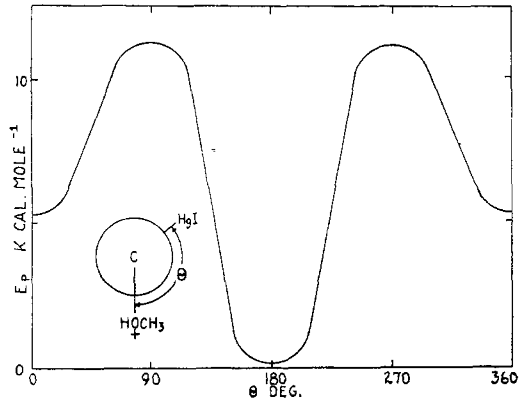

Fig. 1. The potential energy of the deoxymercuration transition state as a function of the dihedral angle, θ

should be comparable to that of III and IV. These predictions are amply borne out by the results.

The success of this theory permits the sketching of an approximate potential energy, E_p, of the transition state as a function of θ for an open chain compound such as I. The height of the peaks at $\theta = 90°$ and $\theta = 270°$ was taken from the estimated rate of unassisted ether cleavage.[14] The plot is shown in Fig. 1.

Two alternative reaction coordinates might be suggested for the *cis* compounds: (1) Carbon-oxygen cleavage might proceed without substantial assistance from any internal rearrangement. In that case the transition state energy would be almost independent of θ. (2) Carbon-oxygen cleavage might be accompanied by the formation of a coordinate bond between mercury and oxygen. In that case the transition state energy would again be minimized when $\theta = 0$.

In the first case similar rates and thermodynamic properties of activation would be predicted for IV and V. In the second case ΔS^* for the *cis* compounds would be consistantly and substantially higher than for the *trans* because less solvent would be immobilized by the *cis* transition states. Since neither of these effects is observed the two alternative reaction coordinates are rejected.

The neglect of solvent in much of this discussion does not imply that it is unimportant. It merely suggests that, within a narrow range of substrate structures, the *change* in solvation on going from the starting state to the transition state, is constant. Even this limited conclusion should be further limited to water as a solvent.

It is noteworthy that no neighboring group participation by carbon[15] needs to be considered to explain the rate, ΔH^*, or ΔS^* for VI. A certain amount of neighboring group participation by carbon is suggested by the formation of VI, rather than its *trans* isomer, in the oxymercuration of norbornene, and the deoxymercuration presumably uses a transition state at least similar to that for oxymercuration. Difficulty in demonstrating neighboring group participation in nonsolvolytic reactions has been previously noted.[16]

EXPERIMENTAL

Kinetic techniques[2,3] and materials[17] used in this investigation have both been previously described.

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[14] C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, N. Y., 1953, p. 334.

[15] S. Winstein, *Bull. soc. chim. France*, C59 (1951).

[16] M. M. Kreevoy, C. R. Morgan, and R. W. Taft, Jr., *J. Am. Chem. Soc.*, **82**, 3064 (1960).

[17] M. M. Kreevoy, John W. Gilje, and Richard A. Kretchmer, *J. Am. Chem. Soc.*, **83**, 4205 (1961).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL COLLEGE]

Steric Factors in the Hydrolysis Rates of Ketimines[1,2]

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The effects of the different stereoisomeric forms of the cyclohexane ring in 2,6-dimethylcyclohexyl phenyl ketimines on the rates of hydrolysis of these ketimines have been compared. In particular the hydrolysis rates of the *meso-cis-* and the *meso-trans*-2,6-dimethylcyclohexyl phenyl ketimine hydrochlorides have been found to be distinctly slower than where the racemic form of this 2,6-dimethylcyclohexyl ring is involved. For comparison, the hydrolysis rates of the monosubstituted 2-, 3-, and 4-methylcyclohexyl phenyl ketimine hydrochlorides have been obtained.

Previous investigations[3] have revealed great differences in the rates of hydrolysis of variously substituted diphenyl ketimine hydrochlorides: $R—C(=NH_2Cl)—R' + HOH \rightarrow R—CO—R' + NH_4Cl$. This difference extends from a half-life (first-order equation)[4] of about two minutes at

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[1] Supported by a grant from the National Science Foundation.

