cyclopropanes have been produced by several general methods. These methods may be listed as: the closure by active metals of 1,3-dihalopropanes; the base catalyzed closure of halo or tosyl esters of nitriles, ketones, esters, nitro compounds, or any compounds having an active hydrogen; carbene insertions and additions; coupling by a modified Grignard reagent. Attempts have been made to utilize all these methods for the synthesis of cyclopropanols. Reviews by Vogel[2,3] furnish a good background of synthetic approaches to cyclopropane derivatives. Freund[1] first used sodium on 1,3-dibromopropane. Later Gustavson[4] reacted zinc dust in ethanol with

---

[1]A. Freund, J. prakt. Chem., 26, 367 (1882).

[2]E. Vogel, Angew. Chem., 72, 4 (1962).

[3]E. Vogel, Fortsch. Chem. Forsch., 3, 430 (1955).

[4]F. Gustavson, J. prakt. Chem., 42, 495 (1890).

1,3-dibromopropane to effect ring closure, a procedure which is still quite widely used. Recent work by Boord[5] and Bartelson[6] in synthesizing some alkyl substituted cyclopropanes shows that yields can be improved by a modification of the Gustavson reaction. Modifications include a lowering of reaction temperature and a change in the solvent.

Magnesium has also been used as an effective metal for ring closure. Boord[7] in a fairly recent paper discloses the use of magnesium to effect ring closure of 1-bromo-3-ethoxypropanes. He also utilized magnesium in tetrahydrofuron to prepare methylene cyclopropane from 3-chloro-2-(chloromethyl)-propene.[8] Anderson[9] also utilized this method to prepare the methylene cyclopropane used in his study of its chemical properties. Although the use of active metals has proven of value in the synthesis of alkyl cyclopropanes, the method has not proven very efficacious for the preparation of cyclopropanols.

---

[5]R. G. Kelso, K. W. Greenlee, J. M. Derfer and C. E. Boord, J. Am. Chem. Soc., 75, 3344 (1953).

[6]J. D. Bartelson, R. E. Burke and H. P. Lankelma, J. Am. Chem. Soc., 68, 2513 (1946).

[7]J. T. Gragson, K. W. Greenlee, J. M. Derfer and C. E. Boord, J. Org. Chem., 20, 275 (1955).

[8]J. T. Gragson, K. W. Greenlee, J. M. Derfer and C. E. Boord, J. Am. Chem. Soc., 75, 3344 (1953).

[9]B. C. Anderson, J. Org. Chem., 27, 2720 (1962).

Hübner,[10] Aschan,[11] and Tornoe[12] report having reacted 1,3-dihalopropan-2-ols with sodium, but only allyl alcohol could be obtained as a product.

The use of a compound having a leaving group $\beta$ to an active hydrogen is a method used quite extensively for the preparation of derivatives of cyclopropane. This method is illustrated in Figure 1. This method was first utilized by Kohler[13,14] and later Smith[15,16,17] for the synthesis of cyclopropanes having ester, carboxyl, ketone, nitrile or nitro substituents. Eilers[18] prepared trans-2-phenyl cyclopropane carboxylic acid and 2-phenyl-1-methylcyclopropane carboxylic acid from the corresponding ethyl-$\gamma$-chloro butanoates (Figure 2).

---

[10]H. Hübner and K. Müller, Ann., 159, 168 (1871).

[11]O. Aschan, Chem. Ber., 23, 183 (1890).

[12]H. Tornoe, Chem. Ber., 24, 2670 (1891).

[13]E. P. Kohler and F. R. Davis, J. Am. Chem. Soc., 41, 992 (1919).

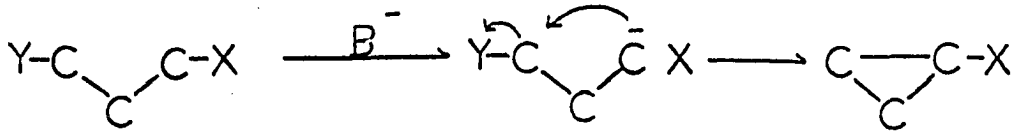
[14]E. P. Kohler and J. B. Conant, J. Am. Chem. Soc., 39, 1404, 1699 (1917).

[15]L. I. Smith and J. S. Showell, J. Org. Chem., 17, 836 (1952).

[16]L. I. Smith and R. E. Kelly, J. Am. Chem. Soc., 74, 3300, 3305 (1952).

[17]L. I. Smith, Record Chem. Progr., 11, 65 (1950).

[18]K. L. Eilers, The synthesis and reactions of substituted cyclopropanols. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1963.



Y = Cl, Br, I, Tos etc.

X = -C(=O)-R, C(=O)-OR, COOH, $NO_2$, CN etc.

Figure 1. The preparation of substituted cyclopropanes by intramolecular displacement

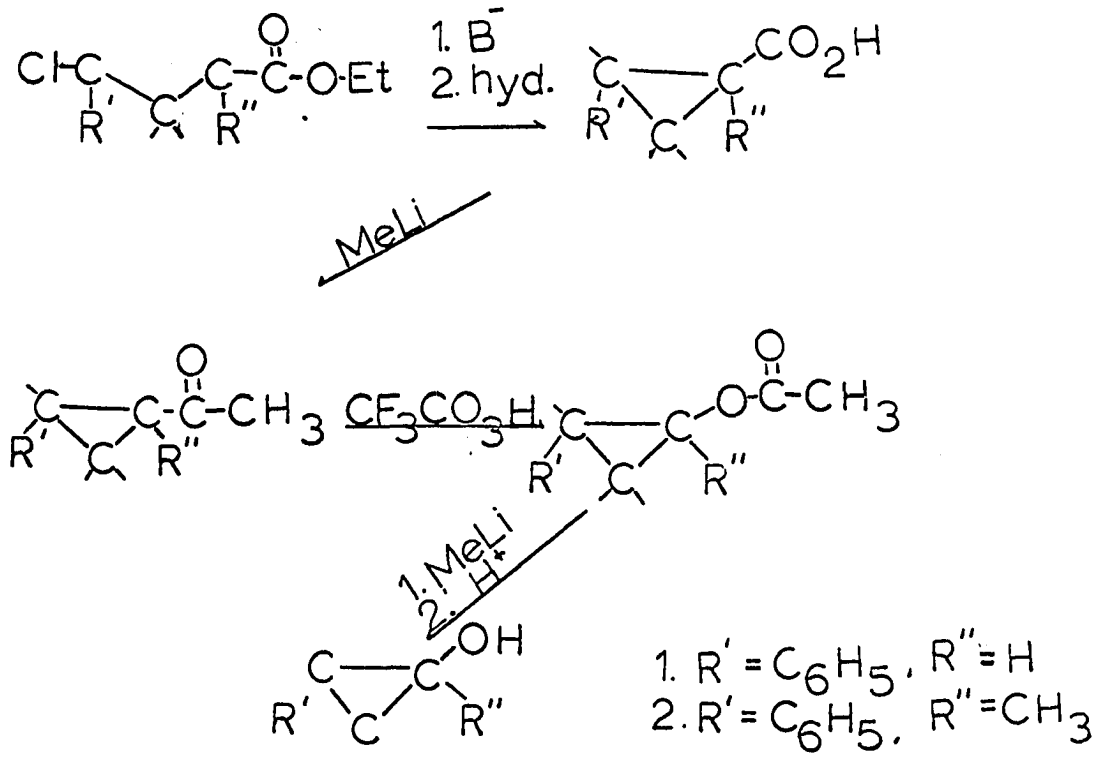



Figure 2. Eiler's method of preparation of substituted cyclopropanols

In order to prepare cyclopropanols corresponding to these acids some recently discovered techniques were used. Eilers was able to prepare the methyl ketones by reaction of the acids with methyl lithium,[19] giving the cyclopropylmethyl ketones in good yield (75%). The ketones were converted to the acetates by reaction with peroxytrifuluoroacetic acid. This reagent was found by Emmons and Lucas[20] to be effective in converting methyl cyclopropyl ketone to the acetate. Peroxybenzoic acid had been found by Friess and Pinson[21] ineffective in oxidizing methyl cyclopropyl ketone to cyclopropyl acetate. The resulting substituted cyclopropyl acetates were then reduced to the cyclopropanols by methyl lithium. This reagent was found to be superior to lithium aluminum hydride.[22,23]

The decomposition of pyrazolines was first found to give

---

[19] C. Tegner, Acta Chem. Scand., 6, 782 (1952).

[20] W. D. Emmons and G. B. Lucas, J. Am. Chem. Soc., 77, 2287 (1955).

[21] S. L. Friess and R. Pinson, J. Am. Chem. Soc., 74, 1302 (1952).

[22] L. R. Mahoney, The solvolysis of cyclopropyl acetate. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1960.

[23] C. H. DePuy and L. R. Mahoney, J. Am. Chem. Soc., 86, 2653 (1964).

cyclopropane derivatives by Büchner.[24] Kohler[25] used this reaction to prepare some cyclopropane carboxylic acids which he found impossible to obtain by the usual base condensations, but yields were very low. Tractenberg[26] used the same reaction to prepare a series of substituted carboxylic acids. He obtained about 25-30 per cent yields of the desired trans-acids, but did not report on the amount of cis acids produced. These workers used these acids in a study of substituent effects on acid strength.[27] Freeman[28] developed a method of preparing various acetoxy pyrazolines by oxidation with lead tetraacetate. These could be decomposed to the corresponding cyclopropyl acetates by thermal or photochemical means (Figure 3). Rodewald[29] has used this procedure to prepare a series of 2-substituted-phenylcyclopropanols in a study of substituent effects on the acid catalyzed ring opening.

---

[24] E. Büchner, Chem. Ber., 28, 221 (1895).

[25] E. P. Kohler and L. L. Steel, J. Am. Chem. Soc., 41, 1093 (1919).

[26] E. N. Tractenberg and G. Odian, J. Am. Chem. Soc., 80, 4015 (1958).

[27] E. N. Tractenberg and G. Odian, J. Am. Chem. Soc., 80, 4018 (1958).

[28] J. P. Freeman, J. Org. Chem., 28, 885 (1963).

[29] L. B. Rodewald, Graduate Assistant, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Synthesis of substituted cyclopropanols. Private communication. 1964.

Simmons and Smith[30] have described the use of zinc-copper alloy with methylene iodide as a quite specific reagent in adding to a double bond to give a cyclopropane. They reported reasonably good yields of cyclopropyl acetate from the use of zinc-copper couple with vinyl acetate. Mahoney[22] only obtained minute yields by this method when substituted vinyl acetates were used as substrates.

The use of zinc-copper couple to make cyclopropanes in some other instances should, perhaps, be mentioned. Dauben[31] found this method quite useful in producing various cyclopropyl carbinols which would have been difficult or impossible to obtain by other approaches. He reacted zinc-copper couple with the corresponding allyl alcohols. Eastman[32] prepared some phenylcyclopropanes in a study of U.V. spectra as affected by steric relations of the cyclopropane ring with the aromatic system.

One very interesting use to which the Simmons-Smith reaction has been put is a reaction sequence given by Wasserman.[33] He found that the Simmons-Smith reagent was capable

---

[30]H. E. Simmons and R. D. Smith, J. Am. Chem. Soc., 81, 4256 (1959).

[31]W. G. Dauben and G. H. Berezin, J. Am. Chem. Soc., 85, 468 (1963).

[32]A. L. Goodman and R. H. Eastman, J. Am. Chem. Soc., 86, 908 (1964).

[33]H. H. Wasserman and D. C. Clogett, Tetr. Letters, No. 7, 341 (1964).

of reacting with 1-ethoxy vinyl acetates and benzoates to form the corresponding 1-ethoxy-1-acetoxy cyclopropanes (Figure 4). The latter could then be reacted with lithium aluminum hydride, methyl magnesium iodide, or phenyl magnesium bromide to give 40-45 per cent yields of 1-substituted cyclopropanols. The method suffers a bit due to the number of steps involved, and although the final step gives good yields, some of the intermediate steps do not.

Magrane and Cottle[34] in 1942 announced the discovery of a low molecular weight alcohol isolated from the reaction of epichlorohydrin and ethylmagnesium bromide. By its properties and by the preparation of several derivatives the compound was identified as the previously unknown cyclopropanol. In a later paper[35] it was found that the addition of ferric chloride caused the reaction to proceed more smoothly. Roberts[36] used both the Cottle procedure and the air oxidation of cyclopropylmagnesium bromide to prepare cyclopropanol. The latter reaction gave only a very small yield of product. Neither Cottle or Roberts were able to obtain pure cyclopropanol, although pure derivatives were obtained.

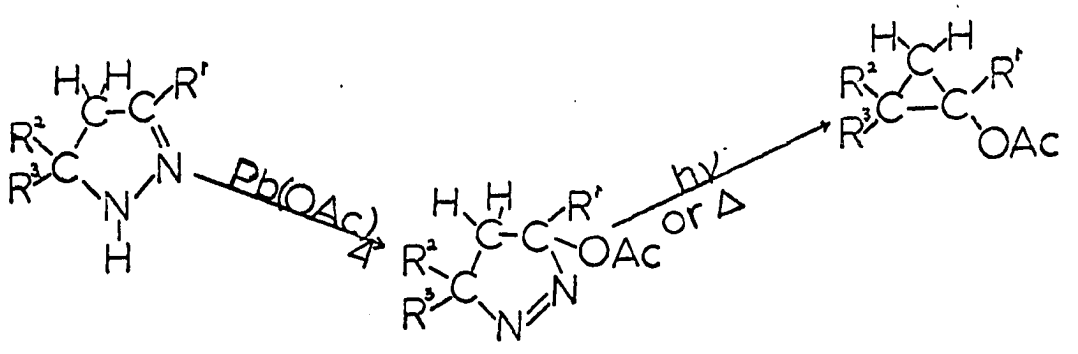
The first isolation of pure cyclopropanol was

---

[34] J. K. Magrane, Jr. and D. L. Cottle, J. Am. Chem. Soc., 64, 484 (1942).

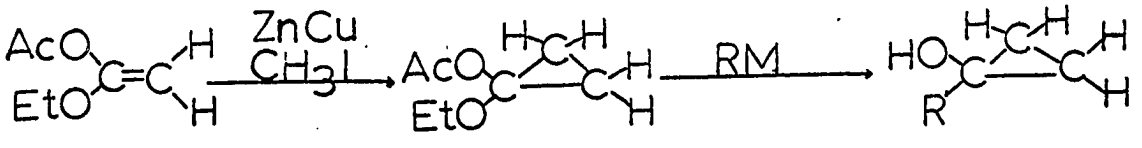
[35] G. W. Stahl and D. L. Cottle, J. Am. Chem. Soc., 65, 1782 (1943).

[36] J. D. Roberts and V. C. Chambers, J. Am. Chem. Soc., 73, 3176 (1961).




| $R^1$ | $R^2$ | $R^3$ | % Yield |
|---|---|---|---|
| $CH_3$ | $CH_3$ | $CH_3$ | 56 |
| H | H | $C_6H_5$ | 10 |
| $C_6H_5$ | $CH_3$ | $CH_3$ | 42 |
| $C_6H_5$ | H | $C_6H_5$ | 61 |
| $C_6H_5$ | H | $C_6H_5$ | 65 |
| $C_2H_5$ | $CH_3$ | $C_2H_5$ | 64 |
| $C_6H_5$ | H | H | 20 |
| $C_6H_5$ | H | $CH_3$ | 60 |

Figure 3. The synthesis of cyclopropyl acetates via pyrazoline decomposition




1. R=H
2. R=$CH_3$
3. R=$C_6H_5$

Figure 4. The synthesis of cyclopropanols by use of zinc-copper couple

accomplished by Mahoney[22] using preparative gas chromatography. Kharasch[37] describes the use of a Grignard reagent with ferric chloride reacting with 1,3-dihalopropanes or 1-halo-3-phenoxypropanes to give cyclopropane in 85% yield, and it seemed probable that the Cottle synthesis involved a similar sequence of reactions.

Dappen[38] investigated the extension of this method to the preparation of substituted cyclopropanols by the use of appropriate substituted epichlorohydrins (Figure 5).

A few other instances of attempted cyclopropanol preparations should be mentioned. Kishner[39] diazotized cyclopropyl amine with sodium nitrite and hydrochloric acid, but obtained allyl alcohol as a product. Lipp and Padberg[40] prepared aphocamphenyl amine and succeeded in diazotizing it to the corresponding alcohol. They found that the alcohol isomerized in acid or to camphinilone (Figure 6).

Nickon,[41] investigating the behavior of optically active camphinilone with potassium t-butoxide in t-butanol, has

---

[37]M. S. Kharasch, M. Weiner, W. Nudenberg, A. Bhattacharya, T. Wang and N. C. Yang, J. Am. Chem. Soc., 83, 3232 (1961).

[38]G. M. Dappen, Synthesis and isomerization of cyclopropanols. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1962.

[39]M. Kishner, Chem. Zentr., 1, 1704, 1709 (1905).

[40]P. Lipp and C. Padberg, Chem. Ber., 54, 1316 (1921).

[41]A. Nickon and J. L. Lambert, J. Am. Chem. Soc., 84, 4604 (1962).

postulated a cyclopropanol anion intermediate formed via a homoenolate anion (Figure 7).

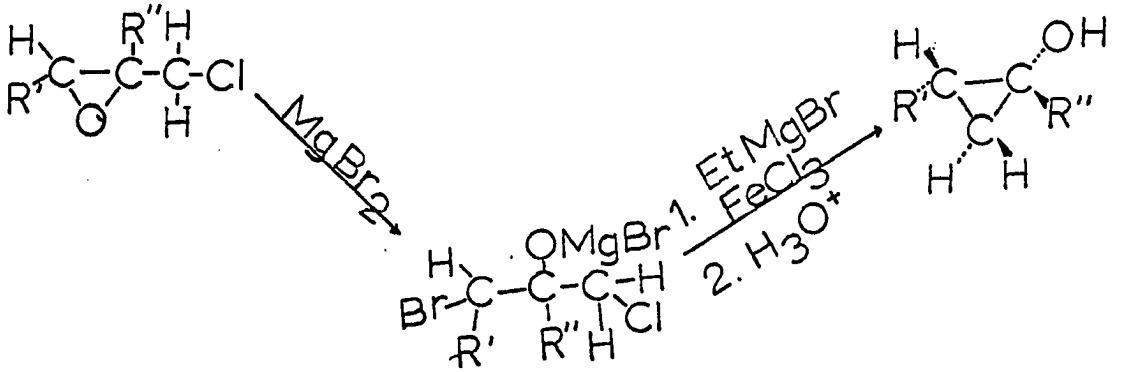
In general, cyclopropane derivatives are unique in both their chemical and physical properties. They behave in a manner which has prompted comparison with ethylene and ethylene derivatives. Cyclopropanols themselves may be compared to enols, tautomerizing to the corresponding aldehydes or ketones. Cyclopropyl ketones have been found to behave somewhat analogously to $\alpha,\beta$-unsaturated aldehydes or ketones.[13,14] Vinyl cyclopropanes have been shown in some instances at least[42] to undergo a Diels-Alder type of addition to maleic anhydride. Their spectra show conjugative effects somewhat intermediate between those of alkanes and alkenes.

The first such effect was noted by Burt and Carr[43] in a study of cyclopropyl ketones. The absorption maximum in the ultraviolet of cyclopropyl ketones was found to be located in a position intermediate to an $\alpha,\beta$ unsaturated ketone and its

---

[42] S. Sarel and E. Breuer, J. Am. Chem. Soc., 81, 6522 (1959).

[43] E. P. Burt and C. P. Carr, J. Am. Chem. Soc., 41, 1590 (1918).




1. R'=phenyl, R"=H

2. R'=H, R"=phenyl

Figure 5. The preparation of cyclopropanols via the use of the Cottle synthesis[34,35]

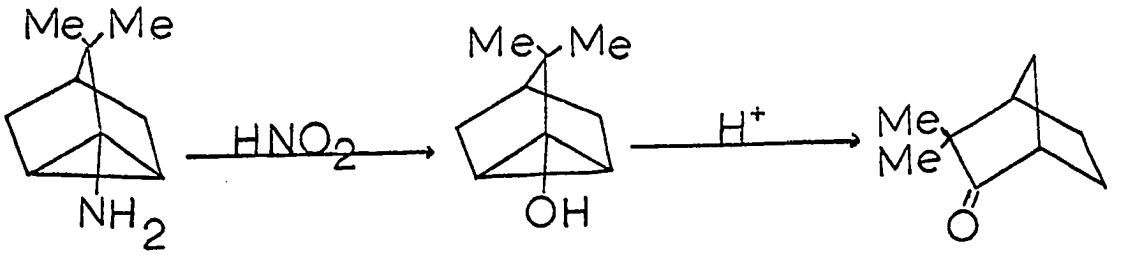



Figure 6. The preparation of aphocamphenol by amine diazotization

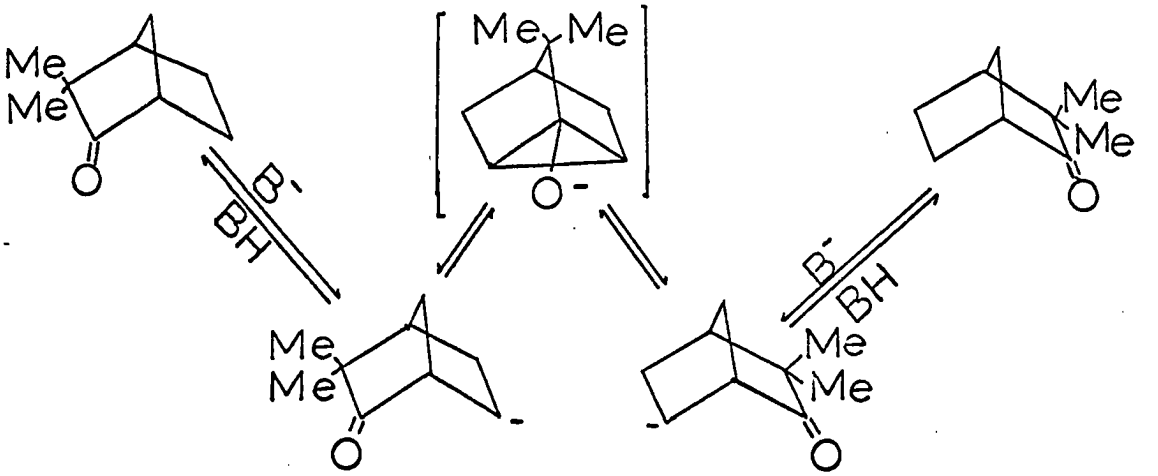



Figure 7. Nickon's postulated cyclopropanol anion intermediate in the racimization of camphinilone

saturated analog. Other workers[44,45,46] have observed essentially the same effect.

