1-(Dimethylnitromethyl)-2,4,6-cycloheptatriene (II).—Sodium (360 mg., 15.7 mmoles) was dissolved in 27 ml. of methanol which had been distilled twice from calcium hydride. To this solution was added at room temperature under nitrogen 1.84 g. (21 mmoles) of 2-nitropropane which had been dried over Drierite. To the mixture was added all at once 2.65 g. (15.5 mmoles) of cycloheptatrienylium bromide with continuous stirring. The stirring was continued for 16 hours. At the end of this time the methanol was removed below room temperature by the water-pump. The residue was extracted with several portions of ether and then evaporated at room temperature with a stream of nitrogen. The crystalline residue remaining had no infrared absorption maxima between 5.86 and 6.35 μ. It had strong sharp maxima at 6.51 and 7.41μ. The product formed star-shaped crystals with a pleasant odor, instantly soluble in methanol or pentane. It was sublimed at 70° under water-pump pressure to give 1.98 g. (69%) of colorless and analytically pure product, m.p. 41.5°.

Anal. Calcd. for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 67.22; H, 7.55; N, 7.95.

Heating at 120° in a sealed tube under nitrogen did not affect the infrared spectrum of a sample of II. Heating for one hour at 200° resulted in charring.

2-Acetamido-2-cycloheptylpropane (III).—Compound II (950 mg., 5.3 mmoles), 500 mg. of 5% palladium-on-charcoal and 20 ml. of ethyl acetate were stirred under one atmosphere of hydrogen; 781 ml. (33 mmoles) was consumed by II. After 10 hours, the catalyst was removed by filtration. The resulting solution was transparent in the ultraviolet. Acetic anhydride (30 ml.) was added to the solution and the mixture was refluxed for 3 hours. The liquids were removed by distillation on the steam-bath under reduced pressure. The residue was recrystallized three times from ethanol–pentane. The yield was 650 mg. (62%) of III, m.p. 111–111.6°, with no absorption in the ultraviolet.

Anal. Calcd. for $C_{12}H_{17}NO$: C, 73.04; H, 11.75. Found: C, 73.36; H, 11.47.

Acknowledgments.[9]—The author is deeply indebted to Professor G. Stork, whose suggestions made a major contribution to this work. Grateful acknowledgment is also made of the experimental advice of Dr. S. D. Darling. Professor N. Kornblum has most kindly and helpfully criticized some of the discussion.

(9) This work was supported in part by a fellowship from 1957 to 1959 from the National Science Foundation.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FLORIDA STATE UNIVERSITY, TALLAHASSEE, FLA.]

Cyclopropanes. VIII.[1] Rates of Ring Opening of Substituted Cyclopropyl Ketones and Carbinols[2]

BY H. M. WALBORSKY AND L. PLONSKER[3]

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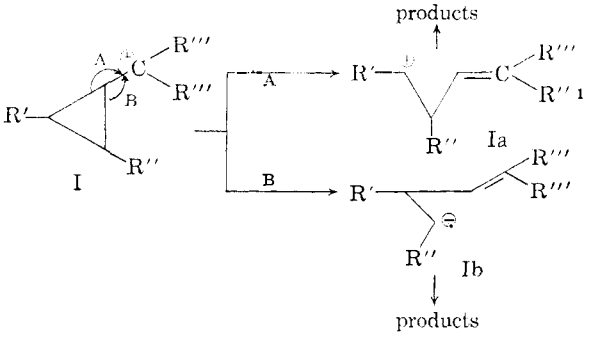
A series of optically active cyclopropyl ketones and carbinols has been prepared in which substituents were varied in the 1- and 2-positions of the ring and on the carbinyl carbon. The rates of acid-catalyzed ring opening have been determined polarimetrically and in some instances by infrared spectroscopy. The effect of geometric isomerism as well as the effect of the substituents on the rates of ring opening is discussed. In certain cases the polarimetric rate was found to be faster than the rate measured by infrared spectroscopy. The implication of this observation on the mechanism of this reaction is discussed.

Examples of the cyclopropylcarbinyl rearrangement can be found in the acid-catalyzed dehydration of cyclopropylcarbinols,[4] solvolysis of certain cyclopropylcarbinyl esters and halides,[5] deamination of cyclopropylcarbinyl amines[6] and the acid-catalyzed rearrangement of cyclopropyl ketones.[7]

Although the rearrangement of unsubstituted cyclopropylcarbinyl derivatives has been studied kinetically[8] no systematic kinetic studies on substituted compounds have been carried out.

Chemical evidence shows that, in general,[9] when the cyclopropylcarbinyl cation I is generated, ring opening will occur toward that carbon atom that can best delocalize a positive charge.



The choice between the intermediates Ia or Ib will depend upon the relative abilities of R′ and R″ to delocalize a positive charge.

The rearrangement products of substituted cyclopropyl ketones can be explained in an analogous manner. In these cases the cyclopropyl-

(1) For paper VII of this series, see H. M. Walborsky, T. Sugita, M. Ohno and Y. Inouye, *J. Am. Chem. Soc.*, **82**, 5255 (1960).

(2) This work was supported by a grant from the National Science Foundation, which is gratefully acknowledged.

(3) Ethyl Corporation Fellowship, 1959–1960.

(4) (a) R. Stoermer, F. Schenk and H. Buchman, *Ber.*, **61**, 2312 (1928); (b) H. M. Walborsky and F. M. Hornyak, *J. Am. Chem. Soc.*, **77**, 6396 (1955); (c) H. M. Walborsky and J. F. Pendleton, *ibid.*, **82**, 1405 (1960).

(5) (a) J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2509 (1951); (b) C. G. Bergstrom and S. Siegel, *ibid.*, **74**, 145 (1952); (c) H. Hart and J. M. Sandri, *ibid.*, **81**, 320 (1959).

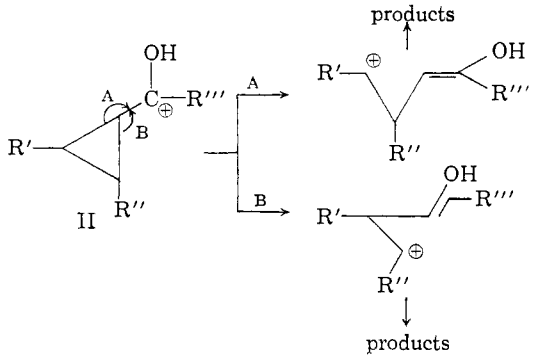
(6) (a) N. J. Demjanow, *Ber.*, **40**, 4393 (1907); (b) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 3542 (1951).