[2] Presented in part at the 137th Meeting of the American Chemical Society in Cleveland, Ohio.

[3] J. B. Culbertson, *J. Am. Chem. Soc.*, **73**, 4818 (1951).

[4] Measurements have been made in 0.01 *M* aqueous solutions.

25° to nearly 9000 minutes at 100°, or 2.3×10^7 minutes calculated to 25°.[5] Several structural factors have been indicated as responsible for these differences, involving tautomerism, resonance, and steric influences. This report represents a continuation of study into steric effects.

In view of the very great retardation in hydrolysis caused by methyl groups in the 2- and 6-positions of one phenyl group in diphenyl ketimines, it was considered of interest to prepare and measure the hydrolysis rates of ketimines with the substituted phenyl ring replaced by the correspondingly substituted, but more flexible, cyclohexyl ring. In the cyclohexyl ring we have both stereoisomeric and conformational structures making possible more varied opportunities for the nucleophilic water molecule in its approach to the relatively positive carbon end of the carbimino group of the ketimine. In particular, for 2,6-dimethylcyclohexyl phenyl ketimine, we may expect for the substituted cyclohexyl ring three stereoisomeric forms, each with its possible variation in conformation. These are the *meso cis*, the *meso trans*, and the *racemic*, with their conformational variations between the boat and chair forms. Thus these different stereoisomeric forms of the 2,6-dimethylcyclohexyl phenyl ketimine hydrochlorides have been prepared and their rates of hydrolysis measured. As it turned out, the preparations for the *meso cis* and the *meso trans* forms gave essentially the same results on measurements of their rates of hydrolysis. As expected because of the steric interference of the methyl substituents in the 2- and the 6- positions of the cyclohexyl ring, these compounds showed a very slow rate of hydrolysis. As with the 2,6-dimethyldiphenyl ketimine hydrochloride, the measurements had to be made at 100°, essentially the temperature of the refluxing dilute aqueous solution. However, their rate of hydrolysis was definitely faster than that of the 2,6-dimethyldiphenyl ketimine salt. Their half life was around 277 minutes compared to 8670 minutes at 100° for the latter. These values calculated to 25° come to 7.6×10^5 and 2.3×10^7 minutes, respectively.[5] The hydrolysis rate for the *racemic* 2,6-dimethylcyclohexyl phenyl compound was distinctly faster. It could be measured at 25° and gave a half life of 1980 minutes at this temperature. Stuart models of these stereoisomeric forms indicated that the *racemic* form should be more open to attack by water than either the *meso cis* or *meso trans* forms—the latter two being about equal in this respect.

For purposes of comparison the 2-, 3-, and 4-monomethylcyclohexyl phenyl ketimines have been prepared and their rates of hydrolysis measured. Since mixed alkyl aryl ketimines have been found to be less stable to hydrolysis than the diaryl ones,[6] at least for the latter two, rapid rates of hydrolysis were expected. However, the 2-methylcyclohexyl phenyl ketimine, considering the very slow rates of the 2,6-dimethylcyclohexyl phenyl ketimines, showed a rather unexpectedly high rate of hydrolysis. It had to be measured at 0°. The hydrolysis rates for the 3- and the 4-methyl substituted compounds were definitely faster than this. Refer to Table I.

TABLE I

HYDROLYSIS RATES OF KETIMINE HYDROCHLORIDES

Ketimine	Kv × 10³ Measured	 Calcd. to 25°	Half-life (minutes at 25°)
2-Methylcyclohexylphenyl	1.9 (0°)	26.6	26
3-Methylcyclohexylphenyl	137 (0°)	1920	0.36
4-Methylcyclohexylphenyl	123 (0°)	1720	0.40
2,6-Dimethylcyclohexylphenyl (meso trans or meso cis)	2.5 (100°)	0.00091	7.6×10^5
2,6-Dimethylcyclohexylphenyl (racemic)	0.40 (25°)	0.40	1750