Eastman[47] and Smith[48] have postulated that the cyclopropane ring is unable to transmit conjugation. Smith prepared phenyl bicyclopropane and found that the second cyclopropane ring had little effect upon the absorption pattern, which was very similar to that of phenyl cyclopropane. Eastman also concluded from his studies that although a cyclopropyl ring at the end of a $\pi$ system was capable of exhibiting conjugation effects, it could not act as a $\pi$ system in transmitting conjugative effects.

However, Cromwell[49] and Cannon[50] disagree. Cromwell noted a small bathochromic shift for both 4' phenylbenzoyl cyclopropane and benzoyl cyclopropane when a phenyl group is placed on the cyclopropane ring (Table 1). Cromwell also

---

[44] J. M. Klotz, J. Am. Chem. Soc., 66, 88 (1944).

[45] J. D. Roberts and C. Green, J. Am. Chem. Soc., 68, 214 (1946).

[46] R. R. Mariella, J. Am. Chem. Soc., 70, 1494 (1948).

[47] R. H. Eastman and S. K. Freeman, J. Am. Chem. Soc., 77, 6642 (1955).

[48] L. R. Smith and E. R. Rogier, J. Am. Chem. Soc., 73, 3840 (1951).

[49] R. J. Mohrbacher and N. H. Cromwell, J. Am. Chem. Soc., 79, 401 (1957).

[50] G. W. Cannon, A. A. Santilli and P. Shenian, J. Am. Chem. Soc., 81, 1660 (1959).

notes a shift in the I. R. of these compounds of up to 6 $cm^{-1}$ in the carbonyl region as further illustration of these effects.

Table 1. Shift in ultra-violet maximum for cyclopropyl ketones

| $CH_2$—$CH$-C-Ar ($CH_2$, O) | | | $C_6H_5CH$—$CH$-C-Ar ($CH_2$, O) | | | Ar=p-$C_6H_5$ |
|---|---|---|---|---|---|---|
| Ia, | 238 | 14.4 | IIa, | 276 | 26.0 | a, R=H |
| Ib, | 242 | 18.2 | IIb, | 280 | 23.0 (cis)<br>28.0 (trans) | b, R=$C_6H_5$ |

Cannon et al.[50] have also cited evidence for both I. R. and U. V. data as proof of the transmission of conjugative effects by the cyclopropane ring. The addition of a 2-methyl group to cyclopropane nitriles, esters, or ketones generally results in a shift to slightly lower frequencies in the I.R. This is interpreted as evidence of conjugative effects exhibited by the cyclopropane ring. Although the U. V. spectra showed little or no shift a small change in absorption intensities was noted. This was considered as also being due to conjugative effects. Lukina[51] has pointed out that enhanced Raman spectral intensities may be attributed to conjugative effects from the cyclopropane ring.

Other evidence of conjugative effects appears from a

[51] M. Yu Lukina, Russian Chem. Rev., 31, 419 (1962). (Eng. trans.).

study of cyclopropane derivatives. Values of dipole moments by Rogers and Roberts[52,53] of cyclopropane derivatives are unusually low in comparison with normal alkyl analogs. This has been interpreted as due to ground state conjugative effects involving electronic interaction of the substituent with the cyclopropane ring.

Tractenberg and Odian[27] determined the for the ionization of trans-2-phenylcyclopropane carboxylic acids. This value was compared with the for two other series, phenylpropionic acids and cinnamic acids. A very small difference in for the -phenylpropionic and cyclopropane carboxylic acids was considered negligable. The for the hydrolysis of the corresponding ethyl esters of the three series of acids was determined by Fuchs and co-workers.[54,55] They found that for this reaction to be intermediate for the three series (Table 2). This was considered as proof that the cyclopropane ring did transmit a conjugative effect. The cyclopropane ring also has some other unique features. Linnett,[56] using

---

[52]M. T. Rogers and J. D. Roberts, J. Am. Chem. Soc., 68, 843 (1946).

[53]M. T. Rogers, J. Am. Chem. Soc., 69, 2544 (1947).

[54]R. Fuchs and J. J. Bloomfield, J. Am. Chem. Soc., 81, 3158 (1959).

[55]R. Fuchs, C. A. Kaplan, J. J. Bloomfield and L. F. Hatch, J. Org. Chem., 27, 733 (1962).

[56]J. W. Linnett, Nature, 160, 162 (1947).

I. R. and Raman spectral data for the C-H bond stretching frequencies, has calculated the force constant of the C-H bond in cyclopropane to be 5.0 units. This is unusual in comparison to value of 4.6-4.8 for the methylene C-H in normal unstrained paraffins. It does, however, compare very closely with a value of 5.1 for the C-H bond stretching in ethylene.

Table 2. Comparison of rho for acid ionization and ester hydrolysis

| Series | $K_{(i)}H_2O$[27] | $K_{(i)}$ (50% $C_2H_5OH$) | Ester hydr. | |
|---|---|---|---|---|
| trans-cinnamic acids | .466 | | 1.301 | 1.329[54] |
| cis-cinnamic acids | | | 1.122 | |
| trans-2-phenyl-cyclopropane | .182 | .473 | .812 | .789 |
| cis-2-phenyl-cyclopropane | | .436 | 1.014 | |
| _-phenylpro-pionic acids | .212 | .344 | .498 | |

Electron diffraction[57,58,59] data also reveals some unusual features of the ring. The H-C-H bond angle is 118.2, almost that for ethylene.[57] The C-C bond distance is 1.54A compared to 1.55A for ethane.

These considerations prompted Coulson and Moffitt[60] to carry out a quantum-mechanical treatment of the cyclopropane ring. The picture that emerged from this work is of the bonds holding the carbon nuclei together being directed at a slight angle away from the line joining the two carbon atoms. This sort of picture has been designated as being a "bent bond description for the molecule. The C-C bond is pictured as having slightly more p character than the normal hybrid orbitals of tetrahedral carbon. The corresponding orbitals have slightly more s character than the normal. Ingraham[61] has shown that the C-C bond can be designated as $sp^{4.12}$ and the C-H bond as $sp^{2.28}$. These values are taken from the wave function given by Coulson and Moffitt for the ring (R)

---

[57] O. Bastiansen and O. Hassel, Tids Kjemi. Bergvesen Met., 6, 71 (1946). Original not available; cited in H. A. Skinner, Nature, 160, 902 (1947).

[58] J. M. O'Gorman and V. Shomaker, J. Am. Chem. Soc., 68, 1138 (1946).

[59] L. Pauling and L. O. Brockway, J. Am. Chem. Soc., 59, 1223 (1937).

[60] C. A. Coulson and W. E. Moffitt, Phil. Mag., 40, 1

[61] L. T. Ingraham, Steric effects on certain physical properties. In M. S. Newman, ed. Steric effects in organic chemistry. New York, N. Y., John Wiley and Sons, Inc. 1956. pp. 481-522.

and C-H orbitals respectively.

1. $\Psi_R = .442[\psi(2S) + 2.03\ \psi(2P_{\sim}R)]$

2. $\Psi_{C-H} = .552[\psi(2S) + 1.51\psi(2P_{\sim}C\text{-}H)]$

In 1, $2.03^2 = 4.12$ hence the Ring orbital is designated as $sp^{4.12}$. The same argument holds for the C-H orbital designation, $sp^{2.28}$.

Coulson and Moffitt[60] point out that the apparent bond shortening which is not expected for the weaker bond in cyclopropane can be partially explained by the greater admixture of p character in the bond. They also point out that since the bonding orbitals are not directed along the line joining the two nuclei, the bond is indeed longer than the interatomic distance as found by electron diffraction measurements. These authors also feel that the amount of electron delocalization (in ev) accounts quite well for the chemical and spectrographic effects of the cyclopropane system. Peters[62] has applied a molecular orbital treatment to cyclopropane and arrives at essentially the same conclusions as Coulson and Moffitt had earlier.

Another description of the ring has been made by Walsh[63] which is somewhat more qualitative in nature. Walsh pictures the cyclopropane ring as composed of three trigonally

---

[62]D. Peters, Tetr., 19, 1539 (1963).

[63]A. D. Walsh, Trans. Faraday Soc., 45, 179 (1949).

hybridized carbons having three $sp^2$ orbitals directed toward the center of the ring, with the p orbitals lying in the plane of the ring (Figure 8a). This arrangement would rise to the electron density picture shown in Figure 8b.

Music and Matsen[64] have carried out some molecular orbital calculations on the ring in connection with the previously mentioned conjugative effects on the U. V. spectra of cyclopropane derivatives. They postulated that the plane of the ring must be perpendicular to the $\pi$ system of the substituent for maximum conjugative effects. Kosower and Ito[65] and Büchi and Loewenthal[66] found a difference in spectra was noted for cyclopropyl ketones where the cyclopropane ring was fixed in its steric relations with the carbonyl group. Eastman did not find this to be the case for phenyl cyclopropanes where the cyclopropane ring was in fixed conformation both parallel and perpendicular to the adjacent phenyl. He postulates the high electron density of the three membered ring as inductively affecting the absorption patterns found.

Chemically, cyclopropanes are affected by both acids and bases. The cleavage of cyclopropane and cyclopropane derivatives by acid is a well known reaction. Kohler[14] has pointed

---

[64] J. F. Music and F. A. Matsen, J. Am. Chem. Soc., 72, 5256 (1950).

[65] E. M. Kosower and M. Ito, Proc. Chem. Soc., 25 (1962).

[66] G. Büchi and H. J. E. Loewenthal, Proc. Chem. Soc., 280 (1962).

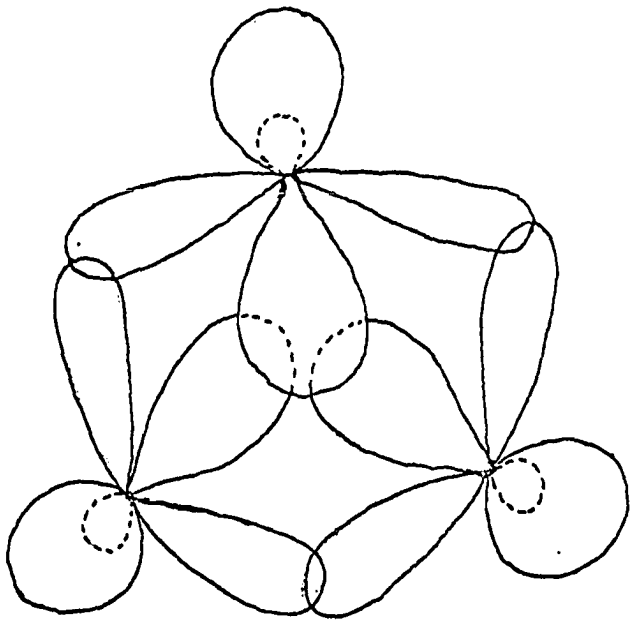


Figure 8a. The molecular orbital picture of cyclopropane according to Walsh[63]

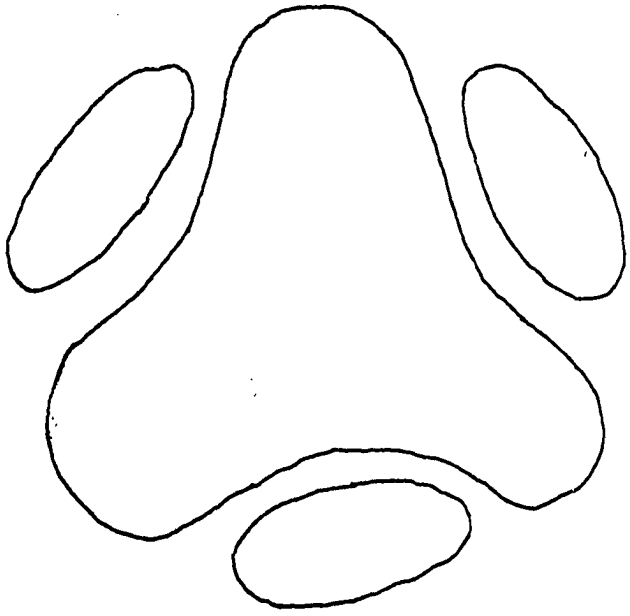


Figure 8b. The electron probability density distribution for cyclopropane[66]

out a type of Markovnikoff rule which states that the ring is broken by acids between the most and the least highly substituted carbon. The anion of the attacking reagent then ends up on the most highly substituted site. This rule may be stated in a more modern manner. The ring opens up to give the most stable carbonium ion. According to LaLonde[67] it may be added that attack of the proton is on the carbon atom which is most highly negative from ground state polarization effects.

LaLonde[67] in some work on the compounds norcarane (Figure 9a), bicyclo [2.1.0] hexane (Figure 9b) and bicyclo [2.1.0] pentane (Figure 9c) found these compounds open primarily by external bond breaking in preference to internal bond breakage. This can be rationized on the basis of structures $x_a$ and $x_b$ (Figure 10) as being important contributers to the polarized state of the ring leading to the preferred direction of ring opening.

This rule is borne out by the preponderance of acetates and olefins which could arise only from external C-C bond breakage. As an example, norcarane gives rise to the products illustrated in Figure 11. It should be mentioned that bicyclo [2.1.0] pentane gives rise to a slightly larger amount of internal bond breakage. This is interpreted by LaLonde as due to internal strain affecting the direction of ring polarization toward the most stable product.

---

[67]R. T. LaLonde and L. S. Forney, J. Am. Chem. Soc., 85, 3767 (1963).

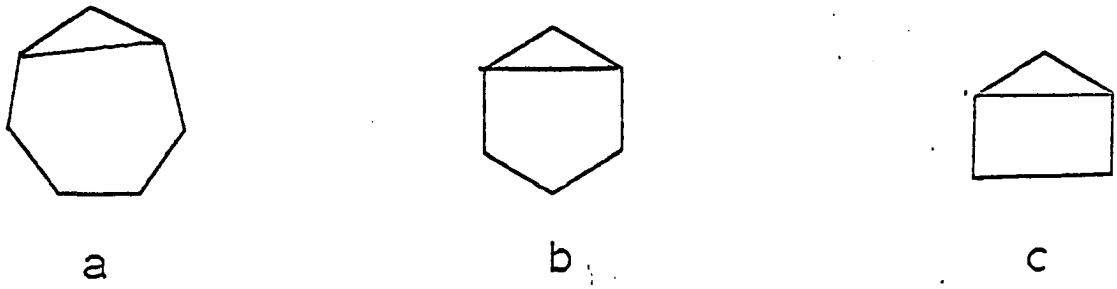



Figure 9. a. Norcarane
b. Bicyclo [3.1.0] hexane
c. Bicyclo [2.1.0] pentane

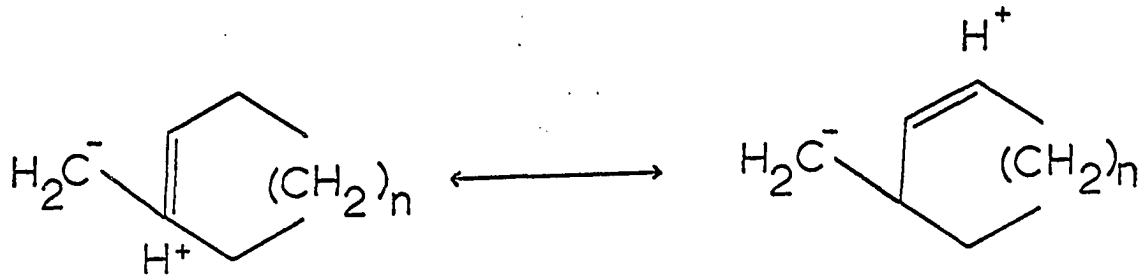



Figure 10. Most probable ground state resonance forms for bicyclo [n.1.0] alkanes

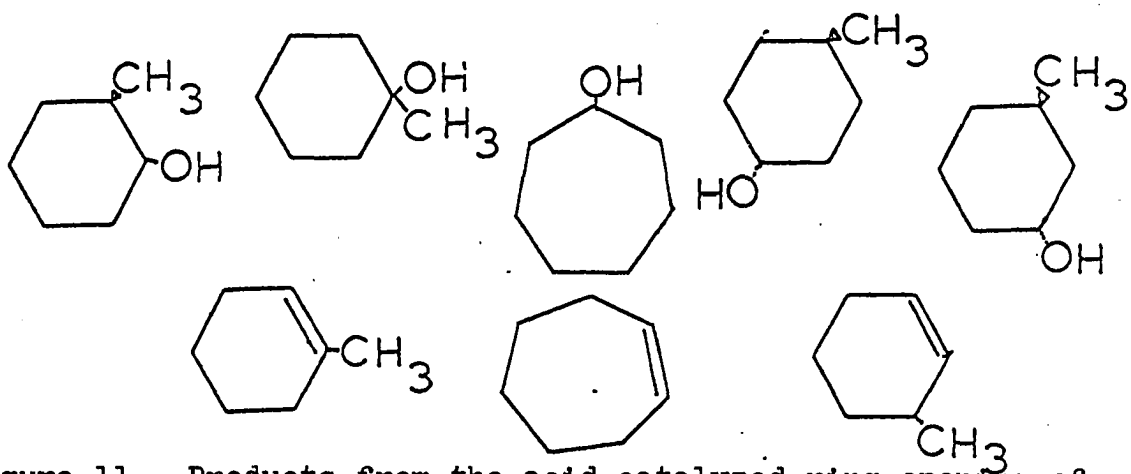



Figure 11. Products from the acid-catalyzed ring opening of norcarane

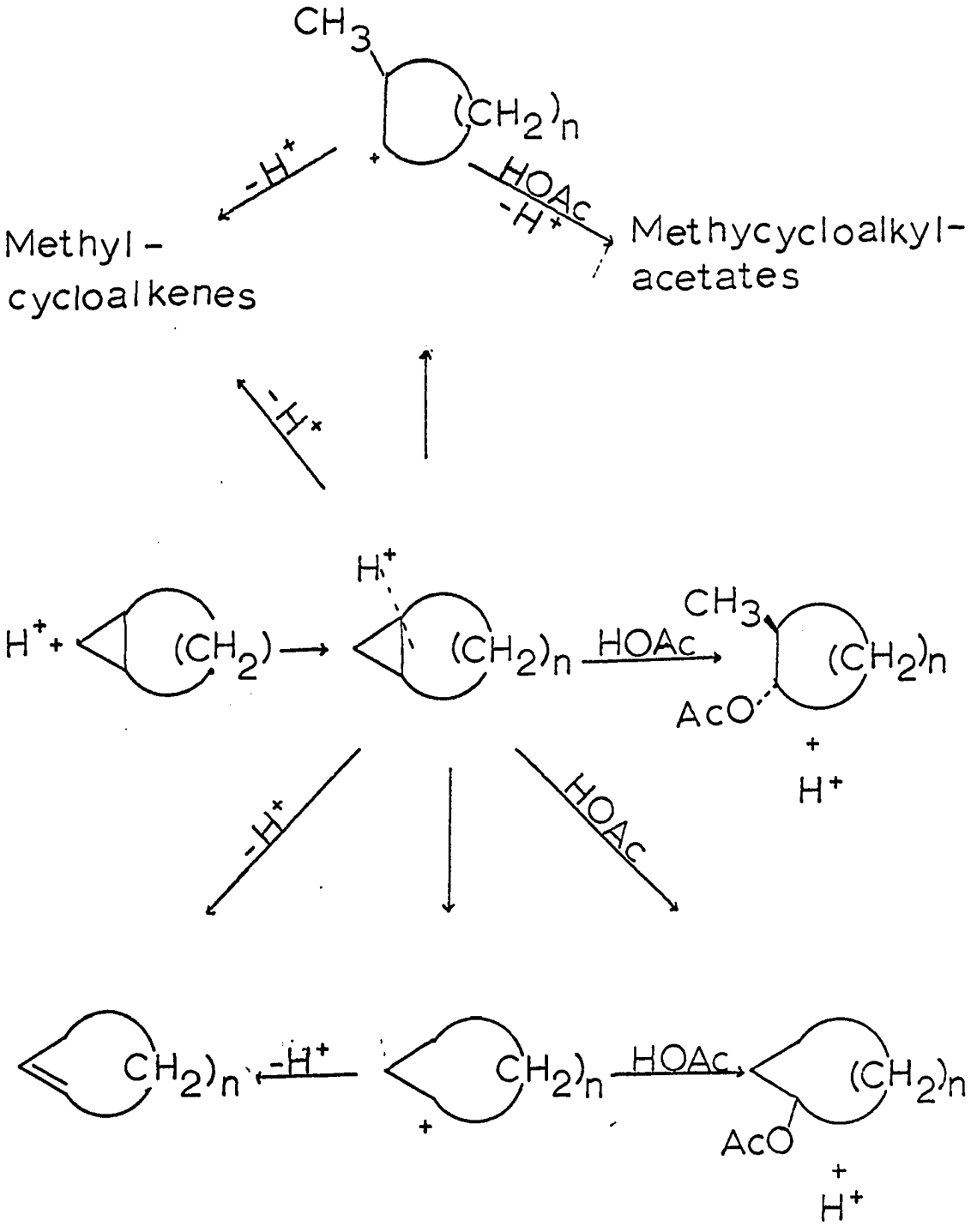



Figure 12. The acid-catalyzed ring-opening of bicyclo n.1.0 alkanes

These authors also noted that a high degree of stereospecificity was indicated. This conclusion was arrived at from the fact that from the acid catalyzed reaction only traces of cis-2-methyl cycloalkanols could be detected by g. p. c. The fact that those products were observed indicates a possible carbonium ion mechanism operating to some extent. The explanation given by these authors involves an attack by a nucleophilic acetate moiety attacking a protonated (or protonating) cyclopropane ring (Figure 12). Some other examples of the stereospecific manner of the ring opening of cyclopropanes might include work by Cope and co-workers.[68,69] They studied the opening of cis-bicyclo [6.1.0] bicyclo nonane and trans bicyclo [6.1.0] nonane. The cis bicyclo [6.1.0] bicyclo octane gave primarily cis-4-methyl cyclooctyle formate and cis-2-methylcyclooctyl formate. The corresponding trans bicyclo [6.1.0] nonane gave primarily trans 2- and -4-methylcyclooctyl formates. These products were postulated by Cope to arise from a stereoregular transannular pathway. This could occur by protonation of the cyclopropane ring, followed by a transannular hydride shift followed by attack of the nucleophilic solvent molecules (Figure 13).