(7) (a) R. C. Fuson and F. N. Baumgartner, *ibid.*, **70**, 3255 (1948); (b) E. P. Kohler and W. N. Jones, *ibid.*, **41**, 1249 (1919); (c) E. G. Ford, P. N. Chakravorty and E. S. Willis, *ibid.*, **60**, 413 (1938).

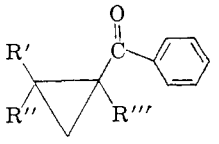
(8) As a leading reference see R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver and J. D. Roberts, *ibid.*, **81**, 4390 (1959).

(9) See, however, S. Julia, M. Julia and C. Huynh, *Bull. soc. chim. France*, 174 (1960); this work indicates that stereochemical factors may also be playing an important role.

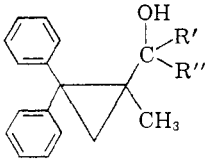
carbinyl cation II is generated by protonation of a carbonyl function,



In the present study the rate of acid-catalyzed ring opening of a series of benzoylcyclopropanes, III–VII, was determined, as well as the rate of ring opening in the acid-catalyzed dehydration of the carbinols VIII–X.



III, R' = H, R'' = C_6H_5, R''' = H
IV, R' = C_6H_5, R'' = H, R''' = H
V, R'R'' = C_6H_5, R''' = H
VI, R' = CH_3O-C_6H_5; R'' = C_6H_5; R''' = H
VII, R', R'' = C_6H_5, R''' = CH_3



VIII, R', R'' = H
IX, R' = C_6H_5, R'' = H
X, R', R'' = C_6H_5

Results

The rates of acid-catalyzed rearrangement of the ketones III-VII and the carbinols VIII–X were measured in chloroform, using *p*-toluenesulfonic acid as the catalyst. The rates were followed polarimetrically,[10] the data being treated by means of eq. 1

$$\ln (\alpha_0/\alpha) = k't \qquad (1)$$

where α_0 represents the optical rotation at zero time and α is the rotation at time t. In some cases the rate of ring opening was also followed by infrared spectroscopy. For the latter method the optical rotation is replaced by the absorbancy in eq. 1.

The pseudo first-order rate constant, k', is composed of an equilibrium constant for the protonation equilibria, a specific rate constant, k, for the loss of activity step, and the acid concentration (TsOH).

In every case studied, except for VI, a linear relationship between ln α_0/α *vs.* t was obtained. In the case of VI the points drifted upward after approximately 35% of reaction and therefore the pseudo first-order rate constant was obtained from the observed half-life. For all of the other reactions, the pseudo first-order rate constants were calculated by the weighted least squares method. It was assumed that the rotation at infinity time was zero. This was found to be the case for those runs where it was convenient to obtain infinity values.

For a typical ketone V, a plot of log k' *vs.* log (TsOH) was linear with a slope of 1 below 0.01 *N*, and linear with slope of 2 between 0.01 and 0.035 *N*. This indicated some second-order acid dependency at higher acid concentrations and therefore all comparisons were made at acid concentrations below 0.01 *N*. Where practical, rate constants were compared at identical acid concentrations. It was also assumed that the equilibrium constant was the same for all phenyl ketones.

In Table I is given an over-all summary of the rates of the acid-catalyzed rearrangements obtained by the polarimetric method.

TABLE I

POLARIMETRIC RATE CONSTANTS FOR THE ACID-CATALYZED REARRANGEMENT OF CYCLOPROPYL KETONES AND CARBINOLS

Compound	Temp., °C.	Acid concn. $\times 10^3$ *M*	k', sec.$^{-1}$	k'/(TsOH)
III	25.2	10.8	4.31×10^{-6}	3.99×10^{-4}
	75.7	6.84	9.14×10^{-6}	1.34×10^{-3}
IV	25.2	10.8	1.92×10^{-7}	1.78×10^{-5}
	75.7	6.84	3.94×10^{-5}	5.76×10^{-3}
V	25.2	1.42	4.05×10^{-7}	2.85×10^{-4}
	25.2	3.54	9.79×10^{-7}	2.77×10^{-4}
	25.2	7.08	2.23×10^{-6}	3.14×10^{-4}
	25.2	10.8	3.06×10^{-6}	2.83×10^{-4}
	25.2	14.2	6.03×10^{-6}	4.24×10^{-4}
	25.2	17.7	1.02×10^{-5}	5.76×10^{-4}
	25.2	29.8	1.88×10^{-5}	6.33×10^{-4}
	25.2	35.4	3.03×10^{-5}	8.56×10^{-4}
VI	25.0	0.0145	3.55×10^{-4}	2.45
VII	25.0	1.45	1.62×10^{-6}	1.12×10^{-3}
VIII	62.3	6.87	9.80×10^{-7}	1.43×10^{-4}
	75.7	6.84	5.74×10^{-6}	8.40×10^{-4}
	25.0[a]			4.5×10^{-7}
IX	25.0	7.26	1.42×10^{-6}	1.96×10^{-4}
X	25.2	0.196	3.79×10^{-4}	1.93×10^{-1}

[a] Extrapolated value.

It is estimated that the accuracy in k'/(TsOH) is ±10% for the polarimetric method. The rate constants determined by the infrared method are estimated to be accurate to ±25%. A comparison of the infrared and polarimetric rate constants is found in Table II. The infrared and polarimetric rate constants were determined under identical conditions.

In the infrared rate measurements, the appearance of a band at 887 cm.$^{-1}$ in the isomerization product of VII was followed. This band, which is not observed in the spectrum of VII, is assigned to the C–H out-of-plane deformation for a trisubstituted double bond. The disappearance of a 985 cm.$^{-1}$ band in III and the 995 cm.$^{-1}$ band in

(10) R. G. Pearson, L. A. Subluskey and L. C. King, *J. Am. Chem. Soc.*, **70**, 3478 (1948); S. Winstein and E. M. Kosower, *ibid.*, **81**, 4399 (1959).