A common procedure for the preparation of these ketimines involves the following reactions:

$$\text{R—Mg—Br} \xrightarrow[\text{dry ether}]{\text{R}'\text{CN}}$$

$$\text{R—C(=N—Mg—Br)—R}' \xrightarrow[-15°]{\text{Ice and NH}_4\text{Cl}}$$

$$\text{R—C(=NH)—R}' \xrightarrow[\text{dry ether}]{\text{dry HCl}} \text{R—C(=NH}_2\text{Cl)—R}'.$$[7]

It happened that the 2-methyl- and the 2,6-dimethyldiphenyl ketimines[3] had been prepared with phenylmagnesium bromide reacting with the appropriately substituted phenyl cyanides. However, considering the availability of 2,6-dimethylcyclohexanol through catalytic hydrogenation of 2,6-dimethylphenol,[8] and the conversion of this alcohol to the bromide, it was thought best to prepare the 2,6-dimethylcyclohexyl phenyl ketimine with the Grignard reagent on the cyclohexyl side. A number of attempts under varying conditions failed in the reaction of 2,6-dimethylcyclohexylmagnesium bromide with benzonitrile to produce the ketimine. It was obtained by the interaction of phenylmagnesium bromide with 2,6-dimethylcyclohexanecarbonitrile. Also, it was found necessary to prepare the 2-methylcyclohexyl phenyl ketimine with the cyanide group on the cyclohexane ring side. Since it was possible to prepare the 3-methyl- and the 4-methylcyclohexyl phenyl ket-

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(5) Refer to Table I and p. 4823 of ref. 3.

(6) C. Moureu and G. Mignonac, *Compt. rend.*, **156**, 1801 (1913); **169**, 237 (1919); **170**, 936 (1920); *Ann. Chim. (Paris)*, (9), 322 (1920). J. B. Cloke, *J. Am. Chem. Soc.*, **62**, 117 (1940).

(7) Refer to p. 4822 of ref. 3.

(8) Carlin, *J. Am. Chem. Soc.*, **67**, 931 (1945).

imines with the Grignard reagent on the cyclohexane ring side, these preparations furnish additional evidence on the steric reaction interference of methyl groups in the 2- and the 2,6- positions of the cyclohexane ring.

Our attempts to prepare the distinctly different *meso cis* and *meso trans* forms of the 2,6-dimethylcyclohexyl phenyl ketimines remain in doubt. When 2,6-dimethylbenzoic acid was converted to 2,6-dimethylcyclohexanecarboxylic acid by hydrogenation with Adam's platinum catalyst (Experimental) the spatial mechanism here dictates the *meso cis* form for the substituted cyclohexane ring. However, when the carboxylic acid is converted to the acid chloride with thionyl chloride, it has appeared likely that the *meso cis* form, through influence of the acid liberated, would be transformed to the more stable *meso trans* form where all three substituents could occupy equatorial positions on the predominating chair conformation of the cyclohexane ring. And presumably this structure would carry on to the cyanide, and from there to the ketimine. Thus to preserve the *meso cis* structure through the series of reactions from the carboxylic acid to the cyanide, triethylamine was introduced to neutralize the hydrochloric acid produced in the formation of the acid chloride.[9] The ketimine prepared from this cyanide gave a hydrolysis rate which checked quite closely with the one obtained for the presumably *meso trans* form. Two possibilities appear here. (1) The *meso cis* form of the ketimine may have essentially the same rate of hydrolysis as the *meso trans*, or (2) the *meso cis* form of the cyclohexane ring may have been transformed to the *meso trans* at the last step in preparation of the nitrile involving the rather high temperature dehydration of the acid amide with phosphorus pentoxide.

Two forms of the 2,6-dimethylcyclohexanecarboxamide were obtained, depending upon whether triethylamine was used or not in preparation of the preceding acid chloride. Their melting points correspond to those reported by Jacobs.[10] However, the two nitriles (obtained by dehydration of these amides on heating with phosphorus pentoxide) had essentially the same physical properties (Experimental). Infrared spectra were taken of the various compounds in this synthetic series—when triethylamine was employed and when not. Although some evidence appeared for different absorptions common to the *meso cis* and the *meso trans* amides and the nitriles produced from each, these differences were insufficient to furnish unequivocal answers to this problem.