---

[68] A. C. Cope and G. L. Woo, J. Am. Chem. Soc., 85, 3601 (1963).

[69] A. C. Cope and J. K. Hecht, J. Am. Chem. Soc., 85, 1780 (1963).

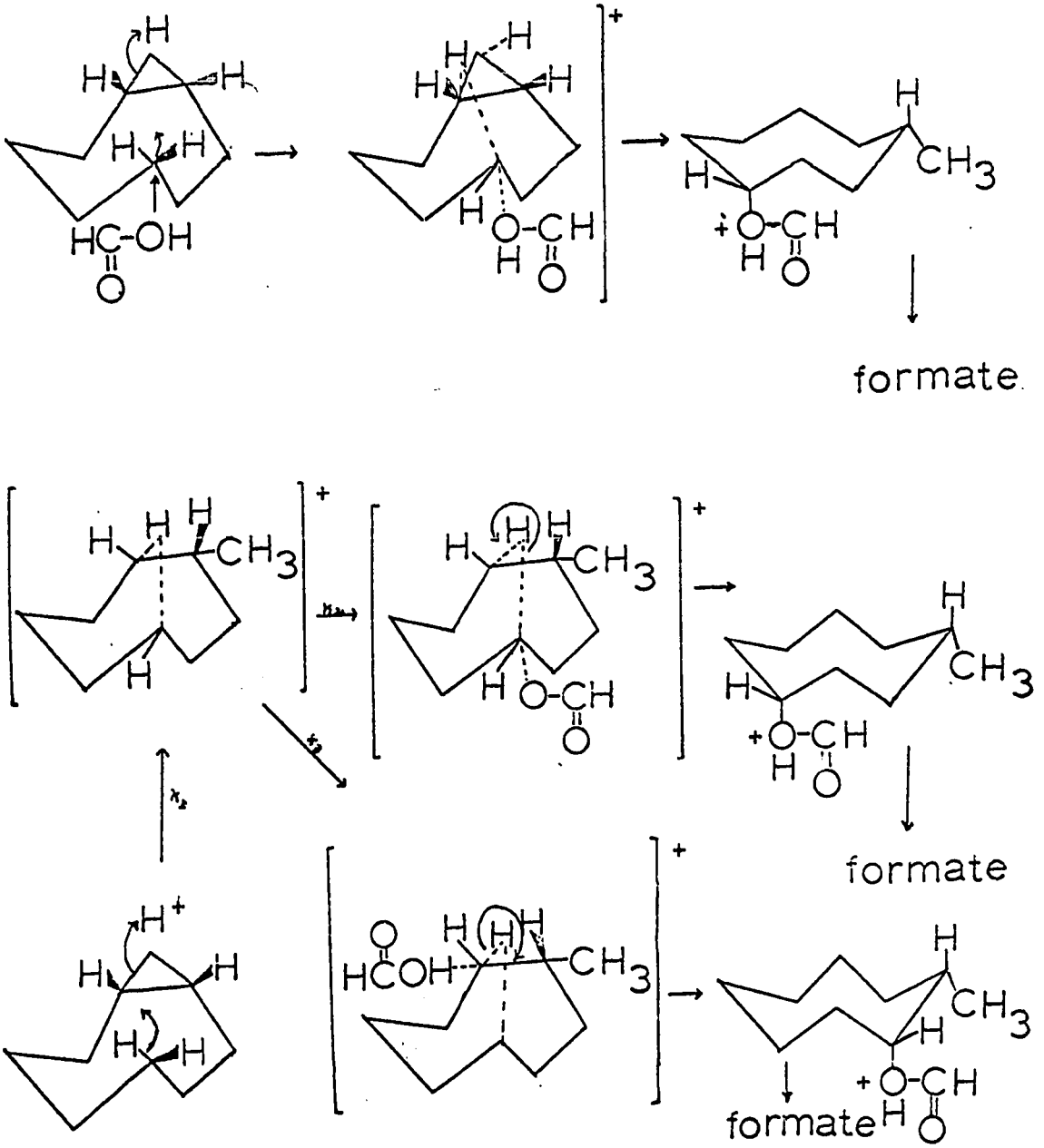
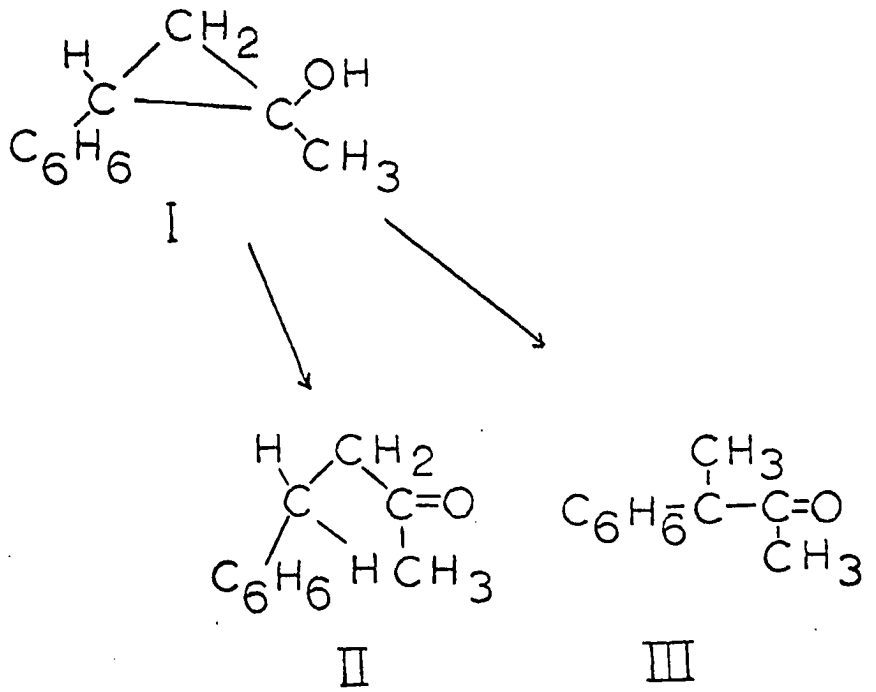



Figure 13. The acid-catalyzed ring opening of cis-bicyclo 6.1.0 nonane




| | | |
|---|---|---|
| Base catalysis | 100% | 0% |
| Acid catalysis | 40% | 60% |

Figure 14. Product distribution from the acid and base catalyzed ring opening of 1-methyl-2-phenyl cyclopropanol

DePuy and Breitbeil[70] have reported some studies on the acid and base catalyzed ring opening of trans 1 methyl-2-phenylcyclopropanol (I) indicated in Figure 14. The acid catalyzed opening gave 60% of II and 40% of III, Figure 14. The base gave 100% of II. In deutero acids or bases an optically active product (III) was obtained. The sign of rotation was dependent upon the reagent used. In analogous open chain compounds inversion of configuration is observed in protonic solvents with base therefore, the authors conclude, retention of configuration is indicated for the ring opening in acidic media. They envision a mechanism for these two reactions as pictured in Figure 15. These results are further supported by Nickon and co-workers[71] in studies on the 1-acetoxytricyclene norbornane. They observed 94.5% inversion of configuration in base (NaOD) for the hydrolysis of the acetate. In deuterosulfuric acid both the acetate and the alcohol showed 90% retention of configuration.

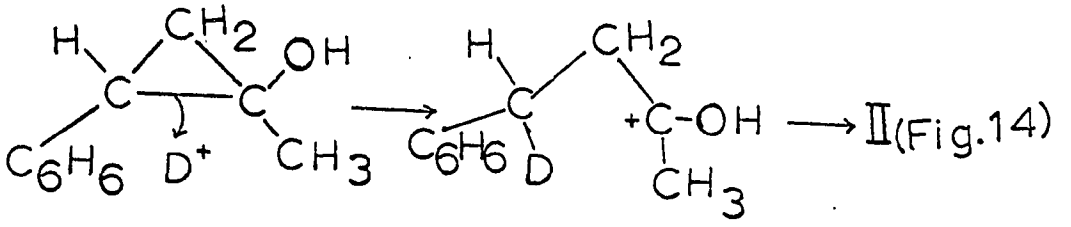
Baird[72] has published some interesting work on the possible intermediates involved in the acid catalyzed ring opening of cyclopropane. On opening cyclopropane in deuterosulfuric

---

[70] C. H. DePuy and F. W. Breitbeil, J. Am. Chem. Soc., 85, 2176 (1963).

[71] A. Nickon, J. N. Hammons, J. L. Lambert and R. O. Williams, J. Am. Chem. Soc., 85, 3714 (1964).

[72] R. L. Baird and A. A. Aboderin, J. Am. Chem. Soc., 86, 252 (1964).



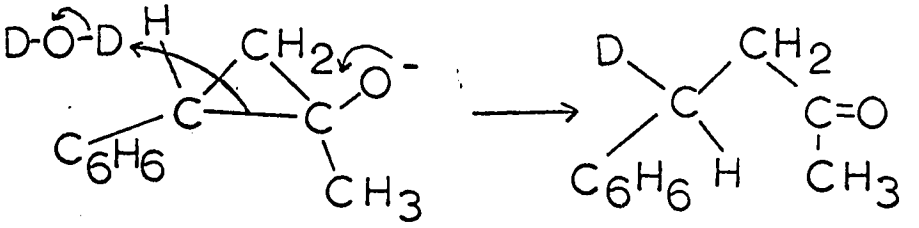




Figure 15. The probable mechanisms for the acid and base catalyzed ring opening of 1 methyl-2-phenyl cyclopropanol

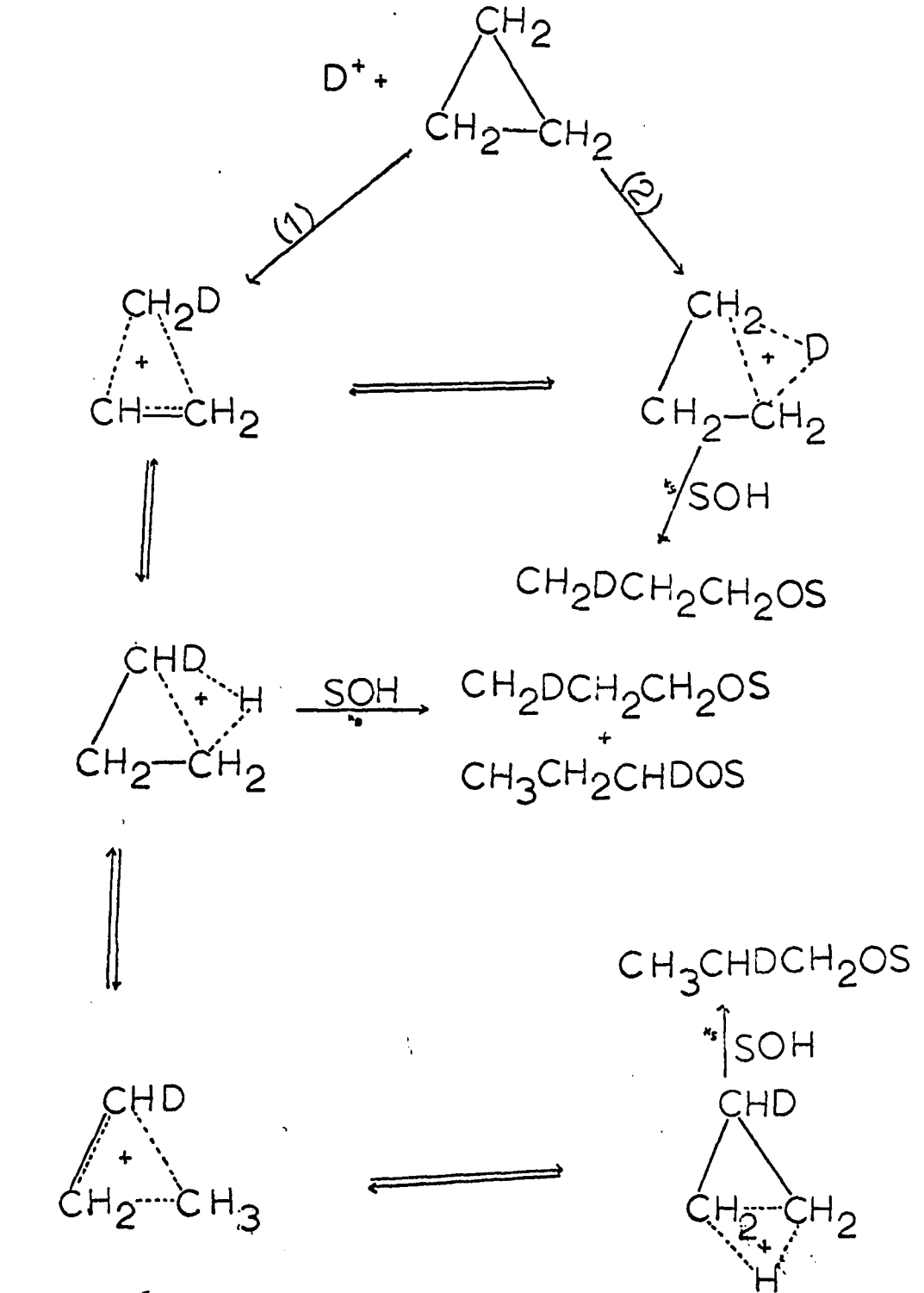



Figure 16. The postulated intermediates in the acid-catalyzed ring opening of cyclopropane

acid, a deuterium distribution of .38, .17, .46 in the 1, 2, and 3 positions respectively is found. This makes methyl shifts unlikely. One could postulate Wagner-Meerwein shifts as giving these results. A lack of isomeric products makes this event rather unlikely.

Instead Baird has been led to propose a bridged protonated cyclopropane intermediate as pictured in Figure 16. That no equilibrium exchange occurred was accounted for by incorporation of only one deuterium into the 1-propanol. In a later paper, Baird[73] observed the deamination of 3,3,3,$d_3$-1-aninopropane and found that $d_2$ and $d_3$ cyclopropane were formed in amounts of 43 and 57% respectively. He has interpreted these results as further evidence for a hydrogen bridged cyclopropane intermediate as this isotope distribution could not be easily accounted for by carbonium ion rearrangements. It is the purpose of this work to further ellucidate factors involved in the acid and base catalyzed ring opening of the cyclopropanol system.

---

[73] A. A. Aboderin and R. L. Baird, J. Am. Chem. Soc., 86, 2301 (1964).

# RESULTS AND DISCUSSION

Although Eilers[18] and Rodewald[29] have developed quite satisfactory procedures for the preparation of 2-substituted-cyclopropanols, a general method for the preparation of 1-substituted cyclopropanols was desired.

Dappen[38] has described a method for the preparation of 1-phenylcyclopropanol and 2-phenylcyclopropanol through the use of a modified Cottle procedure, consisting of the addition of magnesium bromide to epichlorohydrin, followed by ring closure with ethyl Grignard and ferric chloride to give the cyclic alcohol. These reactions are summarized by the equations in Figure 5.

The Cottle reaction was shown to involve magnesium 1,3-dihalo-2-propoxide as an intermediate. This intermediate was considered by us as a more suitable starting point that the substituted epichlorohydrins which took a number of steps to synthesize. Since 1,3-dichloroacetone was a commercially available reagent[74] we considered it as a good starting material. A reaction with the appropriate Grignard reagent would lead to the previously mentioned alkoxide intermediate. This could then be closed by the addition of ethyl Grignard in the presence of ferric chloride.

Upon trying this method we found that several procedural

---

[74]Distillation Products Industries, division of Eastman Kodak Company, Rochester 3, New York.

details had to be worked out. The reaction was found to proceed in highest yields when the ferric chloride and ethylmagnesium bromide were added simultaneously to the alkoxide. When the ferric chloride was added to the alkoxide, followed by the addition of ethylmagnesium bromide, yields were very low. A large excess, 7 moles, of Grignard were found to give complete ring closure. Lesser amounts than this often resulted in some unclosed 1,3-dichloro-2-arylpropanol being found after work-up. The alcohols did not prove too difficult to isolate provided they were distilled immediately following work-up. All but the 1-(m-chlorophenyl)cyclopropanol could be recrystalized from pentane-ether mixtures.

The tosylates of the alcohols were prepared as a further means of identification. All tosylates but the 1-(p-methoxyphenyl)cyclopropyl tosylate were quite stable at room temperature. Data on the alcohols and their tosylates are summarized in Table 3. The yields given are the yields of pure alcohol, the yields before recrystallization were considerably higher.

Table 3. Summary of the data on the substituted aryl cyclopropanols and cyclopropyl tosylates

| Substituent | m.p.(alc.) | m.p.(tos) | %yield(alc.) | %yield (tos) |
|---|---|---|---|---|
| p-$OCH_3$ | 59-60 | decomp. | 31 | 39 |
| p-$CH_3$ | 38-39 | 87.5-88 | 50 | 43 |
| H | ----- | 75-75.5 | 48 | 36.3 |
| m-Cl | ----- | 56-57 | 25 | 14 |
| m-$CF_3$ | 47-48 | 36-36.5 | 36 | -- |

The mechanism of this reaction appears to be similar to the one described by Kharasch and co-workers.[37] These workers noted that 1-phenoxy-3-halopropanes, or 1,3-dihalopropanes when reacted with ethylmagnesium bromide in the presence of ferric chloride produced cyclopropane and propylene in varying amounts. When 3-phenoxy-1-halopropane was the substrate, propylene (90%) is the prime product and cyclopropane is the other major product. If 1,3-dihalopropane is used cyclopropane (85%) is the major product, the remainder being primarily propylene. They postulated a radical mechanism for this reaction. The reasoning is based on the following facts. Grignard exchange followed by displacement is ruled out because it has been shown not to occur to any extent.[75] Furthermore, the decomposition of 3-substituted propylmagnesium bromides gives primarily cyclopropane as the product.[7] The formation of propylene rules this out as a possible reaction pathway. The authors[76] also had found that reactions with Grignard reagents in the presence of transition metal salts involves radical intermediates. They proposed the

---

[75]M. S. Kharasch and C. F. Fuch, J. Org. Chem., 10, 292 (1945).

[76](a)M. S. Kharasch and W. H. Urry, J. Org. Chem., 19, 1477 (1954).

(b)M. S. Kharasch, R. D. Mulley and W. Nudenberg, J. Org. Chem., 19, 1477 (1954).

(c)R. O. C. Norman and W. A. Waters, J. Chem. Soc., 950 (1957).

following mechanism as best fitting experimental details. This is pictured in Figure 17. Step 1 is attack of the Grignard on ferric chloride to give a reduced iron salt with disproportionation of the ethyl radicals involved. The reduced iron salt could then attack a halogen atom on the 3-substituted-1-halopropane to give a radical as shown in step 2. The radical intermediate can then undergo either of two processes. It can rearrange to a secondary radical, followed by attack on group Y to give propylene (step 3), or it may be immediately attacked on group Y by the reduced iron salt to give cyclopropane as illustrated for step 4.