TABLE II

COMPARISON OF INFRARED AND POLARIMETRIC RATE CONSTANTS

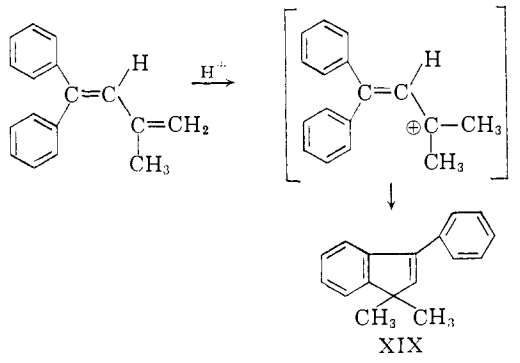
Compound	Temp., °C.	Acid concn. $\times 10^3$ M	k', sec.$^{-1}$ (i.r.)	k', sec.$^{-1}$ (pol.)	k' (pol.)/k'(i.r.)
III	75.7	6.84	8.14×10^{-6}	9.14×10^{-6}	1.1
IV	75.7	6.84	4.7×10^{-5}	3.94×10^{-5}	0.8
V	25.0	34.0	9.2×10^{-6}	4.60×10^{-5}	5.0
VII	25.0	5.94	8.5×10^{-6}	2.08×10^{-5}	2.4
X	25.0	14.9	1.2×10^{-1}	1.13×10^{-1}	1.0

IV was followed. Both of these bands were assigned to a cyclopropane ring deformation.[11] To study the disappearance of V, a 1375 cm.$^{-1}$ band was used. A clear-cut assignment cannot be made for this band, but it seems to be associated with the phenyl cyclopropyl ketone grouping, as it appears in other phenyl cyclopropyl ketones. The absorption bands which are associated with III, IV and V were not found in their respective isomerization products.

Discussion

Products.—The conclusions reached in the introductory section regarding the mode of ring opening of cyclopropylcarbinyl derivatives are also borne out by the present study. That is, ring opening occurs in the direction of that carbon atom whose substituents can best delocalize a positive charge. Table III summarizes the reactions involved in this study. A more detailed analysis of the products is given in the Experimental section.

The dehydration of VIII produced only one identifiable product, the indene XIX. The other component polymerized on standing, which suggests that it is the diene XVIII. It is proposed that the indene was produced from XVIII by the reaction scheme



This is analogous to the mechanism proposed for the transformation[12] of β,β-diphenylethyleneazobenzene to N-anilino-3-phenylindole.

Polarimetric *vs.* Infrared Rate Constants.—Table II contains a comparison of the polarimetric and infrared rate constants. In the case of III and IV it is apparent that the cyclopropane compound disappears as fast as the compounds lose their optical activity. The small differences in the rates are apparently due to the large error in

(11) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., Ltd., London.

(12) H. H. Wasserman and H. R. Nettleton, *Tetrahedron Letters*, **7**, 33 (1960).

TABLE III

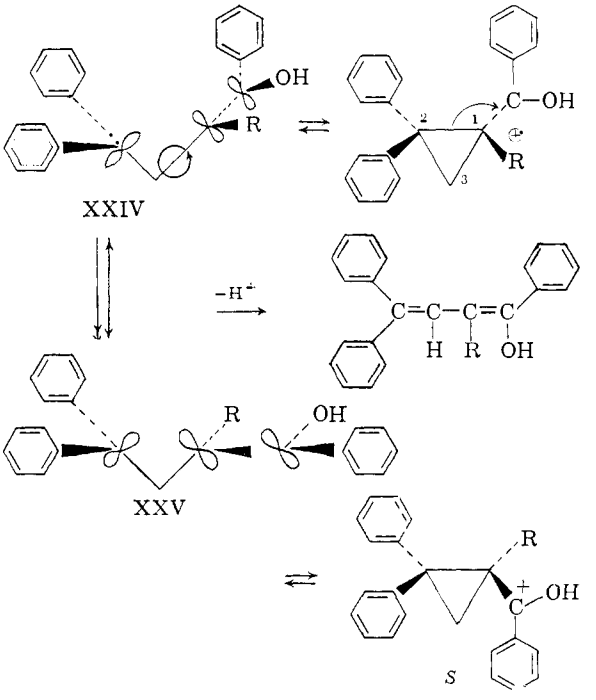
PRODUCTS OF CYCLOPROPANE RING OPENING REACTIONS

Reactant	Major product	Yield, %
III	$C_6H_5CH{=}CHCH_2COC_6H_5$ (XI)	50–60[a]
IV	$C_6H_5CH{=}CHCH_2COC_6H_5$ (XII)	40–50[a]
V	$(C_6H_5)_2C{=}CHCH_2COC_6H_5$ (XIII)	90
VI	p-$CH_3OC_6H_4C(C_6H_5){=}CHCH_2COC_6H_5$ (XIV)	92
VII	$(C_6H_5)_2C{=}CHCHCH_3COC_6H_5$ (XV)	90[b]
X	$(C_6H_5)_2C{=}CHCCH_3{=}C(C_6H_5)_2$ (XVI)	80
IX	$(C_6H_5)_2C{=}CHCCH_3{=}CHC_6H_5$ (XVII)	95
VIII	$(C_6H_5)_2C{=}CHCCH_3{=}CH_2$ (XVIII)	..
VIII	XIX	36

[a] Yield determined by analysis of infrared spectrum at infinity time. [b] Probably a *cis–trans* mixture.

the infrared rate measurements. The loss of activity does not, however, parallel the disappearance of the cyclopropane compound for V or the appearance of the product in VII. It should be mentioned that the disappearance of the 1370 cm.$^{-1}$ band in V paralleled the appearance of a 1320 cm.$^{-1}$ band in the product. The calculated rate constant of the latter was, within experimental error, the same as that obtained for the 1370 cm.$^{-1}$ band. For this reason it is felt that the rate of appearance of products is equivalent to the rate constant for the disappearance of reactants.

