difficulty. The ester, so treated, gave on sodium hydroxide saponification and acidification 25% of the pure 115.5–116.5° product.

The *trans* configuration of this isomer was proved by independent synthesis from the known *trans*-2-(*p*-nitrophenyl)-cyclopropanecarboxylic acid. The latter was reduced with tin and hydrochloric acid and the amine so formed subjected to standard diazotization and Sandmeyer conditions.[16] Recrystallization of the dark, oily product of this reaction from water yielded *trans*-2-(*p*-chlorophenyl)-cyclopropanecarboxylic acid identical in infrared spectrum, melting point and mixed melting point with the compound prepared above from *p*-chlorostyrene.

Anal. Calcd. for $C_{10}H_9O_2Cl$: C, 61.08; H, 4.71; Cl, 18.03. Found: C, 61.23; H, 4.65; Cl, 18.23.

***trans*-2-(*m*-Chlorophenyl)-cyclopropanecarboxylic Acid.**—To a solution of 27.3 g. (0.20 mole) of *m*-chlorostyrene[12] in 25 ml. of xylene heated to 140–150° was added over a period of an hour 33 g. (0.30 mole) of freshly distilled ethyl diazoacetate. Further heating at this temperature was continued until nitrogen evolution ceased at which time the solution was fractionated *in vacuo* to yield 22.0 g. (50% yield) of ethyl 2-(*m*-chlorophenyl)-cyclopropanecarboxylate as a yellow oil, b.p. 114° (0.4 mm.). To avoid the difficulties encountered in several attempts at the saponification of the *p*-chloro compound, the *m*-chloro ester was epimerized directly by treatment with sodium ethoxide in refluxing ethanol for 90 minutes. Saponification was effected by adding water to the above solution and refluxing overnight to yield, after acidification, a pale brown solid which was extracted with 50:50 ethyl acetate–cyclohexane. Concentration of the extract precipitated a lighter colored solid which could be recrystallized from water to give 15% of *trans*-2-(*m*-chlorophenyl)-cyclopropanecarboxylic acid, m.p. 108–109°. This acid had the expected infrared spectrum and did not decolorize permanganate solution.

The *trans* structure of this compound was proved by independent synthesis from the known *trans*-2-(*m*-nitrophenyl)-cyclopropanecarboxylic acid by the same sequence of reactions as was used in the *p*-chloro case (*vide supra*). Identity was established in infrared spectrum, melting point and mixed melting point.

Anal. Calcd. for $C_{10}H_9O_2Cl$: C, 61.08; H, 4.61; Cl, 18.03. Found: C, 61.21; H, 4.61; Cl, 18.16.

***trans*-2-*p*-Tolylcyclopropanecarboxylic Acid.**—A solution of 11.6 g. (0.09 mole) of *p*-methylstyrene[17] and 18.0 g. (0.16 mole) of freshly distilled ethyl diazoacetate was heated cautiously to 110° and the temperature maintained for an hour. The solution was then further heated at 140–150° until nitrogen evolution ceased (*ca.* 3 hours). Vacuum distillation of the product gave 13.5 g. (80% yield) of ethyl 2-*p*-tolylcyclopropanecarboxylate as a clear, colorless oil, b.p. 71–73° (0.08–0.1 mm.). This ester was saponified by refluxing with 12 g. of sodium hydroxide in 60 ml. of 85% ethanol for 13 hours. On acidification, the desired acid precipitated. It melted at 119.5–120.5° after two recrystallizations from water (36% yield), gave a negative test with permanganate solution and had the expected infrared spectrum.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.97; H, 6.87. Found: C, 75.10; H, 6.65.

***trans*-2-(*p*-Acetamidophenyl)-cyclopropanecarboxylic Acid.**—A solution of 2.00 g. (0.0097 mole) of *trans*-2-(*p*-nitrophenyl)-cyclopropanecarboxylic acid and 4.5 g. (0.038 mole) of tin in 12 ml. of concentrated hydrochloric acid was stirred and heated on the steam-bath for an hour. The solution was made alkaline by addition of concentrated ammonium hydroxide and the precipitated tin hydroxides filtered. The filtrate was then made slightly acid with glacial acetic acid and evaporated to dryness. The solid residue was extracted with acetone and the extract evaporated to dryness to yield 1.59 g. (93% yield) of *trans*-2-(*p*-aminophenyl)-cyclopropanecarboxylic acid. This amino acid could not be purified, as also was found to be the case when the reduction had been effected catalytically, but could be acetylated directly with acetic anhydride following the procedure of Markees and Burger to give *trans*-2-(*p*-acetamidophenyl)-cyclopropanecarboxylic acid which after successive recrystallizations from a 1:9 mixture of glacial acetic acid–*n*-butyl ether and then water melted at 206–208° (lit.[5] m. p. 205–208°).

Anal. Calcd. for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39. Found: C, 65.50; H, 6.12; N, 6.49.