Step 1. $2\ EtMgBr + FeCl_3 \longrightarrow (FeCl) + CH_2CH_2 + CH_3CH_3$

Step 2. $(FeCl) + \underset{X}{CH_2}\underset{}{CH_2}\underset{Y}{CH_2} \longrightarrow \cdot CH_2CH_2CH_2Y$

Step 3. $\cdot CH_2CH_2CH\text{-}Y \longrightarrow CH_3\dot{C}H\ CH_2Y \xrightarrow{(FeCl)} CH_3CH{=}CH_2$

or

Step 4. $\cdot CH_2CH_2CH_2Y \longrightarrow \cdot CH_2CH_2CH_2 \cdot \longrightarrow CH_2{<}\begin{matrix}CH_2\\|\\CH_2\end{matrix}$

Figure 17. Proposed sequence of steps in the formation of propylene or cyclopropane via the use of modified Grignard and 3, substituted -1-halopropanes

The extent to which either of these two processes occur can be attributed to the reactivity of the reduced iron salt toward group Y. If group Y is a phenoxy group, attack by the iron salt is much slower allowing time for rearrangement to the secondary radical, giving propylene as the final product. The halogen atoms undergo secondary attack much more rapidly hence, the proportionately higher yield of cyclopropane produced when 1,3-dihalopropanes are the substrate. It is quite likely that cyclopropanols are formed by similar processes when the Cottle method of preparation is used.

## The Acid-catalyzed Ring Opening of 1-(p-methylphenyl)cyclopropanol

We were interested in carrying out some preliminary work with cyclopropanols in acidic media. We chose to examine 1-(p-methylphenyl)cyclopropanol under conditions of different acidities, and under changes of the solvent composition. Originally, the substrate was chosen because of its relative ease of purification. Later investigations also proved this an apt choice as its rate of ring opening was such as to allow kinetic studies to be easily carried out at large acidity extremes. The prime solvent system used for this and some subsequent work was the system of 60/40 volume per cent dioxane-water.

This solvent was chosen because it allowed complete dissolution of the substrate. Also, Bunton and co-workers

had determined values for a Hammett $H_o$ function for this particular solvent system.

The logarithm of the rate constants were plotted against both $H_o$ and pH as shown in Figures 18 and 19 respectively. The pH plot showed a definite curvature. The $H_o$ plot gave a straight line of a slope of 0.685 with little scatter as shown in Figure 18. The data is summarized in Table 4.

Table 4. The rate of the acid-catalized ring opening of 1-(p-methylphenyl)cyclopropanol in 60/40 volume per cent dioxane-water at 50 degrees

| $C_{HClO_4}$ (m/l) | pH | $H_o$ | k x $10^5$ | Log k |
|---|---|---|---|---|
| 0.552 | -0.276 | 1.31 | 1.01 ± .05 | -4.914 |
| 1.005 | -0.002 | 0.67 | 2.75 ± .11 | -4.561 |
| 1.019 | -0.005 | 0.67 | 2.69 ± .07 | -4.570 |
| 1.801 | -0.256 | -0.05 | 9.44 ± .30 | -4.025 |
| 1.819 | -0.260 | -0.07 | 10.3 ± .4 | -3.987 |
| 2.483 | -0.395 | -0.70 | 26.4 ± .4 | -3.578 |
| 2.483 | -0.395 | -0.70 | 26.7 ± 1.1 | -3.573 |
| 3.455 | -0.538 | -1.45 | 81.0 ± 2.7 | -3.092 |
| 3.455 | -0.538 | -1.45 | 87.0 ± 1.9 | -3.061 |
| 3.990 | -0.601 | -1.84 | 172. ± 5. | -2.764 |
| 3.990 | -0.601 | -1.84 | 167. ± 4. | -2.772 |

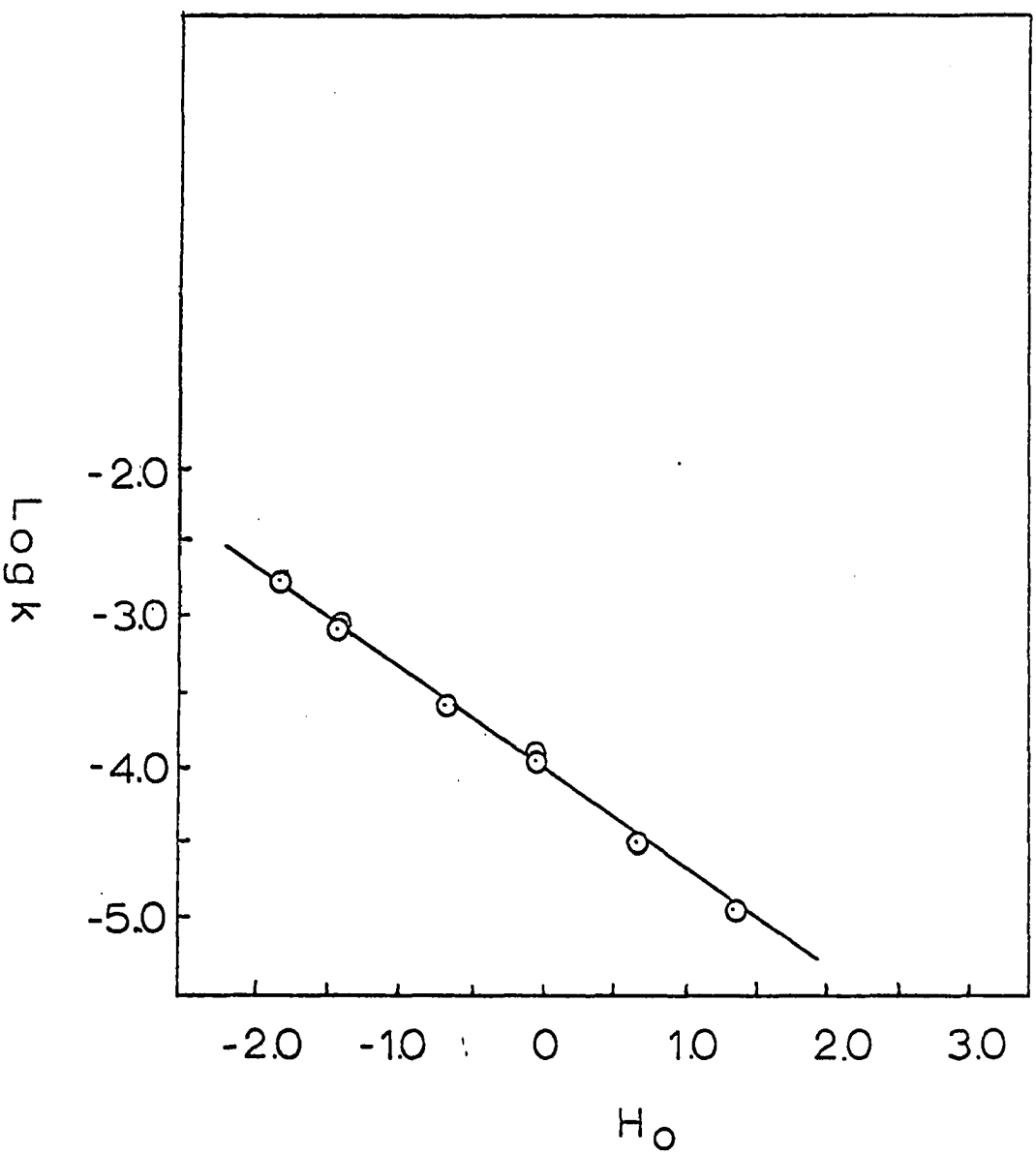



Figure 18. The plot of log k vs. $H_o$ for the acid-catalyzed ring opening of 1-p-methylphenyl cyclopropanol in 60/40 dioxane-water

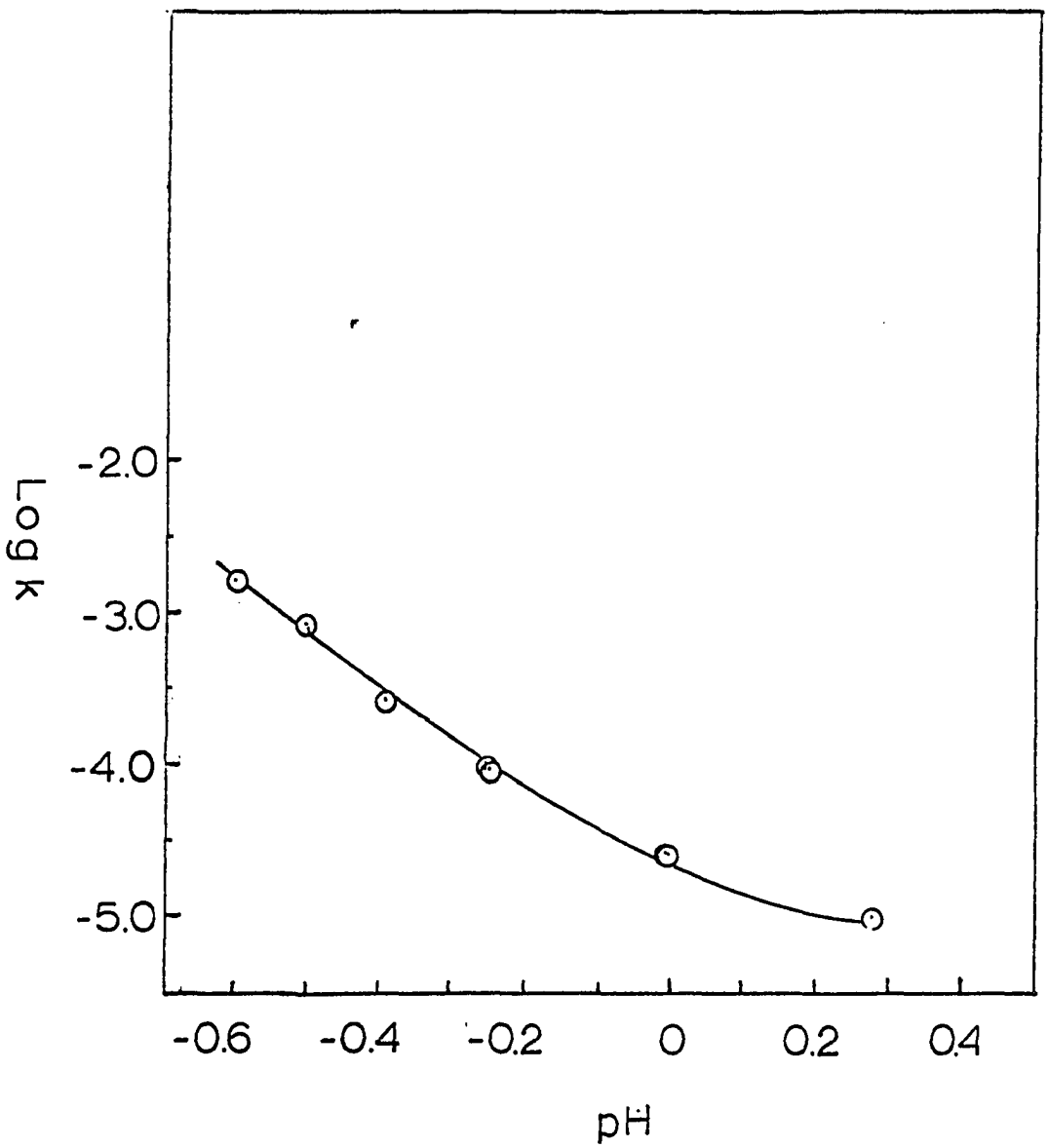



Figure 19. Plot of log k vs. pH for the ring opening of 1-p-methylphenylcyclopropanol

We were also interested in the effects that varying solvent composition at constant acid concentration would have upon the rate of ring opening. For this work two separate sets of kinetic data were obtained. One set of data was obtained for the acid-catalyzed ring opening of 1-(p-methylphenyl)cyclopropanol in dioxane-water mixtures of varying weight percentage composition. The other set of data was obtained for alcohol-water mixtures of varying weight percentage composition. The results are tabulated in Tables 5 and 6.

Table 5. The acid-catalyzed ring opening of 1-(p-methylphenyl)cyclopropanol in dioxane-water mixtures of varying weight percentage combinations

| Per cent Dioxane | $k \times 10^4$ |
|---|---|
| 19.3 | 1.95 ± .08 |
| 33.4 | 1.84 ± .04 |
| 48.3 | 2.00 ± .04 |
| 60.8[a] | (2.46)[a] |
| 70.1 | 3.15 ± .11 |

2.43 M $HClO_4$ in dioxane-water wt. percentage compositions

[a]Extrapolated from the $H_o$ work.

Table 6. The acid-catalyzed ring opening of 1-(p-methylphenyl)cyclopropanol in ethanol-water mixtures of varying weight percentage combinations

| Per cent Ethanol | $k \times 10^5$ | Log I | $Y_o$ | Log k-Log I |
|---|---|---|---|---|
| 31.7 | 1.51 ± .02 | .4410 | .120 | -5.259 |
| 41.8 | 1.21 ± .01 | .0004 | .175 | -4.917 |
| 56.5 | 0.979 ± .029 | -.0580 | .300 | -4.951 |
| 59.9 | 0.875 ± .009 | -.0223 | .352 | -5.036 |
| 76.9 | 0.956 ± .042 | -.0531 | .525 | -4.967 |
| 91.1 | 1.73 ± .05 | -.2492 | .795 | -5.011 |

1.50 N $H_2SO_4$ in ethanol-water mixtures of varying wt. percentage composition.

An interpretation of the results of the $H_o$ and the change of rate in mixed solvent systems is not easily made. One can consider three mechanisms as possibly being operative in acid catalysis. These are designated as A1, A2, and $A_{SE}2$. The A1 reaction is shown in Figure 20. The first step is an equilibrium between the substrate and protonated substrate. This is followed by the step 2 which involves the formation of the transition state complex M which can then react in a fast step (step 3) with solvent to give product and a proton.

$S + H^+ \underset{}{\overset{Keq}{\rightleftharpoons}} SH^+$ Step 1, Equilibrium

$SH^+ \xrightarrow{k_1} M^+$ Step 2, Slow

$M^+ \xrightarrow{k_2}$ Products $+ H^+$ Step 3, Fast

Figure 20. The A-1 mechanism of acid-catalysis

The A-2 mechanism as pictured in Figure 21 involves a prior equilibrium as shown in step 1, followed by a slow reaction with a solvent molecule, usually water, to form a transition state complex M (step 2) which can break down to products plus a proton.

$S + H^+ \underset{}{\overset{Keg}{\rightleftharpoons}} SH^+$ Step 1, Equilibrium

$SH^+ + H_2O \xrightarrow{k_1} M^+$ Step 2, Slow

$M^+ \xrightarrow{k_2}$ Products $+ H^+$ Step 3, Fast

Figure 21. The A-2 mechanism of acid-catalysis

The $A_{SE}2$ mechanism involves first a rate determining proton transfer as pictured in step 1 of Figure 22. This is followed by a fast step which is a reaction with solvent to give product plus a proton (step 2).

$S + H^+ \xrightarrow{k_1} M^+$ Step 1, Slow

$M^+ + H_2O \xrightarrow{k_2}$ Products $+ H^+$ Step 2, Fast

Figure 22. The $A_{SE}2$ mechanism of acid-catalysis

On the basis of a proposal first advanced by Zucker and Hammett[77] and developed by Paul[78] the $H_o$ function was considered as a useful criterion for determining whether a mechanism was A1 or A2. The $H_o$ function does not allow a differentiation between A1 and $A_{SE}2$ since both mechanisms would have the same $H_o$ dependence. The reasoning is as follows: For the A1 reaction the rate is given in equation 1. Dividing rate by concentration of substrate $C_s$ gives the first order rate constant $k_1$ as shown in equation 2. Substituting for $a_{H^+}$ in terms of $h_o$ gives equation 4.

Eq. 1. $$\text{rate} = k\, C_{SH^+} = \frac{k\, C_S\, a_{H^+}}{Keq} \cdot \frac{\gamma s}{\gamma tr}$$

Eq. 2. and $$k_1 = \text{rate}/C_S = k/K_{eq} a_{H^+} \frac{\gamma s}{\gamma tr}$$

Eq. 3. $$a_{H^-} = h_o \frac{\gamma BH^+}{\gamma B}$$

Eq. 4. so $$k_1 = \frac{k}{Keq} h_o \frac{\gamma BH^+}{\gamma B} \frac{\gamma s}{\gamma tr}$$

---

[77] L. Zucker and L. P. Hammett, J. Am. Chem. Soc., 56, 830 (1939).

[78] F. A. Long and M. A. Paul, Chem. Rev., 57, 935 (1957).

Eq. 5. Taking logarithms $\log k_1 = -H_o + \log \frac{\gamma BH^+}{\gamma B} \frac{\gamma s}{\gamma tr} + \text{const.}$

A plot of log $k_1$ should give a straight line of unit slope if the mechanism is A1. Because the A2 mechanism involves the activity of a solvent molecule in the transition state, it would not be expected to follow the above relationship. It can be seen that the assumption must be made that the activities of both substrate and indicator base must change at similar rates for this relationship to hold. This is not always necessarily true. Arnett[79] has found that the indicator structure is very critical and that rather small changes in structure do change the $H_o$ function. Shubert[80] has found a change in rate with increasing acidity, that reflects a change of $SH^+/$ tr. This suggests medium effects not considered in the $H_o$ relationship. These results tend to cast some doubt on the validity of the $H_o$ function as a criterion for determining the mechanism of an acid-catalyzed reaction. Grunwald[81] has also found that the establishment of an acidity function of the $H_o$ type is not always possible in other solvent systems.

---

[79]E. M. Arnett and G. W. Mach, J. Am. Chem. Soc., 86, 2671 (1964).

[80]W. M. Shubert, H. Burkett and A. L. Schy, J. Am. Chem. Soc., 86, 2520 (1964).

[81]B. Gutbezahl and E. Grunwald, J. Am. Chem. Soc., 75, 559 (1953).

Kwart[82,83] has used a kinetic relationship which he believes to be a valid criterion for establishing the type of mechanism operative in acid-catalyzed reactions. The derivation of this relationship comes from the formulation of Grunwald[81] for the $Y_o$ function. The $Y_o$ function represents an effort to compensate for the effect of varying solvent composition on the pKa of a neutral base and its conjugate acid. The $Y_o$ function is given as $(pKa)_w-(pKa)_s = \log f_{H^+} + mY_o$ where the term $mY_o$ represents the ratio $\frac{f_B}{f_{BH^+}}$. The m term represents the contribution of solute structure to the activity coefficient ratio and $Y_o$ represents the solvent contribution to that ratio. The term $\log f_{H^+}$ is another solvent parameter which is a measure of the effect of the solvent composition on the proton activity relative to the proton activity in water. Kwart has postulated that the relationship of log k - log I vs. $Y_o$ can be used as a means of determining mechanism type. If a plot of log k - log I vs. $Y_o$ gives a straight line then the reaction proceeds by an A-1 mechanism. If instead a pronounced curvature is noted, then the reaction proceeds by another mechanistic pathway. A slight curvature is not amenable to interpretation. We have plotted log k - log I vs. $Y_o$ for ethanol-water mixtures of varying composition. The values for I ($BH^+/B$) and $Y_o$ were

---

[82] H. Kwart and A. L. Goodman, J. Am. Chem. Soc., 82, 1947 (1960).

[83] H. Kwart and L. B. Weisfeld, J. Am. Chem. Soc., 80, 4670 (1958).

taken from the values given by Kwart. Values and graphs from Kwart's work are given in Tables 8, 9, 10 and Figures 24, 25 and 26 for comparison with Table 7 and Figure 23, the acid-catalyzed ring opening of 1-(p-methylphenyl)cyclopropanol.

The reason for the presence of curvature is due to the lack of a term for the activity of water when it is involved in the transition state complex. The activity of the water varies with solvent change and the curvature of the line obtained could be considered as representing the extent to which water plays a role in the reaction. As can be seen, the curve for the acid-catalyzed ring opening of 1-(p-methylphenyl)cyclopropanol in varying solvent composition does appear to have a slight curvature. It would appear that until more work appears in the literature on the use of this type of kinetic relationship that a full interpretation of our results must wait.

The 1-arylcyclopropanols previously described were opened in 60/40 dioxane-water at 50 degrees with an acid concentration of 1.45 molar. We were interested in the effects that substituent groups would have on the rate of reaction. A number of runs were made for each substituent and the resulting log k's were plotted against sigma[84] and sigma plus[85] (Figures 27 and 28). The rates as obtained are summarized in

---

[84] H. H. Jaffe, Chem. Rev., 53, 191 (1953).

[85] H. C. Brown and Y. O. Kamoto, J. Am. Chem. Soc., 79, 1913 (1957).