The following mechanism provides a reasonable explanation for the observed differences in the polarimetric and infrared rate constants. Proto-



nation of ketone V or VII produces the cation shown above in the *R*-configuration.[13] In order for racemization to occur the cation XXIV must be converted to cation XXV by rotation about C_1–C_3. The cations XXIV and XXV are epimeric

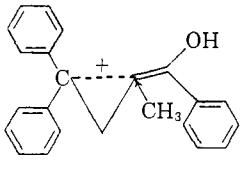
(13) The absolute configurations of these ketones have been established and will be the subject of a forthcoming publication.

and of equal stability. Ring closure of the epimeric cations XXIV and XXV, or loss of a proton to produce the unsaturated ketone, would lead to the observed loss of optical activity. Furthermore, it would also account for the observation that the infrared rate is slower than the polarimetric rate since the loss of activity is a measure of ring opening whereas the infrared rate is a measure of the rate of isomerization to the acyclic ketone.

In contrast to the above observation the polarimetric and infrared rate constants for III and IV are virtually identical. It appears that as soon as the homoallylic cation is formed the loss of a proton occurs very much faster than ring closure. It is not entirely clear why the diphenyl cation undergoes ring closure so readily whereas the phenyl cation does not. This may be due to the greater stability and therefore longer lifetime of the diphenyl cation. This, combined with the greater degree of substitution which seems to favor ring closure[14,15] reactions, may account for the difference in behavior of the two cations.

It should also be noted that no *trans-III* is formed during the reaction of *cis*-IV. This is consistent with the observed similarity of the infrared and polarimetric rate constants. If ring closure were occurring from the cation produced from IV, then the formation of *trans-III* should have been observed, since the *cis*-ketone isomerizes 4.5 times faster than the *trans*.

Effect of 1-Substitution.—A comparison between the polarimetric rate constants listed in Table I shows that VII is 40 times faster than V. It does not seem very likely that this is due solely to an electronic effect, since the methyl group can only exert cross-conjugated interactions as

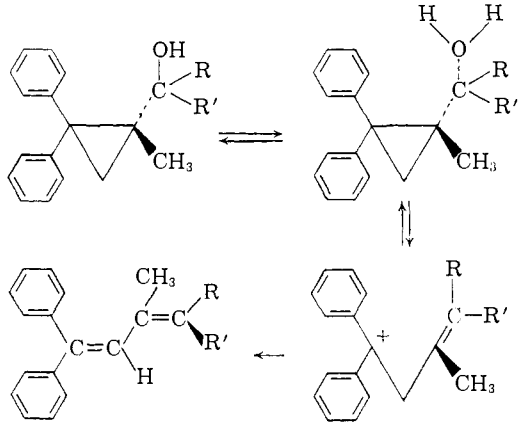


Although a direct comparison with an allylcarbinyl system is not available, comparison with the relative rates of solvolysis in absolute ethanol of allyl chloride and α-methylallyl chloride[16] shows that the latter is only 1.3 times faster than the former.

The enhanced reactivity may be due to steric acceleration since the methyl group can force the benzoyl group into closer proximity with the 2-phenyl substituents. A greater relief of steric compression in the case of the α-methyl than that of the α-hydrogen in going to the open chain isomer would be expected.

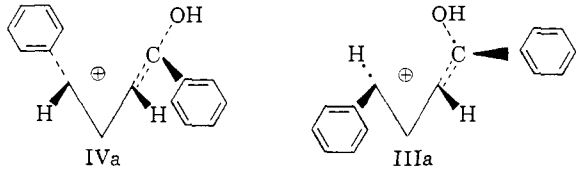
Effect of 2-Substitution.—From the data listed in Table I, comparison of VI, V and III shows that the ring opening reaction is greatly influenced by substitution on the 2-position of the cyclopropane ring. The order is that expected on the basis of carbonium ion intermediates: *p*-methoxyphenyl > phenyl > hydrogen. The relative rates (63×10^4:71:1) seem to be out of line in comparison with the relative rates of solvolysis of benzyl chloride and benzhydryl chloride. The latter solvolyzes 2000 times faster than the former in 2:3 ethanol–ether[17] solvent. The increase in rate in going from V to VI can be attributed to the added stabilizing influence of a *p*-methoxy group. The relative rates of solvolysis of *p*-methoxybenzhydryl chloride to benzhydryl chloride are 5000:1[17] and the analogous tosylates show a 25000:1 ratio in acetone–water. This compares favorably with the 9000:1 ratio that is observed in the present study.

Effect of Substitution on the Carbinyl Carbon.—The polarimetric rates of ring opening in the dehydration of the carbinols VIII, IX and X are given in Table I. The relative rates are again in the order expected on the basis of carbonium ion intermediates (1:430:430,000). The addition of a phenyl group at the site of the initial electron-deficient center (the carbinyl carbon) has a greater effect on the relative rates of ring opening (IX:X = 1000:1) than on the 2-position of the ring (IV:V = 15:1). It should be noted (Table II) that the



polarimetric rate is virtually identical with the infrared rate as determined by the disappearance of the 975 cm.$^{-1}$ band in X. Although the cations derived from the ketones V and VII and the carbinol X have similar degrees of substitution, the ketones exhibited differences in the infrared and polarimetric rates whereas the carbinol did not.

Effect of Geometry on the Ring Opening Reaction.—On a purely electronic basis it would be difficult to predict which geometrical isomer, IV or III, would isomerize faster. The *cis* and *trans* isomers of α-chloromethallyl chloride both solvolyze at approximately the same rate in absolute or aqueous ethanol.[16] To say that the intermediate or transition state IIIa is more or less favorable than that of IVa has no apparent justification.