The 2,6-dimethylcyclohexanecarboxylic acid used toward the preparation of the *racemic* 2,6-dimethylcyclohexyl phenyl ketimine was prepared according to a procedure described by Jacobs, Fenton, and Reed.[11]

As in the previous report[3] on hydrolysis rate of ketimines, the identity of the ketimine hydrochlorides have been indicated (aside from their methods of synthesis) by the ionic chloride analysis, by the nitrogen analysis of the ketimine base, and by melting points of the ketones produced on hydrolysis where these were known. These methylcyclohexyl phenyl ketones are liquids of high boiling point. The ketone from the hydrolysis of racemic 2,6-dimethylcyclohexyl phenyl ketimine (not reported in literature) has been isolated, purified and analyzed for carbon and hydrogen as reported in the Experimental.

EXPERIMENTAL[12]

Preparation of meso-cis- and meso-trans-2,6-dimethylcyclohexyl phenyl ketimines. The hydrochlorides of these ketimines were prepared by the same procedure, employing in each case the appropriate 2,6-dimethylcyclohexyl cyanide in reaction with phenylmagnesium bromide. A preparation of the *meso trans* ketimine salt will be used for illustration.

With 2.10 g. of the *meso-trans*-2,6-dimethylcyclohexyl cyanide available, a Grignard reagent was made from 4.83 g. of bromobenzene and 0.748 g. of magnesium. The cyanide, dissolved in 10 ml. of dry ether, was added dropwise in the course of a few minutes with stirring of the mixture continued for about 2 hr. Then the ether was evaporated through a luke-warmed reflux condenser as dry toluene was added to replace it. This was followed by refluxing at the temperature of the boiling toluene for several hours. The Grignard-cyanide complex was decomposed with ice and ammonium chloride at about −15°. This mixture was extracted with ether and the ether-toluene extract treated to obtain the ketimine hydrochloride as previously described (ref. 3, page 4822). Yield of purified salt was 1.49 g., or 39% of theory.

Anal. Calcd. for $C_{15}H_{22}NCl$: Cl, 14.08. Found (for *meso trans*): 14.46; (for the presumed *meso cis*): 14.38.

Preparation of meso cis and meso trans 2,6-dimethylcyclohexyl cyanides. These compounds were prepared by dehydration of the corresponding stereoisomeric 2,6-dimethylcyclohexanecarboxamides. An intimate mixture of 2.75 g. of the dry *meso trans* amide with 5.50 g. of phosphorus pentoxide was heated in a 100-ml. standard taper flask, attached to a small fractionating unit, until much of the material melted and oily drops began to reflux from the fractionating column. There was a slight darkening of the mixture. After cooling, the mixture was put under reduced pressure and the oily cyanide distilled at 40–44° under 2 mm. pressure. The cyanide from the *meso cis* amide distilled at practically the same temperature range. $n^{25}_{D} = 1.4472$ (*meso trans*) and $n^{20}_{D} = 1.4470$ (*meso cis*). Both showed the cyanide infrared absorption at just under 4.5 μ and the other major absorptions were nearly identical.

The *meso-cis-* and *meso-trans*-2,6-dimethylcyclohexanecarboxylic acid chlorides and the corresponding amides were prepared from the *meso-cis*-carboxylic acid which was obtained by the hydrogenation (Adam's catalyst) of 2,6-dimethylbenzoic acid. It has appeared that this *meso cis* acid (melting at 87.0–87.5°) rearranges to the *meso trans* acid

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[9] Private communication with Prof. T. L. Jacobs, and Ph.D. thesis of Lars Hellberg, at U.C.L.A.

[10] T. L. Jacobs, R. Reed, and E. Pacovska, *J. Am. Chem. Soc.*, **73**, 4505 (1951).

[11] T. L. Jacobs, D. M. Fenton, and R. Reed, *J. Org. Chem.*, **27**, 87 (1962).

[12] The melting points were taken on a Fisher-Johns melting point apparatus except where indicated otherwise, and were uncorrected.

chloride through catalytic action of the hydrochloric acid produced by its reaction with thionyl chloride.[13] Actually the amide produced by the reaction of concentrated aqueous ammonia on this acid chloride melted at 214–215° (sealed capillary tube since it sublimes above 190°). This compares with the value found by Jacobs et al. given as 215–217° for the amide obtained from the *meso trans* carboxylic acid.[10] Moreover, some of our acid chloride on reaction with alcoholic potassium hydroxide followed by acidification produced an acid melting at 103–104° (Jacobs reported 102–103° for the *meso trans* acid).