Table 8. Rates of hydrolysis of epichlorohydrin in aqueous ethanol at 30.02°

| Ethanol wt. % | $H_2SO_4$ | $10^3 k_1$ | log $k_1$ | log $k_1$ - log I |
|---|---|---|---|---|
| 0.00 | 1.43 | 1.41 | 2.851 | -4.052 |
| | 1.93 | 1.53 | 2.815 | -4.500 |
| 15.80 | 1.40 | 1.09 | 2.962 | -3.586 |
| | 1.63 | 1.81 | 2.742 | -3.478 |
| 30.35 | 1.58 | 1.07 | 2.971 | -3.471 |
| | 1.92 | 1.18 | 2.928 | -3.645 |
| 45.57 | 1.46 | 0.68 | 3.167 | -2.967 |
| | 1.89 | .96 | 3.018 | -3.079 |
| 60.52 | 1.26 | .60 | 3.222 | -3.030 |
| | 1.87 | 1.08 | 2.967 | -3.119 |
| 75.53 | 1.20 | 0.61 | 3.215 | -2.987 |
| | 1.57 | 1.04 | 2.983 | -2.950 |
| 100.00 | 1.12 | 3.41 | 2.466 | -3.214 |
| | 1.51 | 4.71 | 2.327 | -3.221 |

Table 9. Rates of hydration of 3-menthene in aqueous ethanol at 44.15°

| Ethanol wt. % | $H_2SO_4$ | log I | log k |
|---|---|---|---|
| 40.79 | 2.20 | .387 | ---- |
| 50.03 | 2.20 | .348 | 4.95 |
| 59.39 | 2.20 | .254 | 5.05 |
| 69.15 | 2.20 | .276 | 5.20 |
| 74.13 | 2.20 | .346 | 5.24 |
| 79.42 | 2.20 | .378 | 5.28 |

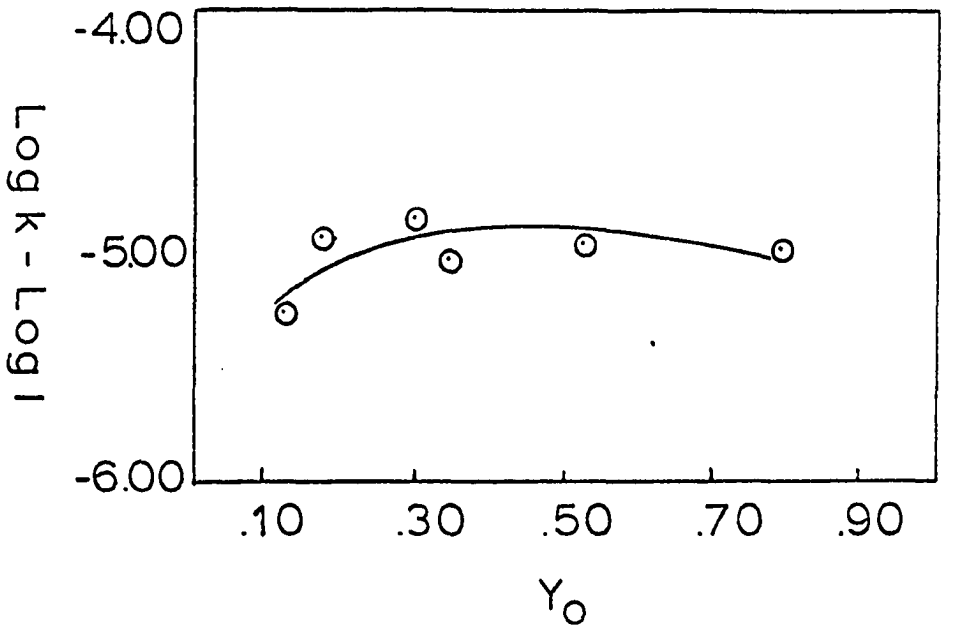



Figure 23. The acid catalyzed ring opening of 1-p-methylphenyl cyclopropanol

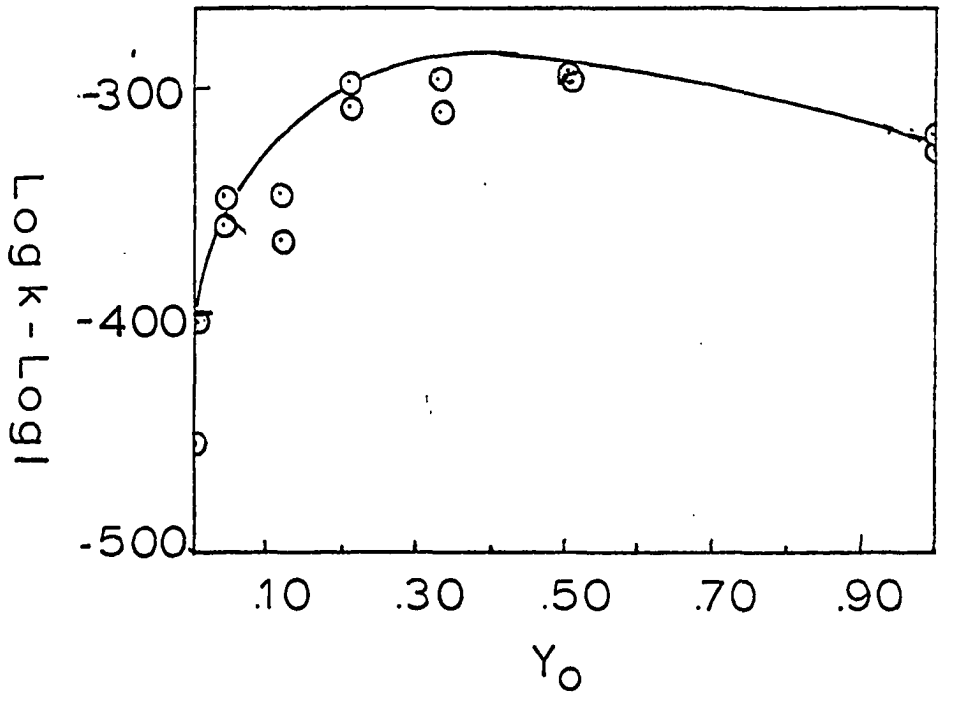



Figure 24. The ring-opening of epichlorohydrin

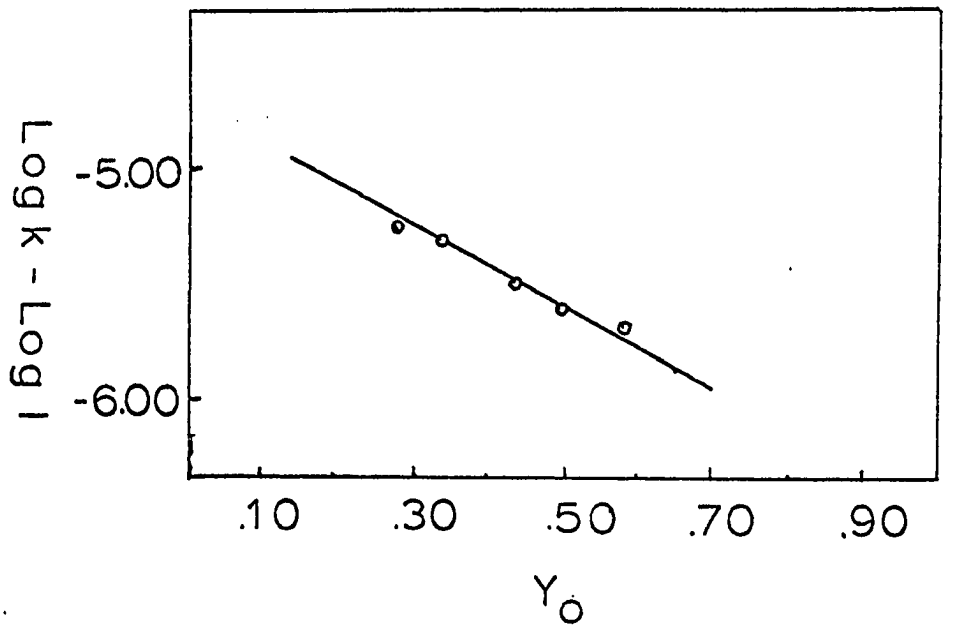



Figure 25. The hydrolysis of 3-menthene

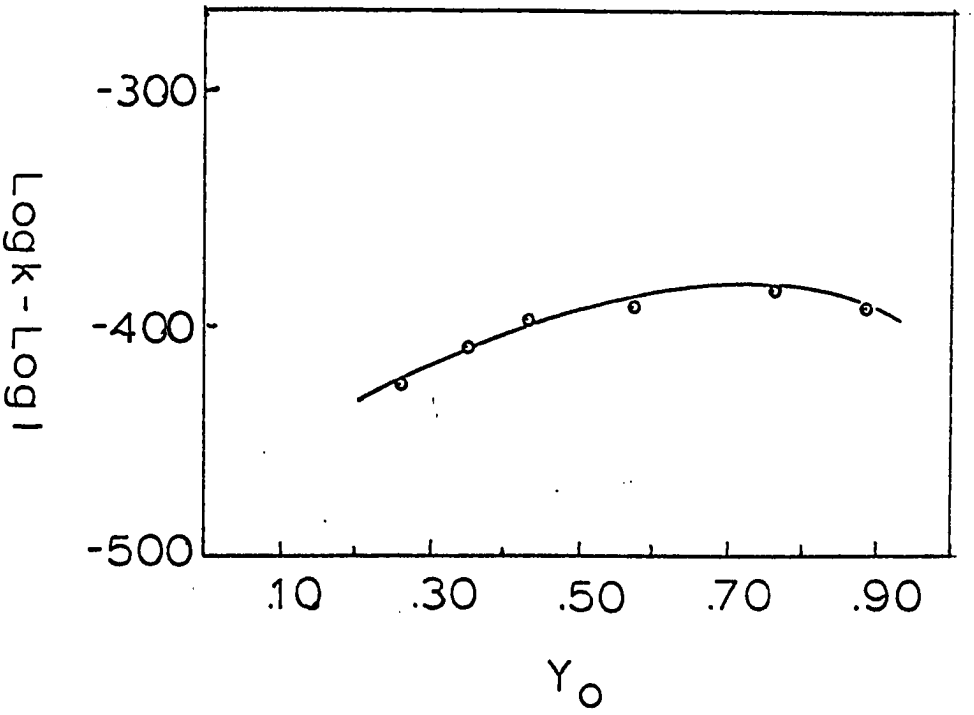
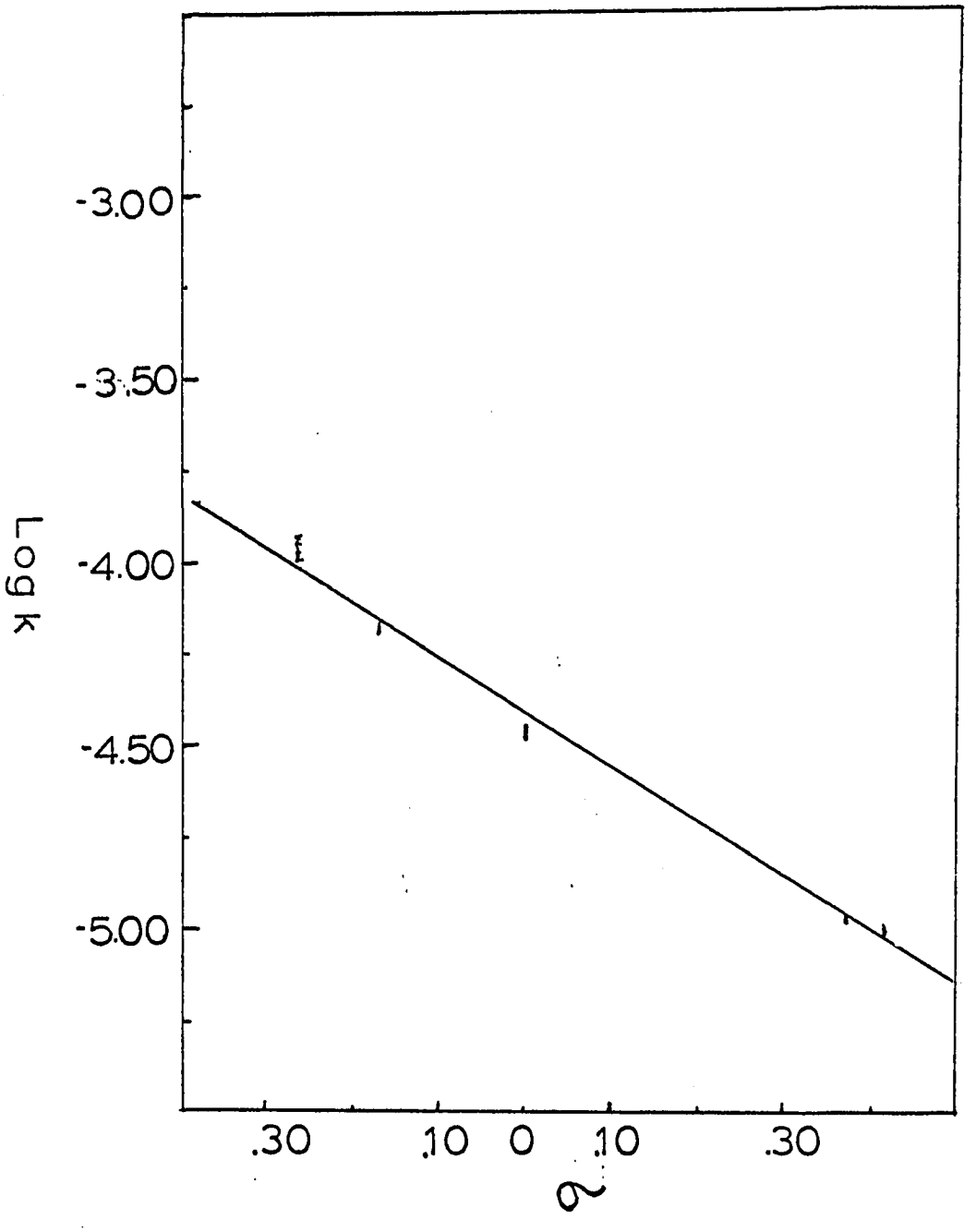



Figure 26. The hydrolysis of phenyl acetate

Figure 27. The plot of log k vs. sigma for the acid-catalyzed ring opening of 1-p-methylphenylcyclopropanol


-3.00
-3.50
-4.00
-4.50
-5.00
Log k
.30
.10
0
.10
.30
σ

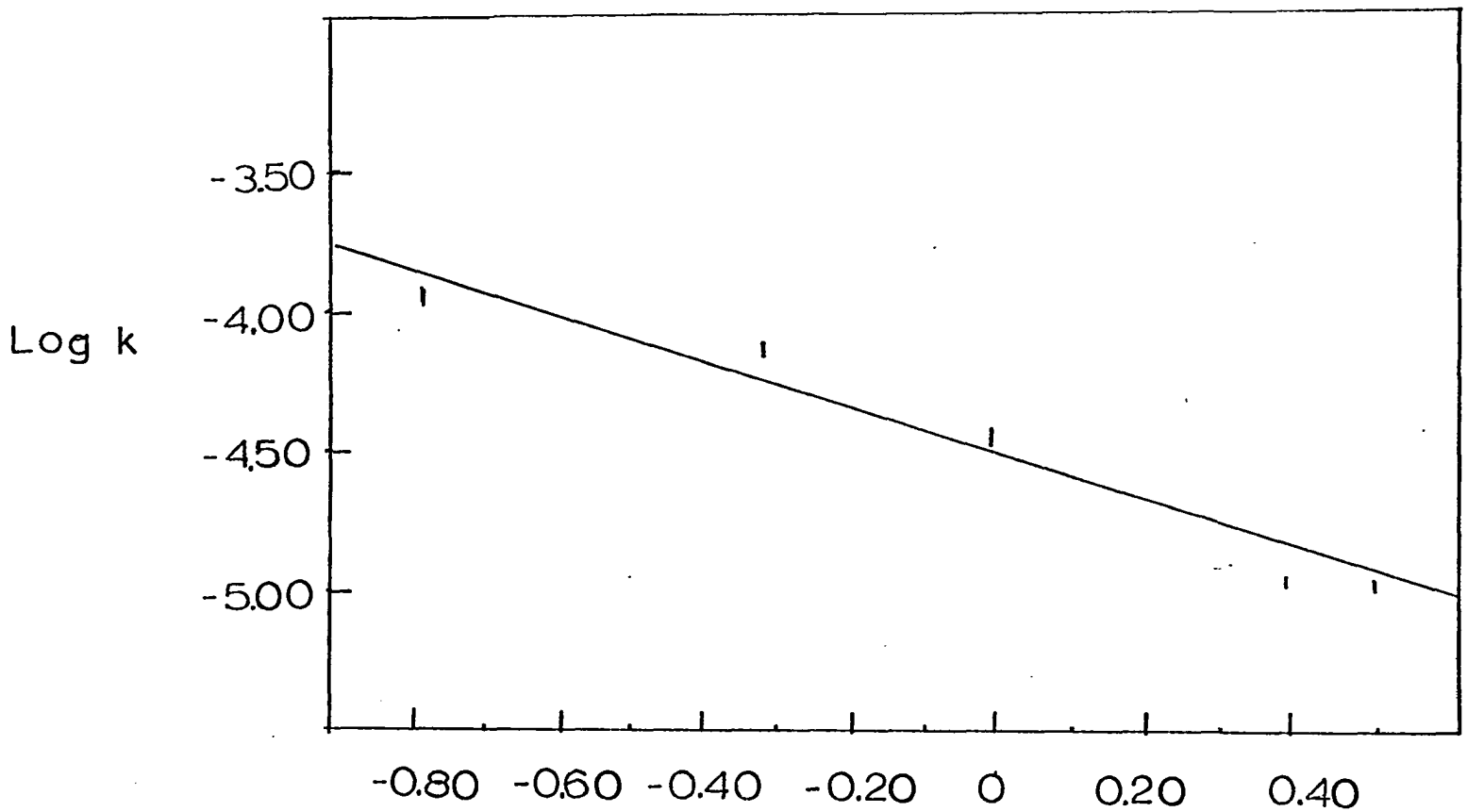



Figure 28. The plot of log k vs. sigma plus $\sigma^+$ for the acid-catalyzed ring opening of 1-arylcyclopropanols

Table 10. Solvolysis of phenyl acetate

| Ethanol wt. % | $10^6$k | log k | log I |
|---|---|---|---|
| 27.87 | 5.75 | 5.24 | -1.01 |
| 36.89 | 6.05 | 5.22 | -1.16 |
| 47.72 | 5.50 | 5.26 | -1.27 |
| 61.03 | 6.08 | 5.22 | -1.31 |
| 76.12 | 7.90 | 5.10 | -1.25 |
| 88.39 | 20 | 4.70 | -0.78 |

Table 11. The rates were found to fit best the sigma values given by Jaffe. The slope of the line obtained had a rho of -1.46 with a root mean error in log k of 0.005. The corresponding values of log k plotted against sigma plus[85] had a root mean error of .095 and had a slope of -0.755.

In considering possible mechanistic pathways one of the most likely would appear that shown in Figure 29.