The observed factor of 4.5 in the relative rates of the *cis* and *trans* isomers is possibly explained by

(14) H. Nilson and L. Smith, *Z. physik. Chem.*, **166A**, 136 (1936).
(15) N. L. Allinger and V. Zalkow, *J. Org. Chem.*, **25**, 701 (1960).
(16) R. H. DeWolfe and W. G. Young, *Chem. Revs.*, **56**, 786 (1956).
(17) A. Streitwieser, Jr., *ibid.*, **56**, 616 (1956).

the calculated activation parameters. The enthalpies of activation for both isomers have nearly identical values, 23.3 kcal./mole, whereas the entropies of activation are −2.9 and −5.6 e.u., respectively. It might be expected that the *cis*-ketone, which has more steric interaction between the 1- and 2-substituents than the *trans*-ketone, would show a greater positive entropy in going to the open chain isomer. If the small difference in the activation entropy is real, the results are consistent with this hypothesis.[18]

Experimental[19]

Resolution.—The optically active carbonyl and hydroxyl compounds used in this study were derived from the corresponding optically active carboxylic acids, employing reactions that did not affect the optically active centers. The carboxylic acids were resolved *via* the brucine or quinine salts. The solvents used were methanol or acetone. Resolution was continued until the alkaloid salts or the derived acids showed no change in rotation in two successive recrystallizations. The carboxylic acids were liberated by adding hydrochloric acid to a slurry of the alkaloid salt in acetone, and then diluting with water. The acids, with the exception of *cis*-2-phenylcyclopropanecarboxylic acid, were water-insoluble solids, and were readily isolated by filtration.

The alkaloid salts were not submitted for elemental analysis, since they were strongly solvated, and purification proved to be a difficult task.

***cis*- and *trans*-2-Phenylcyclopropanecarboxylic Acid.**—Ethyl 2-phenylcyclopropylcarboxylate was prepared according to the method of Burger and Yost.[20] A quantity of 76 g. (0.40 mole) was saponified, yielding 55 g. (0.34 mole) of isomeric acids. Attempts to separate the geometric isomers, as described by Burger and Yost, proved to be very tedious. Separation was attained in the following manner.

To a solution of 4.5 g. (0.121 mole) of sodium hydroxide dissolved in 80 ml. of 75% aqueous ethanol was added 29 g. (0.151 mole) of a *cis*-*trans*-ester mixture. The solution was refluxed for 7 hours, then cooled, diluted with water, and the unreacted ester was extracted with ether. The aqueous phase was acidified and yielded 14 g. (57%) of crude *trans* isomer, m.p. 89–92°, which was recrystallized from petroleum ether (30–60°) to give the pure *trans* isomer, m.p. 91–92°(lit.[20] m.p. 93°).

The unreacted ester was saponified with an excess of sodium hydroxide in aqueous ethanol. Acidification of the basic solution gave 3.0 g. (12%) of pure *cis*-acid, m.p. 106–107° (lit.[20] m.p. 106–107°).

The *trans*-acid was resolved *via* its brucine salt by fractional recrystallization from acetone. The analytical sample of the resolved acid had m.p. 51–52°, $[\alpha]^{24}D$ −368° (*c* 0.931). The infrared spectrum in chloroform was identical with that of the racemic acid.

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.04; H, 6.23. Found: C, 73.81; H, 6.23.

The *cis* isomer was not readily resolved *via* its brucine salt by recrystallization from acetone or methanol. Partial resolution was attained using quinine and recrystallizing from aqueous methanol. The optically active *cis*-acid is quite water soluble, and it was necessary to extract the aqueous solution to recover the acid. The partially resolved acid had a m.p. 78–98°, $[\alpha]^{23}D$ −20°. Its infrared spectrum was identical with that of the racemic acid.

***trans*-1-Benzoyl-2-phenylcyclopropane.**—To a solution of 8.0 g. (0.049 mole) of *trans*-2-phenylcyclopropanecarboxylic acid ($[\alpha]D$ − 368°) in 50 ml. of anhydrous ether was added a filtered solution of phenyllithium (0.148 mole). Upon completion of the addition (30 min.) the solution was allowed to stir for an additional 10 minutes. The ether solution was poured into an excess of aqueous ammonium chloride, the ether layer separated, washed with saturated sodium chloride until the washings were neutral, dried over sodium sulfate, and the solvent stripped. The residual oil was chromatographed on an alumina column, using petroleum ether (30–60°) as the eluent. A total of 9.6 g. (88%) of a white solid, m.p. 72–75°, was obtained. The infrared spectrum showed no hydroxyl bands. The analytical sample was recrystallized from petroleum ether (30–60°) to give transparent needles, m.p. 74–75°, $[\alpha]^{24}D$ −407° (*c* 0.209), near infrared 1.64 μ (cyclopropyl CH_2),[21] infrared 1670 cm.$^{-1}$ (C=O), ultraviolet λ_{max} 241, mμ, log ϵ 4.27 (95% ethanol).

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.44; H, 6.36. Found: C, 86.20; H, 6.41.

The preparation of the racemic ketone is described elsewhere.[22]

***cis*-1-Benzoyl-2-phenylcyclopropane.**—The procedure followed was identical with that of the *trans* isomer. Partially resolved *cis*-acid (1.5 g., 0.0093 mole) yielded 1.2 g. (76%) of a solid, m.p. 63–67°, $[\alpha]^{24}D$ −151°, infrared 1680 cm.$^{-1}$ (C=O), near infrared 1.64 μ.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.44; H, 6.36. Found: C, 86.33; H, 6.33.

The racemic ketone, prepared analogously, had m.p. 69–70°,

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.44; H, 6.36. Found; C, 86.47; H, 6.43.

2,2-Diphenylcyclopropanecarboxylic Acid.—Diphenyldiazomethane[23] (0.19 mole) in petroleum ether (30–60°) was slowly added to an excess of methyl acrylate. After the nitrogen ceased being evolved, the solvent was removed *in vacuo*. The residue was saponified by dissolving in an excess of methanolic sodium hydroxide, then refluxed for 7 hours. Acidification and recrystallization from methanol afforded 31 g. (0.13 mole), m.p. 170.5–172° (lit.[24] 170–171°). The yield was 69% based on diphenyldiazomethane.

The optically active acid was resolved,[24] and the maximum rotation acid had a m.p. 150.5–151.5°, $[\alpha]^{24}D$ −234° (*c* 0.952).

1-Benzoyl-2,2-diphenylcyclopropane.—A solution of 0.023 mole (theoretical) of phenyllithium was added to 2.0 g. (0.0081 mole) of 2,2-diphenylcyclopropanecarboxylic acid ($[\alpha]D$ −234°). After the addition was complete, the solution was allowed to stir for an additional 20 minutes. The reaction mixture was hydrolyzed with an excess of aqueous ammonium chloride and the ether layer was separated, washed with water, and dried over sodium sulfate. The solvent was removed and the residual oil was taken up in methanol and refrigerated. A total of 1.5 g. (62%) was collected, m.p. 99–100.5°, $[\alpha]^{24}D$ −141° (*c* 0.885), near infrared 1.64 μ (cyclopropyl CH_2), infrared 1680 cm.$^{-1}$ (C=O).