To prevent the action of the hydrochloric acid in causing rearrangement of the *meso cis* carboxylic acid to the *meso trans* acid chloride, the preparation was carried out by adding triethylamine[13] along with the thionyl chloride. The amide obtained from this acid chloride melted at 175–179° (Jacobs' value was 181–182.5° for the *meso cis* amide.)

Preparation of racemic 2,6-dimethylcyclohexyl phenyl ketimine. The hydrochloride of this ketimine was prepared in 72% yield by the interaction of racemic 2,6-dimethylcyclohexyl cyanide with phenyl magnesium bromide by the same procedure as described above for the *meso cis* and *meso trans* ketimines.

Anal. Calcd. for $C_{15}H_{22}NCl$: Cl, 14.09. Found: Cl, 14.53.

The racemic 2,6-dimethylcyclohexyl cyanide was prepared from racemic 2,6-dimethylcyclohexanecarboxylic acid *via* the acid chloride and amide. The acid prepared according to ref. 11 melted at 80.0–81.5°. The racemic 2,6-dimethylcyclohexanecarboxamide was obtained from the acid (*via* the acid chloride) in a 74% yield. M.p. = 202–203° (sealed tube).

The racemic 2,6-dimethylcyclohexyl cyanide was prepared from the amide in 90% yield. B.p. = 62° (2 mm.); d = 0.9030 g./ml. at 22.5°; n^{25}D 1.4588.

The free ketimine bases of meso trans and racemic 2,4-dimethylcyclohexyl phenyl ketimine hydrochlorides. These compounds were obtained from the salts by extraction with ether of aqueous solutions with about 25% excess of sodium hydroxide solution added. The ether extracts were dried with anhydrous sodium sulfate and the ether evaporated under reduced pressure.

(a) *Meso-trans* base. *Anal.* Calcd. for $C_{15}H_{21}N$: 6.51. Found: 6.29.

(b) The racemic base boiled at 164–165° under 11 mm. pressure.

n^{25}D = 1.4544. *Anal.* Calcd. for $C_{15}H_{21}N$: N, 6.51. Found: N, 6.40.

The racemic 2,6-dimethylcyclohexyl phenyl ketone. This ketone was obtained by refluxing a dilute aqueous solution of the corresponding ketimine hydrochloride for over 3 hr. It was extracted with ether, the ether extract dried and the ether evaporated under reduced pressure. Under 22 mm. of pressure the ketone distilled at 174–175°.

Anal. Calcd. for $C_{15}H_{20}O$: C, 83.25; H, 9.32. Found: C, 83.00; H, 9.23.[14]

Preparation of monomethylcyclohexyl phenyl ketimines. (1) The 2-methylcyclohexyl phenyl ketimine hydrochloride was prepared by the reaction of 2-methylcyclohexyl cyanide with phenylmagnesium bromide, in a yield of 63%.

Anal. Calcd. for $C_{14}H_{20}NCl$: Cl, 14.91. Found: 15.39.

The cyanide was obtained from 2-methylcyclohexanecarboxylic acid *via* the acid chloride and amide. The carboxylic acid was prepared by the hydrogenation of 2-methylbenzoic acid. For this 27.5 g. of 2-methylbenzoic acid (E. K. No. 1646) was used and 18.90 g. of the hydrogenated acid obtained (66%). It was a liquid boiling at 133–133.5° at 17 mm. From 14.2 g. of the carboxylic acid, 9.6 g. of the amide, melting at 154–155°, was obtained (68%).

The amide, 9.00 g., produced 4.7 g. (60%) of the 2-methylcyclohexyl cyanide boiling at 44° at 2 mm. Density = 0.8987 at 25°; n^{31}D = 1.4480.