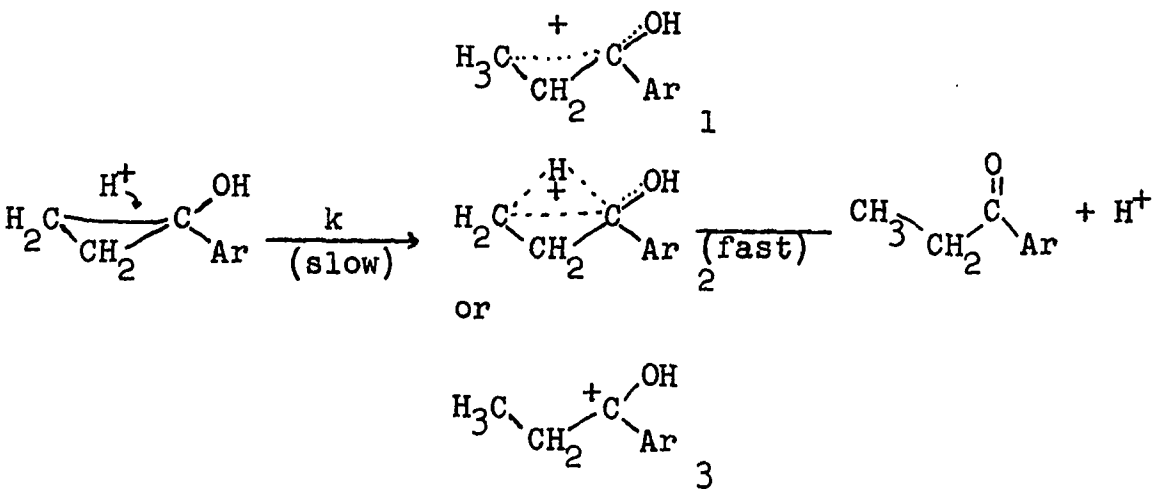



Figure 29. Proposed mechanistic pathway for the acid-catalyzed ring opening of 1-arylcyclopropanols

Table 11. Rates of the acid-catalyzed ring opening of 1-arylcyclopropanols in 60/40 dioxane-water at 50 degrees

| Subst. | k | | Log k | Sigma | Sigma plus |
|---|---|---|---|---|---|
| p-methoxy | 1.15± | .03 x $10^{-4}$ | -3.939 | -0.268 | -0.778 |
| | 1.04± | .03 | -3.983 | | |
| | 1.11± | .09 | -3.955 | | |
| | 1.18± | .06 | -3.928 | | |
| | 1.12± | .05 | -3.951 | | |
| | 1.02± | .02 | -3.991 | | |
| Ave k | 1.10- | .05 | log k calc. for sigma -4.045 | | |
| | | | log k calc. for sigma plus -3.990 | | |
| p-methyl | 6.76± | .23 x $10^{-5}$ | -4.170 | -0.170 | -0.311 |
| | 6.50± | .11 | -4.187 | | |
| | 6.53± | .43 | -4.185 | | |
| | 6.87± | .14 | -4.163 | | |
| Ave k | 6.67± | .15 | log k calc. for sigma -4.188 | | |
| | | | log k calc. for sigma plus -4.342 | | |
| H | 3.29± | .07 x $10^{-5}$ | -4.483 | 0.000 | 0.000 |
| | 3.48± | .07 | -4.458 | | |
| | 3.12± | .26 | -4.506 | | |
| | 2.76± | .16 | -4.559 | | |
| Ave k | 3.18± | .22 | log k calc. for sigma -4.497 | | |
| | | | log k calc. for sigma plus -4.577 | | |
| m-chloro | 1.04± | .03 x $10^{-5}$ | -4.983 | 0.373 | .399 |
| | 1.00± | .06 | -5.000 | | |
| | 1.03± | .04 | -4.987 | | |
| | 1.17± | .04 | -4.932 | | |
| Ave k | 1.06± | .05 | log k calc. for sigma -4.983 | | |
| | | | log k calc. for sigma plus -4.878 | | |
| m-trifluoro-methyl | 9.83± | .26 x $10^{-6}$ | -5.007 | .415 | .520 |
| | 9.40± | .10 | -5.026 | | |
| | 9.37± | .19 | -5.028 | | |
| | 10.0 ± | 1.0 | -5.000 | | |
| Ave k | 9.65± | 0.27 | log k calc. for sigma -5.045 | | |
| | | | log k calc. for sigma plus -4.971 | | |

Table 11 (Continued)

| Subst. | k | Log k | Sigma | Sigma plus |
|---|---|---|---|---|
| log $k_o$ = -4.437 | | | | |
| rms = 0.005 | | | | |
| rho = -1.46 | | | | |
| log $k_o$ = -4.577 | | | | |
| rms = 0.095 | | | | |
| rho plus = -0.755 | | | | |

Whether the protonated intermediate is the protonated intermediate with a carbon or proton bridging or else involves complete charge separation is a question somewhat difficult to answer. As for the question of carbon bridging vs. proton bridging, work by Baird[73] indicates that cyclopropanes are opened via a proton bridged intermediate. Baird has also pointed out that in cyclopropane systems where carbon bridging is favored it may occur. Work by Nickon[86] on nortricyclene indicates a carbon bridged intermediate operative in this system. If either intermediate is operative, the ring opening would be expected to follow sigma rather than sigma plus.[85] If a full positive charge were developed at the reacting site, electronic demands should be much greater. For a comparison to a system with charge separation, work by Stewart and Yates[87] can be referred to. These workers obtained values for the pKa's of twenty substituted acetophenones. The protonated form of the ketones should be similar to intermediate three. Of course, an equilibrium situation is dealt with in their system. However, factors stabilizing the intermediate in the acid-catalyzed ring opening should stabilize the protonated ketone form. These pKa's were found by these workers to correlate well with sigma plus

---

[86]A. Nickon and A. J. Hammons, J. Am. Chem. Soc., 86, 3322 (1964).

[87]R. Stewart and K. Yates, J. Am. Chem. Soc., 80, 6355 (1958).

to give a rho of -2.17 with a correlation coefficient of 0.983. This is in comparison to a rho of -2.22 with a correlation coefficient of 0.905 when the pKa's were plotted against sigma. It is interesting that the p-methoxy and m-methoxy substituted acetophenones were not well correlated with either sigma or sigma plus. Our system fit best, with sigma. A correlation coefficient is not very meaningful statistically for five points and was not made. That inductive effects appear to be of prime importance in relation to resonance effects is indicated by work by Cookson and co-workers[88] on the acid-catalyzed opening of cyclopropane rings incorporated into a steroidal system. The methyl substituted moieties were opened with much greater ease than the phenyl substituted compounds. These workers postulated two factors as possibly operative. The inductive effects of the phenyl group could inhibit initial protonation leading to final product, or the transition state intermediate is so like product that a full charge development does not occur. Because the charge on the carbonium ion is so low only inductive effects are operative and resonance effects cannot be brought into full play.

The rate determining proton transfer illustrated finds some support in the $H_o$ work. The $Y_o$ relationship was found to be inconclusive. Further support of a proton transfer

---

[88] R. C. Cookson, D. P. G. Hamon and J. Hudec, J. Chem. Soc., 5782 (1963).

step is given by work by both Baird[37] and Nickon[86] which indicate no equilibrium prior to ring opening occurs. It would be especially useful to have more definitive data on the effect of substituents on the opening of cyclopropanes so further comparisons with our work can be made.

The ring opening of 1-arylcyclopropanols was also carried out in basic 95% ethanol solution. The results are tabulated in Table 12. A sigma rho plot for 1-arylcyclopropanols did not give a straight line, as shown in Figure 31, but instead gave one which was concave upwards. These results can be explained on the basis of the mechanism in Figure 30.

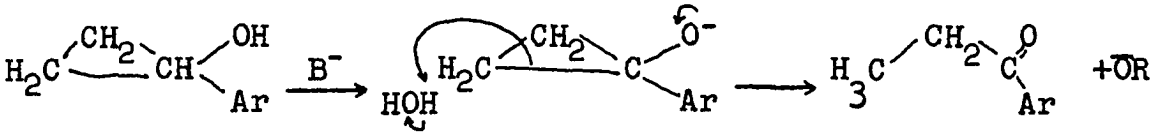


Figure 30. Proposed mechanism for the base-catalyzed ring opening of 1-arylcyclopropanols

Table 12. Ring opening of 1-arylcyclopropanols carried out in basic 95% ethanol solution

| Subst. | k | log k | sigma |
|---|---|---|---|
| p-methoxy | $9.10^{\pm} .12 \times 10^{-5}$ | -4.041 | -0.268 |
| p-methyl | $7.45^{\pm} .07 \times 10^{-5}$ | -4.128 | -0.170 |
| H | $7.02^{\pm} .23 \times 10^{-5}$ | -4.153 | |
| m-chloro | $1.08^{\pm} .02 \times 10^{-4}$ | -3.967 | 0 |
| | $1.12^{\pm} .05 \times 10^{-4}$ | -3.951 | -0.373 |
| m-trifluoro-methyl | $1.33^{\pm} .04 \times 10^{-4}$ | -3.876 | |
| | $1.30^{\pm} .02 \times 10^{-4}$ | -3.886 | .415 |

The transition state complex involves two prime factors contributing to its structure. The alkoxide and the ketone product stability will both combine to exert an effect on the structure of this intermediate. Those factors enhancing alkoxide stability should also enhance a transition complex leaning toward the alkoxide form. On the other hand, factors that stabilize the ketonic product[89] could lead to a transition state more like the ketone in structure. The transition state could be pictured as leaning toward the alkoxide form for electron withdrawing groups and toward the ketonic form for electron donating groups. In the case of the unsubstituted 1-arylcyclopropanol, no particular stability is conferred either to the alkoxide or the ketonic form. This would tend to make the transition state of higher energy than for either electron withdrawing or electron donating

[89] J. W. Baker and H. B. Hopkin, J. Chem. Soc., 1089 (1949).

substituents. The net result would be reflected in the sigma-rho plot obtained as shown in Figure 31. For future work on the base-catalyzed ring opening the rates of reaction in solvents of differing bacicity would be useful, for one could better assess the role of proton transfer from the solvent on the rate of ring opening.

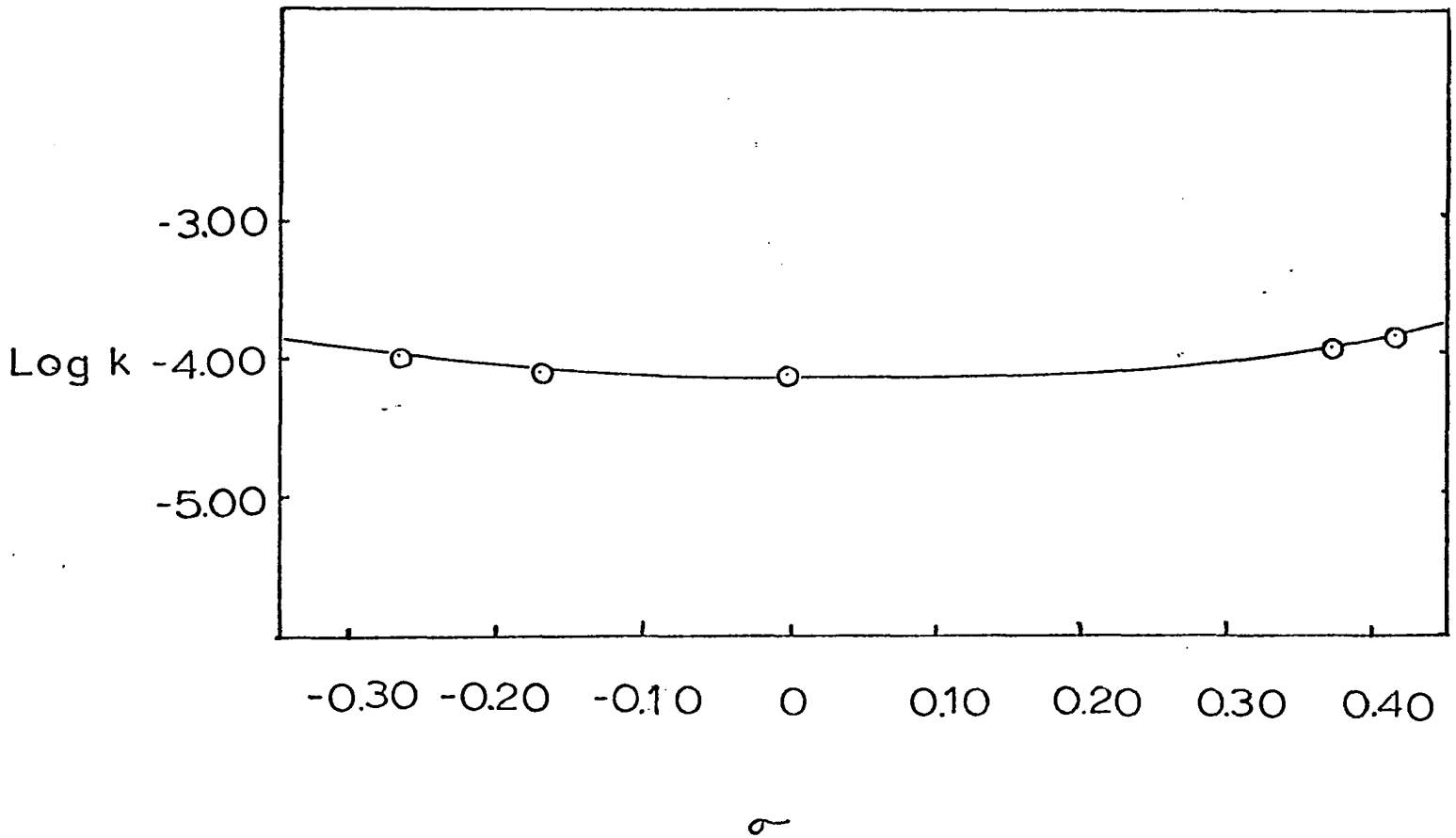



Figure 31. The plot of log k vs. sigma for the base catalyzed ring opening of 1-arylcyclopropanols

# EXPERIMENTAL

## Preparations

### Melting points

All melting points are uncorrected and are reported in degrees Centigrade.

### Infrared spectra

All infrared spectra were recorded on a Perkin-Elmer model 21 spectrometer.

### N. M. R. spectra

All N. M. R. spectra were run on a Varian model HR-60 spectrometer.

### Ultraviolet spectra

All ultraviolet spectra were run on a Beckman model DK-2A recording spectrometer.

### 1-(p-Methylphenyl)cyclopropanol

In general, the preparation of this compound served as a model for the preparation of the succeeding 1-(substituted-phenyl)cyclopropanols. Unless otherwise indicated, the molar amounts of reagents and volumes of solvents used were the same in the succeeding alcohol preparations.

Into a dry 3 l. flask fitted with an efficient reflux condenser, a stirrer, a Y-tube holding a 1 l. and a 250 ml. addition funnel, and protected from moisture by calcium

chloride tubes, was placed 5.76 g. (0.237 g. atom) of magnesium turnings barely covered by anhydrous ether. Forty drops of p-bromotoluene and twenty drops of ethyl bromide were added. The reaction started immediately, and a solution of 35 g. (0.205 mole) of p-bromotoluene in 200 ml. of dry ether was added at such a rate as to maintain mild reflux. After the reaction was complete, a solution of 25.4 g. (0.2 mole) of 1,3 dichloroacetone in 200 ml. of ether was added slowly over a 1-hour period.

At the same time, in a separate 2-l. round bottom flask which was equipped with reflux condenser, stirrer and addition funnel, ethylmagnesium bromide was prepared from 128.6 g. (1.18 moles) of ethyl bromide and 30 g. (1.25 g. atoms) of magnesium turnings in 800 ml. of ether. When the reaction was complete the addition funnel was replaced by a rubber stopper containing a short glass tube. The reflux condenser was replaced with a ground glass exit tube lightly plugged with a small amount of glass wool. The Grignard solution was forced under mild nitrogen pressure through the glass wool plug into the 1 l. addition funnel on the first flask. Into the 250 ml. addition funnel was placed a filtered solution of 2.5 g. (.0154 mole) of anhydrous ferric chloride in 200 ml. of dry ether. The two solutions were added simultaneously over a 2-3 hour period. A large evolution of gas occurred at this time and was vented to a window or hood. Stirring was continued for an additional fourteen hours. The resulting

black suspension was decomposed by adding it slowly to a 4 l. beaker containing a rapidly stirred slurry made of 1,500 g. of ice and 600 ml. of 2 M hydrochloric acid saturated with ammonium chloride. The ether layer was removed and extracted with 200 ml. portions of water until the water layer showed no chloride or acid present. The solution was dried over anhydrous magnesium sulfate. If time did not permit immediate work-up, the ether solution was stored in the refrigerator. The ether was removed by distillation through a Vigreux column. After removal of the ether, the residue, 29 g. (98%), was distilled through a short three inch simple column to give 25.5 g. (86%) distillate which was then fractionated through a short Vigreux column. The fraction boiling at 70-78 degrees at 0.4 mm. was collected to give 19.25 g. (63%) crude carbinol which usually crystallized upon standing in the ice box. Recrystallization from pentane was carried out in a polyethylene bottle by cooling in an ice-salt mixture to give 15.0 g. (50% yield) pure alcohol m. p. 38-39 degrees. The product was identified by N. M. R. and elemental analysis. The N. M. R. showed an $A_2B_2$ pattern at 9.1 τ, a large, sharp single peak corresponding to the methyl protons at 7.8 τ, a broad OH peak at 6.1 τ, and an aromatic region at 3.04 τ.

Analysis

Calcd. for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.49, 80.35; H, 7.96, 8.21.

1-Phenylcyclopropanol

This alcohol was prepared and worked up in the manner described above. After removal of the ether, the residue 23.04 g. (86%) was distilled through a short Vigreux column. The fraction boiling at 67-74 degrees (0.4 mm) was collected to give 12.8 g. (48%) of the alcohol. The remaining traces of isomeric ketone were removed by recrystallization from a pentane-ether mixture at ice box temperature. The recrystallizations were carried out in a polyethylene bottle.

The product was identified by N. M. R., an $A_2B_2$ pattern was found at 9.00 $\tau$, an OH peak at 7.1 $\tau$, and an aromatic region of 2.2 $\tau$. (See Figure 32.)

1-(p-methoxyphenyl)cyclopropanol

This alcohol was prepared and worked up in the manner described as for 1-(p-methylphenyl)cyclopropanol. After removal of the ether, the residue, 40.35 g. (86%), was distilled through a short Vigreux column. The fraction boiling at 110-120 (.35 mm.) was collected to give 25.9 g. (74%) of the crude alcohol. The alcohol was further purified by placing the material into a polyethylene bottle and adding 20-30 ml. of pentane. Sufficient ether was then added to completely dissolve the alcohol. The solution was next placed into an ice bath. It was sometimes necessary to place a few milliliters of the solution into a small Ehrlenmeyer at ice-salt temperatures, scratching the sides of the flask to induce

crystallization. The crystals so obtained were used as seed to promote crystallization of the major portion of product. An attempt was made to crystallize the remaining material by concentrating the mother liquor. Although the material crystallized, it was always contaminated by the inclusion of a yellow colored oil. After several tries at crystallization this effort was discontinued as sufficient alcohol for the kinetic work had been obtained. For identification an N. M. R. spectrum was made. An $A_2B_2$ pattern was found at 9.04 $\tau$, a broad OH bond at 7.95 $\tau$, a single sharp methyl peak at 6.29 $\tau$ and aromatic absorption at 3.10 $\tau$.

1-(m-Chlorophenyl)cyclopropanol

This compound was prepared in a similar way. After removal of the ether, the residue was distilled through a short Vigreux column to give 8.38 g. (25%) yield slightly colored alcohol b. p. 86-91 at .125 mm. For kinetic work the alcohol was purified by molecular distillation. The alcohol was identified by N. M. R. The spectrum showed an $A_2B_2$ pattern at 8.57 $\tau$, a sharp OH bond at 6.45 $\tau$ and aromatic absorption at 2.90 $\tau$.

1-m-trifluoromethylcyclopropanol

The preparation of this alcohol also follows the method of preparation used for 1-p-methylphenylcyclopropanol. After hydrolysis and removal of ether, the residue was taken up into pentane with sufficient ether to completely dissolve all of

the material present. The flask was placed into dry ice but no crystallization could be effected.

A portion of the solution was then placed into a 150 ml. round-bottomed flask and placed on the Roto-vac. The flask was cooled in a salt-ice bath as it rotated. After 1-1.5 minutes crystallization occurred. Meanwhile, the major portion of material was taken out of the Dewar flask and allowed to warm to salt-ice bath temperatures. The crystals previously obtained were added and a large crop of crystals literally fell out of solution. The mother liquor was concentrated to give an additional crop of crystals. A total of 24.3 g. (62%) of crude 1-m-trifluoromethylphenylcyclopropanol was obtained. The crystals were taken up into hot hexane-ether and recrystallized to give 16.4 g. (36% yield) of 1-m-trifluoromethylphenylcyclopropanol melting at 47-48 degrees. As identification of the product, an N. M. R. spectrum was taken. It showed a typical $A_2B_2$ region, a sharp OH peak and an aromatic region. No calculation of $\tau$ values was made on this alcohol.

1-Methylcyclopropanol

This reaction was carried out in the usual manner, using 31 g. (0.21 mole) of methyl iodide and 5.7 g. (0.23 mole) of magnesium turnings to prepare the methyl-magnesium iodide. This was reacted with 25.4 g. (0.2 mole) of dichloroacetone. The product was hydrolyzed with 1,500 g. of ice and 600 ml. of

2 M hydrochloric acid. The water layer was extracted 12 times with 50 ml. portions of ether. The ether was dried over anhydrous magnesium sulfate and removed by distillation through a 12 inch tantalum spiral-packed column. The residue was distilled to give 4.1 g. (28% yield) of 1-methylcyclopropanol, b. p. 102-104.5 degrees, reported 103.5 degrees.[38]

Identification An N. M. R. analysis gave a spectral pattern identical with that reported.[38]

1-Arylcyclopropyl tosylates

For additional identification of the alcohols, tosylates were prepared using slight modifications of the Tipson[90] procedure. The identity of the tosylates was confirmed by N. M. R. and elemental analysis except for the 1-p-methoxycyclopropyl tosylate which decomposed quite rapidly at room temperature.

1-(p-Methylphenyl)cyclopropyl tosylate

Into a 50 ml. Ehrlenmeyer flask was placed 30 ml. of dry pyridine. The pyridine was cooled at -5 degrees in a salt-ice bath and 2 g. (.01 mole) of 1-(p-methylphenyl)cyclopropanol was added. After the alcohol completely dissolved, 2.85 g. (.015 mole) of p-toluenesulfonyl chloride was added. The flask was swirled occasionally. After one hour the flask was placed into the ice-box and allowed to stand for two days.

---

[90]R. S. Tipson, J. Org. Chem., 9, 235 (1944).

The flask was removed from the refrigerator and its contents were poured into an ice-water slurry. A white amorphous precipitate formed which was removed by filtration. The solid was washed with ice-cold 10% hydrochloric acid until it appeared all pyridine had been removed. The solid was washed with ice-water until the water was chloride free. The solid was allowed to dry on the suction funnel.

The solid was weighed (2.38 g.) and then was placed into hot purified Skelly B. Sufficient ether was added to dissolve the solid. A little anhydrous magnesium sulfate and some charcoal were added and the solution was filtered to remove the drying agent and charcoal. Some of the ether was removed by evaporation, pentane was added to the cloud point, and the flask was allowed to stand at room temperature. When crystal formation began, the flask was transferred to the refrigerator. The resulting white needle-like crystals were removed from the solid by filtration. These were left for 24 hours in a vacuum dessicator in which strips of paraffin had been placed. After removal of solvent, 1.76 g. (43% yield) of product melting at 87.5-88 degrees was obtained. The N. M. R. spectrum gave an $A_2B_2$ pattern at 8.69 $\tau$, two large single peaks at 7.75 $\tau$ and 7.67 $\tau$ corresponding to the two aromatic methyl groups, and aromatic absorption at 3.00 $\tau$.