Anal. Calcd. for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.18; H, 6.31.

The racemic material was prepared in 78% yield using the above procedure.[25] The infrared spectrum of the racemic ketone, in carbon tetrachloride was identical with that of the optically active ketone.

2-(*p*-Methoxyphenyl)-2-phenylcyclopropanecarboxylic Acid.—To a heated (120°) mixture of 22 g. (0.105 mole) 1-(*p*-methoxyphenyl)-1-phenylethylene[26] was added 19.3 g. (0.171 mole) of ethyl diazoacetate.[27] There was an immediate evolution of nitrogen, which continued until all of the ethyl diazoacetate was added. Upon completion of addition (*ca.* 40 min.), heating was continued for an additional 0.5 hour. The mixture was cooled, added to an excess of alcoholic potassium hydroxide, and refluxed for

(18) However, see R. A. Sneen, B. R. Smith and I. A. I. Taha, American Chemical Society Abstracts, 138th Meeting, New York City, 1960, p. 35, who have recently reported that the *trans*-2-phenylcyclopropylcarbinyl naphthalenesulfonate solvolyzed 3.5 times faster than the *cis*.

(19) All melting points are uncorrected. All rotations were taken in chloroform.

(20) A. Burger and W. L. Yost, *J. Am. Chem. Soc.*, **70**, 2196 (1948).

(21) W. H. Washburn and J. H. Mahoney, *ibid.*, **80**, 504 (1958).

(22) R. J. Mohrbacher and N. H. Cromwell, *ibid.*, **79**, 401 (1957).

(23) L. F. Smith and K. L. Howard, *Org. Syntheses*, **24**, 53 (1944).

(24) H. M. Walborsky and F. M. Hornyak, *J. Am. Chem. Soc.*, **77**, 6026 (1955).

(25) F. J. Impastato, Ph.D. Dissertation, Florida State University, 1959.

(26) C. D. Hurd and C. N. Webb, *J. Am. Chem. Soc.*, **49**, 549 (1927).

(27) E. B. Womack and A. B. Nelson, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 392.

12 hours. After dilution with water, the basic solution was acidified, and yielded 20 g. (70%) of a crude mixture of isomeric acids. Several recrystallizations yielded a total of 3.7 g. (13%) of one pure isomer, m.p. 177.5–179°. The other isomer could not be obtained pure.

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 75.89; H, 6.01.

The acid was resolved *via* its brucine salt by fractional recrystallization from methanol. The optically pure acid had m.p. 113–114°, $[\alpha]^{22}D$ −176°.

The infrared spectra of the racemic and optically active acids were identical.

Anal. Calcd. for $C_{17}H_{16}O$: C, 76.10; H, 6.01. Found: C, 76.07; H, 6.16.

1-Benzoyl-2-(*p*-methoxyphenyl)-2-phenylcyclopropane.—To 1.7 g. (0.0068 mole) of 2-(*p*-methoxyphenyl)-2-phenylcyclopropanecarboxylic acid ($[\alpha]D$ −176°) was added 0.017 mole (theoretical) of phenyllithium in 60 ml. of dry ether. After stirring for an additional 10 minutes the solution was hydrolyzed with ammonium chloride. The ether layer was separated, washed with water, and dried over sodium sulfate. The ether was removed, and the solid residue recrystallized from ethanol to give 0.60 g. (41%), of white needles, m.p. 143.5–148°. The analytical sample had m.p. 147–148.5°, $[\alpha]^{23}D$ −88° (*c* 0.803), infrared 1670 cm.$^{-1}$ (C=O), near infrared 1.63 μ.

Anal. Calcd. for $C_{23}H_{21}O_2$: C, 84.12; H, 6.14. Found: C, 83.87; H, 6.21.

1-Methyl-2,2-diphenylcyclopropanecarboxylic Acid.—The racemic and optically active acids were prepared as previously described.[25,28]

1-Methyl-1-benzoyl-2,2-diphenylcyclopropane.—The racemic and optically active ketones were prepared as previously described.[25,28]

1-Methyl-2,2-diphenylcyclopropylcarbinol.—Racemic 1-methyl-2,2-diphenylcyclopropanecarboxylic acid (26 g., 0.103 mole) was dissolved in 750 ml. of dry ether and added to a slurry of 16 g. of lithium aluminum hydride and 500 ml. of dry ether. The solution was allowed to stir for 12 hours. The complex was decomposed by the addition of aqueous ammonium chloride. The ether was separated, dried, and removed to yield a solid residue, m.p. 101–102°, in quantitative yield; infrared 3800, 3640 cm.$^{-1}$ (-OH), near infrared 1.64μ.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.68; H, 7.61. Found: C, 85.50; H, 7.71.

The optically active carbinol, prepared in an analogous manner from the levorotating acid, had m.p. 117–117.5°, $[\alpha]^{22}D$ −32° (*c* 0.984). The infrared spectra of the racemic and optically active carbinols were identical.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.68; H, 7.61. Found: C, 85.76; H, 7.56.

1-Methyl-2,2-diphenylcyclopropylphenylcarbinol.—A solution of 5.0 g. (0.021 mole) of racemic 1-methyl-2,2-diphenylcyclopropylcarboxaldehyde in 40 ml. of dry ether was added to 0.03 mole of phenylmagnesium bromide in 70 ml. of dry ether, and allowed to stand for 2 hours. The complex was decomposed by adding aqueous ammonium chloride and the ether was separated, dried, and stripped to yield a white solid which on recrystallization from methanol afforded 4.7 g. (68%) of the desired product, m.p. 173–175°, infrared 3720 cm.$^{-1}$ (OH), near infrared 1.64μ.

Anal. Calcd. for $C_{23}H_{22}O$: C, 87.86; H, 7.05. Found: C, 87.87; H, 7.35.

The optically active phenylcarbinol was prepared in 67% yield by lithium aluminum hydride reduction of 1-methyl-1-benzoyl-2,2-diphenylcyclopropane ($[\alpha]D$ −33°). The analytical sample, recrystallized from ethanol, had m.p. 159–160.5°, $[\alpha]^{23}D$ −114° (*c* 0.968).