(2) The 3-methylcyclohexyl phenyl ketimine hydrochloride was prepared by the interaction of 3-methylcyclohexylmagnesium bromide with phenyl cyanide. Due to the great ease of hydrolysis of this ketimine salt, some modification was necessary in its preparation. Instead of breaking up the Grignard reagent cyanide complex with ice and ammonium chloride at −15°, dry HCl gas was passed into the complex suspended in ether with the apparatus well protected from air moisture and thinning with more ether as a solid mass separated. Dry ammonia gas was then introduced producing white granular ammonium chloride with the liberated ketimine base dissolving in the ether. After complete neutralization of the hydrochloric acid, the ether was refluxed with the escape of excess ammonia. This mixture was drawn through a sintered glass filter under a stream of well dried air. Under suction it was washed with dry ether until no more ammonia could be detected. Dry hydrogen chloride was passed into this ether filtrate with separation of the ketimine hydrochloride. This was dry filtered and washed with dry ether. The ketimine salt was purified by solution in dry chloroform and reprecipitated by addition of dry ether-all filtrations carried out in a stream of dry air. Yield of purified material was 24%.

Anal. Calcd. for $C_{14}H_{20}NCl$: Cl, 14.91. Found: Cl, 15.17.

(3) The 4-methylcyclohexyl phenyl ketimine hydrochloride was prepared by the same procedure as for the 3-methylcyclohexyl phenyl ketimine salt.

Anal. Calcd. for $C_{14}H_{20}NCl$: Cl, 14.91. Found: Cl, 15.20.

The methylcyclohexyl bromides were obtained from the methylcyclohexanols (Eastman Organic Chemicals) reacting with phosphorus tribromide.

Measurement of hydrolysis rates. The procedure employed in determining the rates of hydrolysis of these ketimine hydrochlorides has been essentially the same as reported previously.[3] A 0.01 M aqueous solution is prepared at a noted time. At observed intervals of time 50-ml. aliquots of this solution are withdrawn and quickly introduced to an excess of standard base (around 0.100 N), with a layer of carbon tetrachloride present, in a separatory funnel. The ketimine base is liberated and extracted several times with carbon tetrachloride. The excess standard base is then determined by titration with standard acid using Methyl Orange or equivalent pH range indicator. The equivalents of base consumed represent the moles of ketimine salt remaining unhydrolyzed up to each observed time.

Hydrolysis of the *meso-cis-* and *meso-trans-*2,6-dimethylcyclohexyl phenyl ketimine hydrochlorides was carried out at the temperature of their refluxing solutions (approximately 100°). The racemic 2,6-dimethylcyclohexyl phenyl ketimine hydrochloride was run in a thermostat at 25° ± 0.02.

For the very rapidly hydrolyzing solutions of the monomethylcyclohexyl phenyl ketimine hydrochlorides, instead of withdrawing samples for a given analysis series from one solution, the equivalent amount of the salt for each analysis was weighed into separate small flasks placed in the thermostat (0° for these) and quickly dissolved in water (0°) at an observed time. Then each of these was quickly introduced to the separatory funnel, containing the standard base and carbon tetrachloride, etc., at observed time interval for that sample.

The hydrolysis rate constants and the half-life values were determined from the usual plot and calculation based on the equation for a first-order reaction.

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[13] Ph.D. dissertation, Lars Hellberg, University of California at Los Angeles.

[14] Analysis made by C. F. Geiger, 312 East Yale St., Ontario, Calif.

the Ipatiev High Pressure Laboratory, and at the State University of Iowa for the use of high pressure autoclave equipment. Also our appreciation goes to the Petroleum Research Fund of the American Chemical Society for a grant in partial payment for a Beckman infrared spectrophotometer used in part on this research.

MOUNT VERNON, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Transmission of Electronic Effects by the Cyclopropane Ring. Ionization Constants of *m*- and *p*-Substituted β-Phenylpropionic, *cis*- and *trans*-2-Phenylcyclopropanecarboxylic Acids in 50% Ethanol

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Ionization constants of three series of *m*- and *p*-substituted acids have been measured in 50% ethanol: β-phenylpropionic, *cis*- and *trans*-2-phenylcyclopropanecarboxylic. Hammett rho constants are 0.344, 0.436, and 0.473, respectively, which, by contract with previous measurements in water, suggests that the cyclopropane ring transmits electronic effects somewhat better than does the dimethylene group.