Analysis Calcd. for $C_{17}H_{18}O_3S$: C, 67.52; H, 6.00. Found: C, 67.16; H, 6.09.

1-(p-Methoxyphenyl)cyclopropyl tosylate

This compound was prepared from 2 g. (.012 mole) of 1-(p-methoxyphenyl)cyclopropanol, 3.1 g. (.018 mole) of toluenesulfonate, and 20 ml. of dry pyridine in the same manner described for the preceding 1-p-methylphenylcyclopropanol. Identification was not positive as the 1.5 g. (39% yield) of product obtained was so unstable at room temperature, no N. M. R. or elemental analysis could be made. The compound decomposed too rapidly to give a melting point.

1-Phenylcyclopropyl tosylate

This compound was prepared in the usual manner from 4 g. (.03 mole) of 1-phenylcyclopropanol and 8.6 g. (.045 mole) of P-toluenesulfonylchloride in 40 ml. of dry pyridine. Work-up and recrystallization gave 3.12 g. (36.3% yield) of crystals melting at 75-75.5 degrees. The N. M. R. spectrum showed an $A_2B_2$ pattern at 8.69 $\tau$, a single aromatic methyl peak at 7.66 $\tau$ and an aromatic absorption at 2.95 $\tau$ (Figure 33).

Analysis Calcd. for $H_{16}C_{16}SO_3$: C, 66.63; H, 5.59. Found: C, 66.65; H, 5.49.

1-(m-Chlorophenyl)cyclopropyl tosylate

This compound was prepared in the usual manner from 2 g. (.019 mole) of 1-m-chlorophenylcyclopropanol and 5.4 g. (.028 mole) of P-toluenesulfonylchloride in 30 ml. of dry pyridine. As the material did not crystallize in the ice-water slurry,

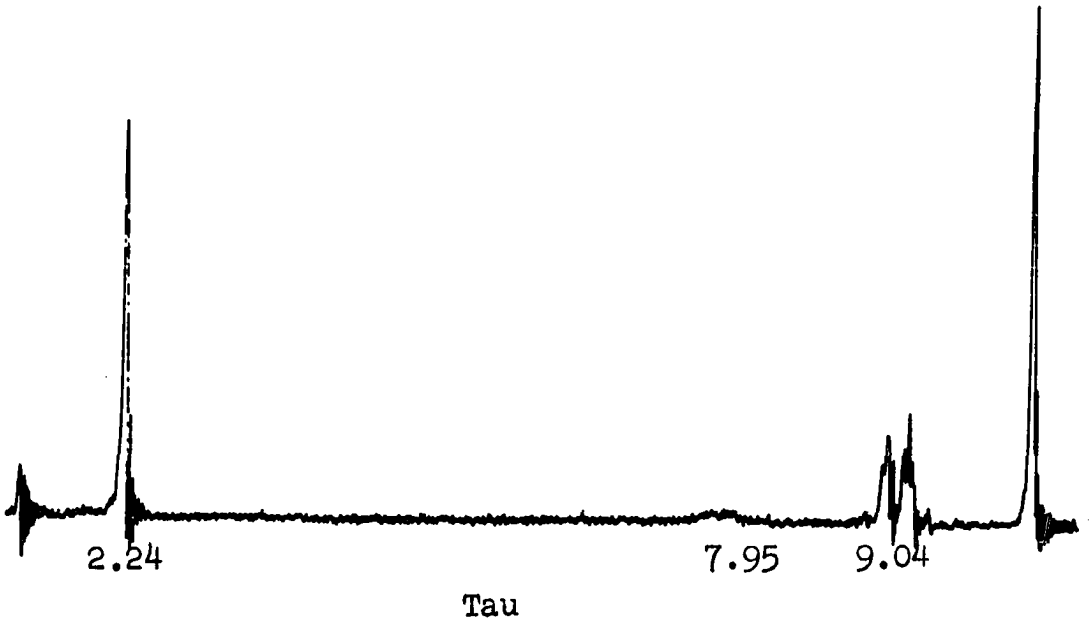



Figure 32. N.M.R. spectrum of 1-phenylcyclopropanol

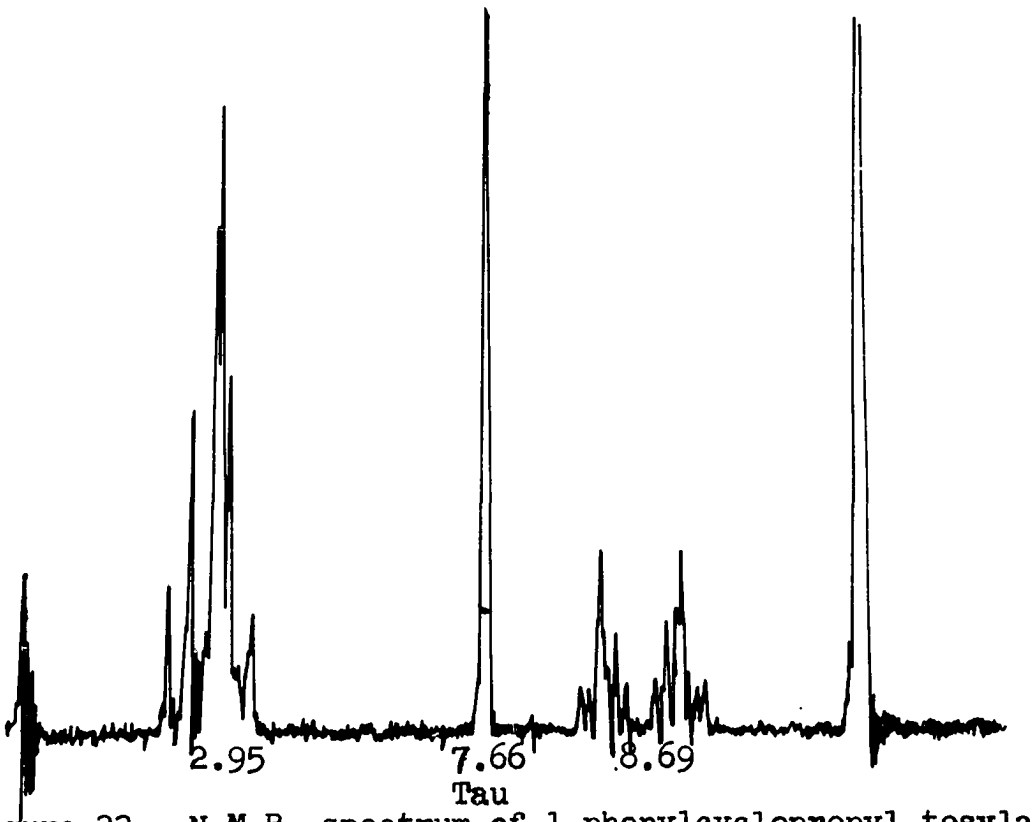



Figure 33. N.M.R. spectrum of 1-phenylcyclopropyl tosylate

the water was extracted six times with 10 ml. portions of methylene chloride. The methylene chloride was washed six times with 10 ml. portions of 1.5 M hydrochloric acid. The hydrochloric acid was removed by washing with cold water until the water was chloride free. The methylene chloride layer was dried over anhydrous magnesium sulfate. The drying agent was removed by filtration. Most of the methylene chloride was evaporated and the residue was taken up in 20 ml. of Skelly B. The flask containing the Skelly B solution of tosylate was wrapped in a towel and placed into a Dewar containing dry ice. A pink solid formed which was removed by filtration and put into 20 ml. of Skelly B. Ether was added until the material dissolved. The flask containing the solution was placed into the ice-box, but the crystals were still slightly colored. Three more recrystallizations from Skelly B and chloroform gave 0.86 g. (14% yield) which melted at 56-57 degrees. An N. M. R. spectrum showed an $A_2B_2$ pattern at 8.57 $\tau$, a single peak at 7.68 $\tau$ and an aromatic absorption at 2.85 $\tau$.

Analysis Calcd. for $H_{15}C_{16}SO_3Cl$: C, 59.53; H, 4.68. Found: C, 59.53; H, 4.67.

1-(m-trifluoromethylphenyl)cyclopropyl tosylate

Its melting point is 36-36.5 degrees. The N. M. R. spectrum showed an $A_2B_2$ pattern at 8.57 $\tau$, a single peak at 7.69 $\tau$, and aromatic absorption at 2.68 $\tau$.

Analysis Calcd. for $C_{17}H_{15}F_3SO_3$: C, 57.30; H, 4.24. Found: C, 57.55; H, 4.94.

Kinetic procedure

These kinetics were run in either dioxane-water or ethanol solution. For the Hammett $\sigma_1$ kinetic runs and the $H_o$ kinetic runs the solvent system was 60/40 vol. % dioxane-water. As the composition of the solvent was to be kept as nearly constant as possible, it was necessary to take into account the amount of water present in the perchloric acid. The use of tables taken from the Handbook of Chemistry and Physics[91] gave the percentage by weight of perchloric acid and water at 25 degrees vs. the specific gravity. Sodium hydroxide solution standardized against potassium acid pthalate was used to titrate 1 ml. aliquots of the concentrated acid which turned out to be 12.26 M. This was equivalent to a 72.5% perchloric acid solution which has a density of 1.698 g./ml.

For each milliliter of acid there was calculated to be present .47 ml. of water. A 60/40 dioxane-water solution was placed into a 250 ml., 500 ml., or 1 l. volumetric flask. The requisite amount of acid was added followed by the addition of .71 ml. of dioxane per ml. of acid used. The flask

---

[91]C. D. Hodgman, ed., Handbook of chemistry and physics. Cleveland, Ohio, Chemical Rubber Publishing Company. 1955. pp. 1870.

was then warmed to 50 degrees in the bath and 60/40 dioxane-water, preheated to 50 degrees, was added to fill the flask to the mark.

Preparation of dioxane The dioxane was purified by two methods. For most of the runs the dioxane was purified by the method given by Fieser.[92] The remainder was purified by allowing the dioxane to reflux over anhydrous sodium hydroxide for a week or more. The dioxane was distilled through an 18 inch Vigreux column taking only the center cut. The solvent was then distilled from fresh sodium hydroxide through a Todd column having approximately 50 plates to remove any benzene, which is the principal impurity. The center cut boiling at 102.5 degrees (uncorrected) was collected. This was placed in a 2 l. round bottomed flask and kept refluxing until use under nitrogen in the presence of anhydrous sodium hydroxide. The distillation apparatus was set up so water flow through the reflux condenser could be shut off so as to allow distillation through the reflux condenser to another condenser. The forerun was discarded and the freshly distilled dioxane was used as needed for each kinetic run. A g. p. c. analysis showed only a single peak.*

---

[92]L. F. Fieser, Experiments in organic chemistry. D. C. Heath and Company. 1957. pp. 284.

*Retention time: 16.5 minutes on a 1 m. O.D.P.N. column followed by a 1 m. Perkin-Elmer "A" column with a flow rate of 112 cc/min. at 86 degrees.

An ultraviolet spectrum showed no aromatic absorptions.

The kinetic runs were carried out by weighing an appropriate amount of alcohol into a 100 ml. flask. The amount of alcohol needed was determined by allowing the alcohol present to react in acid for ten or more half-lives. The absorption at this time was determined. The extinction coefficients determined in this manner for the ketones agreed well with reported values. The extinction coefficient for 1-(m-trifluormethylpropiophenone) is not reported. The amounts of alcohols (0.015 g.-0.022 g.) were calculated so as to give a final absorption of 0.85. The amounts of 1-phenylcyclopropanol and 1-(m-chlorophenyl)cyclopropanol were measured by a syringe to give approximately 0.04 ml. of liquid alcohol.

The flask and alcohol were placed into a constant temperature bath for one minute. The acid or base solutions which were used for a particular run had been placed into the bath several hours earlier. The flask containing 1-arylcyclopropanol was filled to the mark with the acid or base solution and vigorously shaken. A 5 ml. sample was removed immediately and quenched by diluting into a 100 ml. volumetric flask containing about 75 ml. of ethanol. The flask was filled to the mark with ethanol. The ethanol effectively quenched the reaction, for samples which were allowed to stand at room temperature for ten hours showed only an almost

imperceptible change in U.V. absorption. Other samples were taken at suitable intervals; the time was recorded when the pipette was one-half empty.

The rate constants were determined from the 1st order rate expression $\log \frac{(A_\infty - A_o)}{(A_\infty - A_t)} = kt$ where $A_o$, $A_t$ and $A_\infty$ are the absorbances at zero time, intermediate times, and the absorbance after ten or more half-lives. Careful check to make certain that the wavelength is the same for all samples must be made, otherwise error is introduced.

Table 13. Kinetics of 1-p-methylphenylcyclopropanol in 60/40 dioxane-water and 1.819 M perchloric acid at 50 degrees

| Sample | Absorbance | Time | k x $10^3$ uncorrected |
|---|---|---|---|
| 1 | .064 | 0 | ---- |
| 2 | .120 | 12.0 | ---- |
| 3 | .170 | 27.0 | 2.44 |
| 4 | .233 | 42.9 | 2.58 |
| 5 | .302 | 58.5 | 2.83 |
| 6 | .340 | 76.7 | 2.59 |
| 7 | .383 | 89.0 | 2.69 |
| 8 | .408 | 103.5 | 2.57 |
| 9 | .490 | 138.2 | 2.63 |
| 10 | .617 | 210.2 | 2.75 |
| 11 | .680 | ----- | ---- |
| 12 | .790 | 402.7 | 2.76 |
| 13 | .816 | ----- | |

$k_{sec}^{-1} = 1.03 \pm .04 \times 10^{-4}$.

Ultraviolet lambda max. 252.5. Log epsilon = 4.17.

Calculated infinity point .819.

Table 14. Kinetics of 1-(p-methylphenyl)cyclopropanol in 60/40 dioxane-water and 1.801 M perchloric acid at 50 degrees

| Sample | Absorbance | Time (min) | k x $10^3$ |
|---|---|---|---|
| 1 | .021 | 0 | |
| 2 | .138 | 24.95 | 2.68 |
| 3 | .230 | 50.75 | 2.53 |
| 4 | .324 | 82.21 | 2.46 |
| 5 | .400 | 110.24 | 2.47 |
| 6 | .483 | 147.23 | 2.47 |
| 7 | .530 | 181.21 | 2.35 |
| 8 | .600 | 227.72 | 2.27 |
| 9 | .723 | 352.24 | 2.44 |
| 10 | .748 | 464.44 | 2.39 |
| 11 | .805 | 553.44 | 2.57 |
| 12 | .870 | | |

$k_{sec}^{-1} = 9.44 \pm .30 \times 10^{-5}\ sec^{-1}$.

Ultraviolet lambda max. = 252.5 m . Log epsilon = 4.17.

Calculated infinity point .838.

Table 15. Kinetics of 1-p-methylphenylcyclopropanol in 60/40 dioxane-water and 1.005 M perchloric acid at 50 degrees

| Sample | Absorbance | Time (min) | $k \times 10^4$ |
|---|---|---|---|
| 1 | .015 | 0 | ---- |
| 2 | .026 | 18.07 | ---- |
| 3 | .586 | 37.74 | ---- |
| 4 | .084 | 57.54 | 6.63 |
| 5 | .113 | 77.41 | 7.31 |
| 6 | .158 | 111.59 | 7.46 |
| 7 | .208 | 163.70 | 7.12 |
| 8 | .300 | 271.56 | 6.83 |
| 9 | .434 | 453.74 | 6.85 |
| 10 | .775 | 1,436.61 | 7.91 |
| 11 | .835 | | |

$k_{sec}^{-1} = 2.75 \pm .11 \times 10^{-5}{}_{sec}^{-1}$.

Ultraviolet lambda max. = 252.5 m . Log epsilon = 4.17.

Calculated infinity point .824.

Table 16. Kinetics of 1-p-methylphenylcyclopropanol in 60/40 dioxane-water and 1.019 M perchloric acid at 50 degrees

| Sample | Absorbance | Time (sec) | k x $10^5$ |
|---|---|---|---|
| 1 | .082 | 0 | ---- |
| 2 | .101 | 1,754 | ---- |
| 3 | .139 | 3,578 | ---- |
| 4 | .190 | 5,788 | 1.10 |
| 5 | .254 | 9,201 | 1.15 |
| 6 | .330 | 13,785 | 1.18 |
| 7 | .392 | 18,600 | 1.15 |
| 8 | .490 | 25,986 | 1.20 |
| 9 | .555 | 32,875 | 1.19 |
| 10 | .614 | 39,608 | 1.21 |
| 11 | .667 | 48,338 | 1.20 |
| 12 | .877 | ------ | |

$k_{sec}^{-1} = 2.69 \pm .07 \times 10^{-5}\ sec^{-1}$.

Ultraviolet lambda max. = 252.5. Log epsilon = 4.17.

Calculated infinity point .879.

Table 17. Kinetics of 1-p-methylphenylcyclopropanol in 60/40 dioxane-water and 2.483 M perchloric acid at 50 degrees

| Sample | Absorbance | Time (min) | k x $10^3$ |
|---|---|---|---|
| 1 | .181 | 0 | ---- |
| 2 | .257 | 11.20 | ---- |
| 3 | .342 | 21.52 | 6.41 |
| 4 | .437 | 36.51 | 6.74 |
| 5 | .543 | 59.74 | 6.87 |
| 6 | .625 | 85.05 | 7.08 |
| 7 | .674 | 110.74 | 7.01 |
| 8 | .730 | 149.60 | 7.61 |
| 9 | .764 | 208.36 | ---- |
| 10 | .773 | ------ | |

$k_{sec}^{-1} = 2.67 \pm .11 \times 10^{-4}\ sec^{-1}$.

Ultraviolet lambda max. = 252.5. Log epsilon = 4.17.

Calculated infinity point .773.

Table 18. Kinetics of 1-p-methylphenylcyclopropanol in 60/40 dioxane-water and 2.48 M perchloric acid at 50 degrees

| Sample | Absorbance | Time (min) | $k \times 10^3$ |
|---|---|---|---|
| 1 | .160 | 0 | ---- |
| 2 | .218 | 6.62 | ---- |
| 3 | .274 | 12.95 | 6.58 |
| 4 | .318 | 18.35 | 6.71 |
| 5 | .375 | 26.54 | 6.71 |
| 6 | .425 | 34.10 | 6.81 |
| 7 | .475 | 42.53 | 6.92 |
| 8 | .527 | 52.43 | 7.06 |
| 9 | .583 | 68.52 | 6.86 |
| 10 | .639 | 84.88 | 7.06 |
| 11 | .689 | 106.09 | 7.17 |
| 12 | .810 | | |

$k_{sec}^{-1} = 2.64 \pm .04 \times 10^{-4}$.

Lambda max. = 252.5 m .

Calculated infinity point .796.

Table 19. Kinetics of 1-p-methylphenylcyclopropanol in 60/40 dioxane-water and 3.455 M perchloric acid at 50 degrees

| Sample | Absorbance | Time (min) | k x $10^2$ uncorr. |
|---|---|---|---|
| 1 | .045 | 0 | ---- |
| 2 | .056 | 0.41 | ---- |
| 3 | .070 | 0.81 | ---- |
| 4 | .083 | 1.21 | ---- |
| 5 | .101 | 1.66 | 1.91 |
| 6 | .124 | 2.27 | 2.00 |
| 7 | .137 | 2.66 | 2.01 |
| 8 | .155 | 3.10 | 2.13 |
| 9 | .173 | 3.56 | 2.14 |
| 10 | .190 | 4.07 | 2.15 |
| 11 | .207 | 4.62 | 2.14 |
| 12 | .246 | 5.78 | 2.19 |
| 13 | .268 | 6.47 | 2.21 |
| 14 | .285 | 7.21 | 2.16 |
| 15 | .340 | 9.24 | 2.17 |
| 16 | .841* | | |

$k_{sec}^{-1} = 8.10 \pm .27 \times 10^{-4} sec^{-1}$.

Ultraviolet lambda max. = 252.5. Log epsilon = 4.17.

*Calculated infinity point.

Table 20. Kinetics of 1-p-methylphenylcyclopropanol in 60/40 dioxane-water and 3.455 M perchloric acid at 50 degrees

| Sample | Absorbance | Time (min) | k x $10^2$ |
|---|---|---|---|
| 1 | .071 | 0 | ---- |
| 2 | .088 | 0.55 | ---- |
| 3 | .127 | 1.62 | 2.12 |
| 4 | .169 | 2.67 | 2.33 |
| 5 | .198 | 3.64 | 2.26 |
| 6 | .221 | 4.60 | 2.16 |
| 7 | .260 | 5.86 | 2.20 |
| 8 | .289 | 6.91 | 2.21 |
| 9 | .318 | 7.99 | 2.23 |
| 10 | .343 | 9.09 | 2.21 |
| 11 | .376 | 10.29 | 2.25 |
| 12 | .400 | 11.08 | 2.33 |
| 13 | .436 | 13.23 | 2.25 |
| 14 | .565 | 20.73 | 2.34 |
| 15 | .086* | ----- | ---- |

$k_{sec}^{-1} = 8.70 \pm .19 \times 10^{-4}$.

Ultraviolet lambda max. = 252.5. Log epsilon = 4.17.

*Calculated infinity point.