The optically active carbinol and the racemic carbinol had identical infrared spectra.

Anal. Calcd. for $C_{23}H_{22}O$: C, 87.86; H, 7.05. Found: C, 88.12; H, 7.21.

(+)-Methyl 1-Methyl-2,2-diphenylcyclopropylcarboxylate.—A solution of 6.3 g. (0.025 mole) of 1-methyl-2,2-diphenylcyclopropanecarboxylic acid ($[\alpha]D$ +27°) in ether was treated with an excess of diazomethane,[29] and allowed to stand at room temperature for 24 hours. After removal of the solvent and recrystallization from methanol, there was obtained 6.0 g. (91%) of the desired ester, m.p. 75.5–77.5°, $[\alpha]^{24}D$ +16° (*c* 0.960), infrared 1690 cm.$^{-1}$ (C=O). The ester was estimated to be 80% optically pure.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.29; H, 6.81.

1-Methyl-2,2-diphenylcyclopropyldiphenylcarbinol.—To an excess of phenylmagnesium bromide was added a solution of 2.7 g. (0.01 mole) of methyl 1-methyl-2,2-diphenylcyclopropylcarboxylate ($[\alpha]D$ +16°) in 150 ml. of dry ether. After 18 hours of stirring, the complex was decomposed by addition of aqueous ammonium chloride. The ether layer was filtered, and the ether removed. The oily residue was crystallized from 95% ethanol to yield 2.3 g. (58%) of the desired carbinol, m.p. 133.5–135°, $[\alpha]^{22}D$ −48° (*c* 1.43). The analytical sample was recrystallized from 95% ethanol, raising the m.p. to 136–137°.

Anal. Calcd. for $C_{29}H_{25}O$: C, 89.19; H, 6.71. Found: C, 89.34; H, 7.00.

The preparation of the racemic alcohol is described elsewhere.[25]

Product Analysis.—All of the product analyses were performed in a similar manner. The conditions used were essentially the same as those employed for the rate determinations. A quantity of carbonyl or hydroxyl compound was treated with toluenesulfonic acid in chloroform, for a period of time that was sufficient to complete the reaction. The acid was neutralized with saturated sodium bicarbonate, and the chloroform dried over sodium sulfate. After removal of the solvent, the physical properties of the product were determined. In the cases where the product was unknown, the structure was characterized by oxidation of the olefin with ozone, or potassium permanganate, and the fragments analyzed.

Acid Treatment of *trans*-1-Benzoyl-2-phenylcyclopropane.—A solution of 2.8 g. of the *trans*-ketone dissolved in 50 ml. of 0.03 *N* toluenesulfonic acid in chloroform was heated in a sealed tube for 9 hours, at 100°. The product was a noncrystalline mixture. Dissolving the semi-solid in 95% ethanol and cooling gave 1.7 g. of impure product, m.p. 69–85°. Recrystallization from petroleum ether (30–60°) gave 1.0 g. (41%), m.p. 89.5–90.5°, oxime m.p. 106.5–108°, infrared 1680 cm.$^{-1}$ (C=O); near infrared, no 1.64μ band. Attempted mixed melting with starting material resulted in an oil. The product reacted immediately with potassium permanganate reagent. The physical properties agree well for the known β-benzylidenepropiophenone (lit.[30] m.p. 93°, oxime m.p. 104–106°). The side products of this reaction were not determined.

Acid Treatment of *cis*-1-Benzoyl-2-phenylcyclopropane.—A solution of 1.0 g. of the *cis*-ketone dissolved in 20 ml. of 0.01*N* toluenesulfonic acid in chloroform was heated in a sealed tube at 75° for 38 hours. The product was recrystallized from petroleum ether (30–60°), yielding 0.1 g. (10%) of β-benzylidinepropiophenone, m.p. 90–91°.

Acid Treatment of 1-Benzoyl-2,2-diphenylcyclopropane.—The racemic ketone (2 g.) was treated with 100 ml. of 0.05 *N* toluenesulfonic acid in chloroform, and refluxed for 20 hours. After the usual workup, 2 g. of material, m.p. 122–125°, was obtained. Trituration with petroleum ether (30–60°), and filtration yielded 1.8 g. of 1,1,4-triphenylbutene-1-one-4. The analytical sample was chromatographed, recrystallized from ether–petroleum ether, m.p. 126–126.5°. Mixed m.p. with starting material gave m.p. 106–133°, infrared 1690 cm.$^{-1}$ (C=O); near infrared, no 1.64 μ absorption band.

Anal. Calcd. for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.28; H, 6.20.

Ozonolysis of the product in ethyl acetate gave benzoic acid, m.p. and mixed m.p. 120–121°. From the neutral fraction was obtained benzophenone characterized by its 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 232–235°.

Acid Treatment of 1-Benzoyl-1-methyl-2,2-diphenylcyclopropane.—The active ketone (54 mg.) was treated with 0.02 *N* toluenesulfonic acid in chloroform for 3 hours. The solvent was removed, and the residue chromatographed on

(28) H. M. Walborsky and F. J. Impastato, *Chemistry & Industry*, 1690 (1960).

(29) H. M. Redemann, R. O. Rice, R. Roberts and H. P. Ward, ref. 27, p. 244.

(30) H. Wieland and H. Stenzl, *Ber.*, **40**, 4830 (1907).

alumina. A total of 50 mg. of 1,1,4-triphenyl-3-methylbutene-1-one-4, m.p. 102–102.5°, was collected. The product gave a slow positive permanganate test.

Anal. Calcd. for $C_{23}H_{20}O$: C, 88.42; H, 6.45. Found: C, 88.26; H, 6.49.

Ozonolysis gave benzophenone, m.p. 47–49.5°, and benzoic acid, m.p. 121–122°. Mixed m.p. with authentic samples showed no depression.

Acid Treatment of 1-Methyl-2,2-diphenylcyclopropylphenylcarbinol.—The racemic carbinol (2.0 g.) was refluxed with 100 ml. of 0.02 *N* toluenesulfonic acid in chloroform for 11 hours. The product, 1,1,4-triphenyl-3-methylbutadiene (1.8 g.), was an oil that could not be crystallized, b.p. 171–177° (0.2 mm.); ultraviolet λ_{max} 245, 317 mμ; log ϵ 4.31, 4.37.