The "double bond character" of the cyclopropane ring in simple electrophilic addition reactions and hydrogenation has been recognized for many years. More recently nucleophilic addition[2a] to cyclopropylcarbonyl compounds and Diels-Alder addition to the vinylcyclopropane linkages[2b] have been observed. During the past fifteen years a considerable body of evidence from spectra,[3] dipole moments,[3a] and chemical reactivity[2] has supported the idea of cyclopropane conjugation. The cyclopropane ring shows strong conjugation with a cationic carbon atom.[4] Two proposed molecular-orbital structures of cyclopropane[5] attribute to it a considerable degree of pi bond character. Stereochemical requirements for conjugation with three-membered rings have been examined.[6]

Controverting this are several reports of the failure of the cyclopropane ring to transmit conjugative effects in an excited state (ultraviolet spectra[7]), in reactions involving carbanion formation,[7] and (presumably in the ground state) in the ionization process of a series of *m*- and *p*-substituted 2-phenylcyclopropanecarboxylic acids.[8] More recently the measurement of rates of alkaline hydrolysis of *cis*-[9] and *trans*-[3a,9] ethyl *m*- and *p*-substituted 2-phenylcyclopropanecarboxylates has led to the conclusion that the three-membered ring transmits electronic effects considerably better than does the dimethylene (—CH_2CH_2—) group of the ethyl β-phenylpropionates.

The conflicting conclusions based on ionization constant data[8] and rate data[3a,9] have suggested a further examination of the former. The choice of 50% ethanol, rather than water,[8] as the medium results in small but uniform deviations from thermodynamic values of K_i. Certain advantages meanwhile accrue, including enhanced substituent effects and solubility of the compounds. The ionization constants are listed in Table I for the β-phenylpropionic acids and for the *cis*- and *trans*-2-phenylcyclopropanecarboxylic acids.

An examination of Hammett equation rho values (Table II) reveals some of the differences between ester hydrolysis and K_i in water data, and between K_i data in water and in 50% ethanol.

In ester hydrolysis rho increases as the transmitting linkage is varied in the order —CH_2CH_2— < *trans*-cyclopropane < *cis*-cyclopropane < *cis*—CH=CH— < *trans*—CH=CH—. The K_i data in water show *trans*-cyclopropane $\cong$ —CH_2CH_2— < *trans* —CH=CH—. In 50% ethanol the K_i order is —CH_2CH_2— < *cis*-cyclopropane < *trans*-cyclopropane, in agreement with spectral evidence.[4,9] Considering only the work herein reported, one

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[1] (a) Based, in part, on the Ph.D. dissertation of C. A. K., The University of Texas, 1962. (b) Department of Chemistry, University of Oklahoma, Norman, Okla.

[2] (a) See, for example, R. W. Kierstead, R. P. Linstead, and B. C. L. Weedon, *J. Chem. Soc.*, 3616 (1952); (b) S. Sarel and E. Breuer, *J. Am. Chem. Soc.*, **81**, 6522 (1959).

[3] (a) See references in R. Fuchs and J. J. Bloomfield, *J. Am. Chem. Soc.*, **81**, 3158 (1959); (b) M. F. Hawthorne, *J. Org. Chem.*, **21**, 1523 (1956); (c) G. W. Cannon, A. A. Santilli, and P. Shenian, *J. Am. Chem. Soc.*, **81**, 1660 (1959); R. J. Mohrbacker and N. H. Cromwell, *J. Am. Chem. Soc.*, **79**, 401 (1957).

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[6] N. H. Cromwell and G. V. Hudson, *J. Am. Chem. Soc.*, **75**, 872 (1958). J. W. Rowe, Doctoral thesis, Swiss Federal Institute of Technology, Zurich, 1957.

[7] L. I. Smith and E. R. Rogier, *J. Am. Chem. Soc.*, **73**, 3840 (1951); R. H. Eastman and S. K. Freeman, *J. Am. Chem. Soc.*, **77**, 6642 (1955); G. W. Cannon, A. A. Santilli, and P. Shenian, *J. Am. Chem. Soc.*, **81**, 4264 (1959).

[8] E. N. Trachtenberg and G. Odian, *J. Am. Chem. Soc.*, **80**, 4018 (1958).

[9] R. Fuchs and J. J. Bloomfield, manuscript in preparation.