Table 21. Kinetics of 1-p-methylphenylcyclopropanol in 60/40 dioxane-water and 3.990 M perchloric acid at 50 degrees

| Sample | Absorbance | Time (min) | k x $10^2$ |
|---|---|---|---|
| 1 | .103 | 0 | ---- |
| 2 | .130 | 0.43 | 3.96 |
| 3 | .165 | 0.91 | 4.41 |
| 4 | .198 | 1.44 | 4.39 |
| 5 | .224 | 1.92 | 4.29 |
| 6 | .250 | 2.45 | 4.18 |
| 7 | .284 | 3.00 | 4.33 |
| 8 | .320 | 3.62 | 4.46 |
| 9 | .352 | 4.22 | 4.51 |
| 10 | .387 | 4.78 | 4.74 |
| 11 | .406 | 5.43 | 4.55 |
| 12 | .436 | 6.08 | 4.62 |
| 13 | .460 | 6.90 | 4.50 |
| 14 | .503 | 7.60 | 4.85 |
| 15 | .806 | ---- | ---- |

$k_{sec}^{-1} = 1.72 \pm .05 \times 10^{-3}{}_{sec}^{-1}$.

Ultraviolet lambda max. = 252.5. Log epsilon = 4.17.

Calculated infinity point .803.

Table 22. Kinetics of 1-p-methylphenylcyclopropanol in 60/40 dioxane-water and 3.990 M perchloric acid at 50 degrees

| Sample | Absorbance | Time (min) | k x $10^2$ |
|---|---|---|---|
| 1 | .113 | 0 | ---- |
| 2 | .143 | 0.50 | ---- |
| 3 | .182 | 0.95 | 4.54 |
| 4 | .204 | 1.53 | 3.78 |
| 5 | .246 | 2.05 | 4.31 |
| 6 | .279 | 2.52 | 4.45 |
| 7 | .308 | 3.07 | 4.40 |
| 8 | .336 | 3.62 | 4.37 |
| 9 | .374 | 4.20 | 4.58 |
| 10 | .407 | 4.90 | 4.57 |
| 11 | .447 | 5.45 | 4.87 |
| 12 | .477 | 6.45 | 4.65 |
| 13 | .524 | 7.71 | 4.66 |
| 14 | .840 | | |

$k_{sec}^{-1} = 1.72 \pm .07 \times 10^{-3}$.

Ultraviolet lambda max. = 252.5. Log epsilon = 4.17.

Calculated infinity point .843.

Table 23. Kinetics of 1-p-methylphenylcyclopropanol in dioxane-water and 0.552 M perchloric acid at 50 degrees

| Sample | Absorbance | Time (min) | k x $10^4$ |
|---|---|---|---|
| 1 | .074 | 0 | ---- |
| 2 | .098 | 72.72 | ---- |
| 3 | .127 | 130.59 | 2.71 |
| 4 | .170 | 249.35 | 2.67 |
| 5 | .196 | 344.70 | 2.51 |
| 6 | .220 | 430.63 | 2.46 |
| 7 | .234 | 494.56 | 2.37 |
| 8 | .287 | 636.38 | 2.59 |
| 9 | .305 | 715.27 | 2.55 |
| 10 | .440 | 1,212.03 | 2.82 |
| 11 | .495 | 1,439.95 | 2.95 |
| 12 | .757* | | |

$k_{sec}^{-1} = 1.01 \pm .05 \times 10^{-5}{}_{sec}^{-1}$.

Ultraviolet lambda max. = 252.5. Log epsilon = 4.17.

*Calculated infinity point.

Table 24. Kinetics of p-methylphenylcyclopropanol in sulfuric-acid-ethanol at 50 degrees

| Sample | Absorbancy | Time (min) | k x $10^4$ |
|---|---|---|---|
| 1 | .023 | 0 | ---- |
| 2 | .068 | 61.23 | 3.86 |
| 3 | .140 | 164.27 | 3.95 |
| 4 | .195 | 253.75 | 3.90 |
| 5 | .269 | 379.80 | 3.94 |
| 6 | .318 | 466.73 | 3.99 |
| 7 | .402 | 639.20 | 4.05 |
| 8 | .487 | 838.57 | 4.13 |
| 9 | .561 | 1,119.32 | 3.94 |
| - | .867 | ------ | |

$k = 1.52 \pm .03 \times 10^{-5}$.

1.50 N $H_2SO_4$ in 31.7 per cent ethanol.

Ultraviolet lambda max. = 252.5 m . Log epsilon = 4.17.

Calculated infinity point .861.

Table 25. Kinetics of p-methylphenylcyclopropanol in sulfuric acid-ethanol at 50 degrees

| Sample | Absorbancy | Time (min) | k x $10^4$ |
|---|---|---|---|
| 1 | .016 | 0 | ---- |
| 2 | .052 | 60.56 | 3.22 |
| 3 | .110 | 166.31 | 3.26 |
| 4 | .150 | 251.87 | 3.17 |
| 5 | .207 | 378.56 | 3.13 |
| 6 | .243 | 466.19 | 3.12 |
| 7 | .310 | 638.03 | 3.12 |
| 8 | .390 | 878.69 | 3.12 |
| 9 | .460 | 1,120.41 | 3.15 |
| - | .815 | ------ | ---- |

$k_{sec}^{-1} = 3.16 \pm .04 \times 10^{-4}$.

1.50 N $H_2SO_4$ in 41.8% ethanol.

Ultraviolet lambda max. = 252.5. Log epsilon = 4.17.

Calculated infinity point .811.

Table 26. Kinetics of p-methylphenylcyclopropanol in sulfuric acid-ethanol at 50 degrees

| Sample | Absorbancy | Time (min) | k x $10^4$ |
|---|---|---|---|
| 1 | .020 | 0 | ---- |
| 2 | .049 | 60.52 | ---- |
| 3 | .098 | 166.32 | 3.10 |
| 4 | .125 | 252.55 | 2.64 |
| 5 | .180 | 379.02 | 2.63 |
| 6 | .213 | 467.34 | 2.59 |
| 7 | .270 | 638.62 | 2.50 |
| 8 | .347 | 879.41 | 2.49 |
| 9 | .408 | 1,126.58 | 2.42 |
| - | .897 | ------ | |

$k = 1.00 \pm .07 \times 10^{-5}_{sec^{-1}}$.

1.50 N $H_2SO_4$ in 56.5% ethanol.

Ultraviolet lambda max. = 252.5. Log epsilon = 4.17.

Calculated infinity point .893.

Table 27. Kinetics of p-methylphenylcyclopropanol in sulfuric acid-ethanol at 50 degrees

| Sample | Absorbance | Time (min) | k x $10^4$ |
|---|---|---|---|
| 1 | .021 | 0 | ---- |
| 2 | .069 | 118.83 | 2.27 |
| 3 | .118 | 252.01 | 2.21 |
| 4 | .191 | 455.37 | 2.27 |
| 5 | .252 | 638.64 | 2.31 |
| 6 | .323 | 879.35 | 2.33 |
| 7 | .381 | 1,121.60 | 2.31 |
| - | .823 | | |

$k = 8.75 \pm .09 \times 10^{-6}$.

1.50 M $H_2SO_4$ in 59.9% ethanol.

Ultraviolet lambda max. = 252.5. Log epsilon = 4.17.

Calculated infinity point .822.

Table 28. Kinetics of p-methylphenylcyclopropanol in sulfuric acid-ethanol at 50 degrees

| Sample | Absorbance | Time | $k \times 10^4$ |
|---|---|---|---|
| 1 | .028 | 0 | ---- |
| 2 | .070 | 100.32 | 2.19 |
| 3 | .115 | 202.42 | 2.30 |
| 4 | .160 | 300.37 | 2.43 |
| 5 | .213 | 410.42 | 2.59 |
| 6 | .253 | 506.98 | 2.62 |
| 7 | .283 | 613.98 | 2.51 |
| - | .882 | ------ | ---- |

$k = 9.56 \pm .42 \times 10^{-6}_{sec}{}^{-1}$.

1.50 M $H_2SO_4$ in 76.9% ethanol.

Ultraviolet lambda max. = 252.5. Log epsilon = 4.17.

Calculated infinity point .881.

Table 29. Kinetics of p-methylphenylcyclopropanol in sulfuric acid-ethanol at 50 degrees

| Sample | Absorbance | Time | k x $10^4$ |
|---|---|---|---|
| 1 | .060 | 0 | ---- |
| 2 | .117 | 73.19 | 4.51 |
| 3 | .170 | 145.38 | 4.56 |
| 4 | .214 | 229.06 | 4.19 |
| 5 | .269 | 300.59 | 4.53 |
| 6 | .334 | 409.94 | 4.61 |
| 7 | .372 | 506.84 | 4.40 |
| 8 | .428 | 614.38 | 4.86 |
| - | .837 | | |

$k = 1.73 \pm .05 \times 10^{-5}$.

1.50 M $H_2SO_4$ in 91.2% ethanol.

Ultraviolet lambda max. = 252.5. Log epsilon = 4.17.

Calculated infinity point .838.

Table 30. Kinetics of 1-p-methoxyphenylcyclopropanol in 60/40 dioxane-water at 50 degrees

| Sample | Absorbance | Time | $k \times 10^3$ |
|---|---|---|---|
| 1 | .167 | 0 | ---- |
| 2 | .205 | 9.00 | 3.10 |
| 3 | .240 | 18.96 | 2.94 |
| 4 | .277 | 30.35 | 2.88 |
| 5 | .325 | 42.96 | 3.10 |
| 6 | .353 | 54.12 | 2.97 |
| 7 | .400 | 68.20 | 3.11 |
| 8 | .443 | 82.18 | 3.24 |
| 9 | .483 | 101.98 | 3.20 |
| 10 | .768 | ----- | |

$k = 1.15 \pm .03 \times 10^{-4}\ sec^{-1}$.

$HClO_4 = 1.44 \pm .01$ N.

Ultraviolet lambda max. = 273. Log epsilon = 4.20.

Calculated infinity point .813.

Other k's for the same compound:

$1.04 \pm .03 \times 10^{-4}$

$1.11 \pm .09 \times 10^{-4}$

$1.18 \pm .06 \times 10^{-4}$

$1.12 \pm .05 \times 10^{-4}$

$1.02 \pm .02 \times 10^{-4}$

Average $k = 1.10 \pm .05 \times 10^{-4}$

Table 31. Kinetics for 1-p-methylphenylcyclopropanol in 60/40 dioxane-water at 50 degrees

| Sample | Absorbance | Time | $k \times 10^3$ |
|---|---|---|---|
| 1 | .028 | 0 | ---- |
| 2 | .075 | 17.47 | 1.61 |
| 3 | .136 | 38.72 | 1.75 |
| 4 | .187 | 58.89 | 1.89 |
| 5 | .233 | 79.33 | 1.72 |
| 6 | .282 | 107.72 | 1.73 |
| 7 | .348 | 130.93 | 1.70 |
| 8 | .380 | 154.60 | 1.74 |
| 9 | .427 | 180.20 | 1.78 |
| 10 | .468 | 205.09 | 1.82 |
| 11 | .505 | 237.51 | 1.80 |
| 12 | .538 | 266.67 | 1.82 |
| 13 | .790 | | |

$k = 6.76 \pm .23 \times 10^{-5}$.

$HClO_4 = 1.44 \pm .01$ N.

Ultraviolet lambda max. = 252.5. Log epsilon = 4.17.

Calculated infinity point .795.

Other k's for same compound:

$6.50 \pm .11 \times 10^{-5}$

$6.53 \pm .43 \times 10^{-5}$

$6.87 \pm .14 \times 10^{-5}$

Average $k = 6.67 \pm .15 \times 10^{-5}$

Table 32. Kinetics of 1-phenylcyclopropanol in 60/40 dioxane-water at 50 degrees

| Sample | Absorbance | Time (sec) | k x $10^3$ |
|---|---|---|---|
| 1 | .063 | 0 | |
| 2 | .075 | 779 | ---- |
| 3 | .115 | 2,571 | 1.48 |
| 4 | .174 | 6,193 | 1.42 |
| 5 | .248 | 11,393 | 1.39 |
| 6 | .307 | 15,887 | 1.41 |
| 7 | .407 | 26,716 | 1.37 |
| 8 | .494 | 37,759 | 1.47 |
| 9 | .543 | 47,522 | 1.44 |
| 10 | .643 | 85,282 | ---- |
| 11 | .668 | | |

k sec = $3.29 \pm .07 \times 10^{-5}$.

$HClO_4 = 1.44 \pm .01$.

Ultraviolet lambda max. = 241. Epsilon undetermined.

Infinity point undetermined.

Other k's for same compound:

$3.48 \pm .07 \times 10^{-5}$

$3.12 \pm .26 \times 10^{-5}$

$2.76 \pm .16 \times 10^{-5}$

Average k = $3.18 \pm .22 \times 10^{-5}$

Table 33. Kinetics of 1 m-chlorophenylcyclopropanol in 60/40 dioxane-water at 50 degrees

| Sample | Absorbance | Time | $k \times 10^4$ |
|---|---|---|---|
| 1 | 0.280 | 0 | ---- |
| 2 | 0.320 | 85.09 | 2.70 |
| 3 | 0.336 | 149.49 | 2.48 |
| 4 | 0.482 | 558.27 | 2.78 |
| 5 | 0.673 | 1,376.03 | 2.77 |
| 6 | 0.836 | 2,676.82 | 2.83 |
| 7 | 0.930 | 5,264.88 | 2.73 |
| 8 | 0.954 | ------- | ---- |

$k = 1.04 \pm .03 \times 10^{-5}_{sec}{}^{-1}$.

Concentration $HClO_4 = 1.44 \pm .01$.

Lambda max. = 240 m . Log epsilon = undetermined.

Calculated infinity point (undetermined).

Other k's for the same compound:

$1.00 \pm .06 \times 10^{-5}$

$1.03 \pm .04 \times 10^{-5}$

$1.17 \pm .04 \times 10^{-5}$ (1.48 M)

Average $k = 1.06 \pm .05 \times 10^{-5}_{sec}{}^{-1}$

Table 34. Kinetics of 1-m-trifluoromethylcyclopropanol in perchloric acid and 60/40 dioxane-water at 50 degrees

| Sample | Absorbance | Time | $k \times 10^4$ |
|---|---|---|---|
| 1 | .376 | 0 | ---- |
| 2 | .433 | 279.73 | 2.57 |
| 3 | .517 | 830.38 | 2.48 |
| 4 | .578 | 1,350.41 | 2.50 |
| 5 | .627 | 1,898.71 | 2.54 |
| 6 | .690 | 2,913.46 | 2.72 |
| 7 | .750 | ------ | |

$k_{sec}^{-1} = 9.83 \pm .26 \times 10^{-6}$.

Concentration of $HClO_4 = 1.44 \pm .01$.

Ultraviolet lambda max. = 235. Log epsilon = 4.022.

Calculated infinity point

Other k's for same compound:

$9.40 \pm .10 \times 10^{-6}_{sec}{}^{-1}$

$9.37 \pm .19 \times 10^{-6}_{sec}{}^{-1}$

$10.00 \pm 1.00 \times 10^{-5}_{sec}{}^{-1}$

Ave $k = 9.65 \times 10^{-6}$

Table 35. Kinetics of 1-(p-methoxyphenyl)cyclopropanol with base in 95% ethanol at 50 degrees

| Sample | Absorbance | Time | $k \times 10^3$ |
|---|---|---|---|
| 1 | .105 | 0 | ---- |
| 2 | .150 | 12.57 | 2.37 |
| 3 | .227 | 36.43 | 2.35 |
| 4 | .283 | 55.41 | 2.37 |
| 5 | .352 | 81.12 | 2.41 |
| 6 | .428 | 114.98 | 2.43 |
| 7 | .477 | 144.90 | 2.36 |
| 8 | .525 | 177.87 | 2.34 |
| 9 | .570 | 214.51 | 2.32 |
| 10 | .610 | 252.18 | 2.34 |
| -- | .787 | ------ | |

$k = 9.10 \pm .12 \times 10^{-5}$.

N. NaOH = .0112 N. in 95% ethanol.

Ultraviolet lambda max. = 272 m . Log epsilon = 4.20.

Calculated infinity point .773.

Table 36. Kinetics of 1-methylphenylcyclopropanol with base in 95% ethanol at 50 degrees

| Sample | Absorbance | Time | $k \times 10^3$ |
|---|---|---|---|
| 1 | .023 | 0 | ---- |
| 2 | .105 | 24.49 | 1.96 |
| 3 | .177 | 48.84 | 1.94 |
| 4 | .240 | 72.50 | 1.94 |
| 5 | .296 | 96.41 | 1.93 |
| 6 | .355 | 121.27 | 1.97 |
| 7 | .403 | 148.97 | 1.93 |
| 8 | .447 | 173.17 | 1.95 |
| 9 | .479 | 196.24 | 1.92 |
| 10 | .528 | 235.72 | 1.90 |
| -- | .808 | | |

$k_{sec}^{-1} = 7.45 \pm .07 \times 10^{-5}$.

NaOH = .0112 N. in 95% ethanol.

Lambda max. = 252.5. Log epsilon = 4.17.

Calculated infinity point .807.

Table 37. Kinetics of 1-m-chlorophenylcyclopropanol with base in 95% ethanol at 50 degrees

| Sample | Absorbance | Time | $k \times 10^3$ |
|---|---|---|---|
| 1 | .340 | 0 | ---- |
| 2 | .437 | 38.87 | 2.75 |
| 3 | .512 | 76.54 | 2.81 |
| 4 | .603 | 134.95 | 2.92 |
| 5 | .647 | 190.89 | 2.71 |
| 6 | .680 | 227.10 | 2.82 |
| 7 | .781 | | |

$k = 1.08 \pm .02 \times 10^{-4}$.

N. NaOH = .0112 N in 95% ethanol.

Lambda max. = 240 m . Log epsilon (undetermined).

Other k for the same compound:

$1.12 \pm .05 \times 10^{-4}$

Table 38. Kinetics of 1-m-trifluoromethylphenylcyclopropanol with base in 95% ethanol at 50 degrees

| Sample | Absorbance | Time | k x $10^5$ |
|---|---|---|---|
| 1 | .250 | 0 | ---- |
| 2 | .298 | 14.76 | 3.68 |
| 3 | .357 | 38.53 | 3.43 |
| 4 | .400 | 56.88 | 3.49 |
| 5 | .447 | 83.17 | 3.44 |
| 6 | .500 | 116.23 | 3.68 |
| 7 | .528 | 146.88 | 3.38 |
| 8 | .555 | 180.00 | 3.32 |
| 9 | .580 | 216.62 | 3.32 |
| 10 | .604 | 254.07 | 3.46 |
| -- | .658 | ------ | |

$k = 1.33 \pm .04 \times 10^{-4}$.

NaOH = .01 126 N in 95% ethanol.

Lambda max. = 235. Log epsilon = 4.02.

Calculated infinity point

Other k for same compound:

$1.28 \pm .02$

Average $k = 1.30 \pm .02 \times 10^{-4}$.

Table 39. Kinetics of 1-phenylcyclopropanol with base in 95% ethanol

| Sample | Absorbance | Time | $k \times 10^3$ |
|---|---|---|---|
| 1 | .015 | 0 | ----- |
| 2 | .064 | 21.92 | 1.98 |
| 3 | .123 | 57.87 | 1.76 |
| 4 | .154 | 74.01 | 1.85 |
| 5 | .188 | 100.22 | 1.77 |
| 6 | .224 | 125.32 | 1.80 |
| 7 | .260 | 156.77 | 1.79 |
| 8 | .294 | 191.53 | 1.77 |
| 9 | .328 | 216.88 | 1.88 |
| - | .530 | | |

$k = 7.02 \pm .23 \times 10^{-5}$.

NaOH = .0112 N in 95% ethanol.

Lambda max. = 241 m . Log epsilon undetermined.

## SUMMARY

A variety of 1-arylcyclopropanols were prepared by the addition of the appropriate aryl Grignard to 1,3 dichloroacetone followed by ring closure with ethylmagnesium bromide in the presence of anhydrous ferric chloride. One member of the series, 1-p-methylphenylcyclopropanol, was opened in 60/40 dioxane-water mixtures of varying acidity.

In another study on this compound the effect of varying solvent compositions on the rate of the acid-catalyzed ring opening was determined.

The results of the first study gave a good $H_0$ correlation indicating a possible A-1 or $A_{SE}2$ mechanism operative.

The second study gave inconclusive results. From comparisons with other work which was performed on cyclopropane the most probable mechanism involves a proton transfer to the cyclopropane ring followed by ring opening.

The entire series of 1-arylcyclopropanols was used in a Hammett $\sigma, \rho$ study to investigate the effects of substituents on the acid-catalyzed ring opening. It was found that the rates were correlated best with sigma. This indicated a fairly low charge build-up in the transition state such that resonance effects could not be brought into full play.

These results agreed with some studies on the acid-catalyzed ring opening of cyclopropanes in which inductive effects were found to be the primary contributors to their

reactivity.

The base-catalyzed ring opening of 1-arylcyclopropanols was found to be quite insensitive to substituent effects. This was explained on the basis of a variation in the transition state from an alkoxide formulation to a ketonic type of transition state complex.

ACKNOWLEDGEMENT

The author wishes to thank his major professor, Dr. C. H. DePuy, for patience, consideration and understanding during the course of this work. The author is also grateful to his parents who have contributed much toward the furthering of his education.