Anal. Calcd. for $C_{23}H_{20}$: C, 93.19; H, 6.80. Found: C, 92.92; H, 6.93.

Permanganate oxidation in aqueous acetone gave benzophenone, characterized by its 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 238–240°. From the basic aqueous solution was obtained, after acidification, benzoic acid, m.p. and mixed m.p. 119–120°.

Acid Treatment of 1-Methyl-2,2-diphenylcyclopropyldiphenylcarbinol.—The carbinol (0.60 g.) was treated with 25 ml. of 0.03 *N* toluenesulfonic acid in chloroform for 14 hours. The product was recrystallized from ethanol, yielding 0.45 g. of 1,1,4,4-tetraphenylisoprene, m.p. 134–136°. A second recrystallization from ethanol raised the melting point to 137–138°. A mixed m.p. with an authentic sample[25] showed no depression.

Acid Treatment of 1-Benzoyl-2-(*p*-methoxyphenyl)-2-phenylcyclopropane.—The racemic ketone (1.0 g.) was dissolved in 20 ml. of 0.03 *N* toluenesulfonic acid in chloroform and allowed to react for 12 hours. The product was recrystallized from methanol, yielding 0.8 g. of 1-(*p*-methoxyphenyl)-1,4-diphenylbutene-1-one-4, m.p. 82–89°, infrared 1685 cm.$^{-1}$.

Anal. Calcd. for $C_{23}H_{21}O_2$: C, 84.12; H, 6.14. Found: C, 83.87; H, 6.21.

Permanganate oxidation gave *p*-methoxybenzophenone, m.p. and mixed m.p. 60–61.5°, and benzoic acid m.p. and mixed m.p. 118–120°.

Acid Treatment of 1-Methyl-2,2-diphenylcyclopropylcarbinol.—The racemic carbinol (24 g., 0.10 mole) was refluxed in 500 ml. of 0.04 *N* toluenesulfonic acid in chloroform for 48 hours. The crude product was an oil. Distillation yielded 18 g., b.p. 105–124° (0.5 mm.) with slight decomposition. The pot residue weighed 4.0 g. Redistillation gave 7.9 g. (36%) of material, b.p. 150–158° (1.2 mm.), that solidified on standing, m.p. 42–48°. The residue (8.6 g.) did not distil, and became viscous on standing. Recrystallization from methanol raised the melting point to 48–50°. Oxidation with permanganate yielded a solid acid, m.p. 196–198°. Treatment with nitric acid gave a solid nitro derivative, m.p. 138–140°. The physical properties of the product are in agreement with those of the known 1,1-dimethyl-3-phenylindene,[31] m.p. 50–51°; dimethyl-(2-benzoyl)-phenylacetic acid, m.p. 198°; nitro derivative, m.p. 141–142°.

The residue was probably 1,1-diphenyl-3-methylbutadiene, which polymerized on standing.

Kinetic Method. Polarimetry.—The instrument used was a Bellingham and Stanley precision polarimeter, equipped with a sodium vapor lamp. The instrument could be read directly to 0.01°, and estimated to ±0.002°. For a large number of observations a precision of ±0.006° was obtained.

The number of observations made for any point varied with the conditions of the run. For the fast runs, the average of 3–6 observations were taken as the point. For the long runs, 6–10 observations were made from both ends of the tube, and the average was taken as the reading.

Standard Solutions.—Technical *p*-toluenesulfonic acid was recrystallized from chloroform; m.p. 101–103°. A quantity was weighed into a volumetric flask, and chloroform (Eastman Kodak Co. spectrograde) was added to mark. The exact concentration was determined by titration with a standard sodium hydroxide solution. The solutions were stored in the dark and found to be stable, since less than a 2% change was observed after 3 months.

For the high temperature runs, the concentration change due to the expansion of chloroform was determined experimentally, and found to agree, within less than 1% of the calculated value.

Solutions for Rate Experiments.—A quantity of optically active material was weighed and dissolved in the standard acid solution, such that a 0.5° rotation or greater could be observed at zero time. It had been determined that the rate constant is not affected by changes in concentration of the optically active species.

Kinetic Procedure.—There were essentially three methods used for the rate experiments.

Method A.—The solutions were placed in a 2 or 4 decimeter jacketed polarimeter tube, and left there for the entire course of the reaction. The temperature was kept constant by circulating water from a thermostated bath around the tube. It was necessary to use Tygon or Teflon washers for the tubes, as the rubber washers swell in contact with chloroform over a period of several hours. The increased pressure usually resulted in cracked polarimeter windows.

Method B.—The solutions were made up in glass stoppered volumetric flasks, and placed in a thermostated bath. At the appropriate times the solutions were poured into the polarimeter tube, and the rotations were taken at room temperature (*ca.* 24°). The solutions were poured back into the flasks and returned to the bath.

Method C.—The solutions were poured into test-tubes. The test-tubes were sealed and placed into a 75.7 or 62.8° thermostated bath. At the appropriate times, the tubes were withdrawn and the reaction was rapidly stopped by immersing into an ice-water-bath. An aliquot was withdrawn and the rotation taken at room temperature. The solution was poured back into the tube and returned to the bath after sealing. The amount of time necessary for a known volume of chloroform to heat from room temperature to 75.7° and cooled to 25° was determined experimentally and subtracted from the measurement time.

Rate measurements were made until 50–80% of loss of activity. In some cases infinity readings were taken.

Infrared Rate Measurements.—The instrument used was a Perkin–Elmer model 221.

Kinetic Procedure.—The procedure used was essentially the same as that used for the polarimetric rate determinations. For the high temperature runs of the *cis*- and *trans*-benzoyl-2-phenylcyclopropane, an aliquot was withdrawn from each polarimetric point, and the infrared value determined. For the 25° runs, the solutions were kept in thermostated baths. At the appropriate times, an aliquot was withdrawn and the transmittancy determined.

(31) C. F. Koelsch and P. R. Johnson, *J. Am. Chem. Soc.*, **65**, 567 (1943).