***trans*-2-*p*-Anisylcyclopropanecarboxylic Acid.**—A solution of 10 g. (0.077 mole) of *p*-methoxystyrene[12] and 15.0 g. (0.135 mole) of freshly distilled ethyl diazoacetate was heated at 130–140° until nitrogen evolution ceased (*ca.* 3 hours. Fractionation of the reaction mixture *in vacuo* yielded 11.3 g. (77% yield) of ethyl 2-*p*-anisylcyclopropanecarboxylate as a clear, colorless oil, b.p. 150° (3 mm.), which solidified in the receiver vessel. This ester was saponified by refluxing with 12 g. of potassium hydroxide in 25 ml. of 85% ethanol for 8 hours to yield 15% of the corresponding acid, m.p. 112–113° after three recrystallizations from water. This acid gave a negative test with permanganate solution and had the expected infrared spectrum.

The *trans* stereochemistry of this compound was proved by its independent synthesis from the known *trans*-2-(*p*-nitrophenyl)-cyclopropanecarboxylic acid following the procedure of Hodgson and Foster involving a sequence of reactions in which the nitro group is reduced with tin and hydrochloric acid and the amine group so formed diazotized and replaced by methoxyl.[18] The compound formed in this way agreed with that synthesized from *p*-methoxystyrene in infrared spectrum, melting point and mixed melting point.

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29. Found: C, 68.60; H, 6.15.

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[16] C. S. Marvel and S. M. McElvain, "Organic Syntheses," Coll. Vol. 1, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 170.

[17] N. Sulzbacher and E. Bergmann, *J. Org. Chem.*, **13**, 303 (1948).

[18] H. H. Hodgson and C. K. Foster, *J. Chem. Soc.*, 581 (1942).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Conjugative Transmission in Cyclopropane Systems

BY EDWARD N. TRACHTENBERG AND GEORGE ODIAN[1]

RECEIVED FEBRUARY 21, 1958

The *pK*'s of a series of *m*- and *p*-substituted *trans*-2-phenylcyclopropanecarboxylic acids in dilute aqueous solution at 25° were determined potentiometrically and the Hammett ρ for the reaction calculated. Comparison to the ρ for the dissociation of *trans*-cinnamic acid and β-phenylpropionic acid indicates that the cyclopropane ring does not transmit conjugation.

It has long been recognized that cyclopropane is quite different in both its physical and chemical properties from its strainless higher homologs and that it bears some marked resemblance to an olefin. One of the most interesting properties is the ability of the three-membered ring to enter into conjugation. It is well known that there is delocalization of electrons in an alternating system of single and double bonds with concomitant transmission of electrical effects along the chain. In the case of

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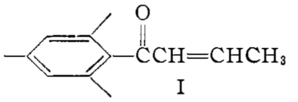
(1) This paper represents part of the work to be submitted by Mr. George Odian to the Graduate Faculties of Columbia University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

cyclopropane, it appears necessary, however, to draw a distinction between extension and transmission of conjugation. Thus, although there is a good deal of evidence in support of the former, the situation relative to the latter is far from conclusive. It is the purpose of this study to cast more light on the problem of whether cyclopropane is able to transmit conjugative effects.

That the electrons of the cyclopropane ring are delocalized is predicted on theoretical grounds[2] and supported by a wide variety of experimental evidence. Ultraviolet studies of cyclopropane in conjugation with carbonyl groups,[3] double bonds[4] and aromatic systems[5] all reveal bathochromic shifts indicative of such delocalization either in the excited or both ground and excited states. Dipole moment measurements,[3b,6] infrared spectroscopy,[3c,7] study of molecular refraction[3e,8] and boiling point differences[8] all offer data in support of this hypothesis. Chemical evidence also has been offered in cases involving conjugation to such groups as the carbonyl,[9] the double bond[8] and carbonium ion intermediates.[10] That the situation is not completely parallel to that of the olefins is shown, however, by the fact that the conjugative properties appear to be more limited in scope than in the case of the double bond. Thus, whereas mesityl propenyl ketone (I) adds both Grignard reagents and active methylene compounds in the 1,4-manner, the same is not true for mesityl cyclopropyl ketone (II), direct addition to the carbonyl being forbidden in either case by excessive steric hindrance.[9d] Furthermore, there appears no evidence of a successful Diels–Alder reaction involving either a vinylcyclopropane[8] or a bicyclopropyl system.[5a] It is true that Gascoigne has reported the addition of maleic anhydride and benzoquinone to such compounds as α-thujene (III), Δ^4-carene (IV) and Δ^3-carene (V), but the products in all cases were the corresponding adducts of α-phellandrene (VI) and α-terpinene (VII).[11] In view of the fact that the experimental conditions used were sufficient to isomerize the compounds to α-phellandrene and α-terpinene prior to Diels–Alder addition and in view of the fact that Δ^3-carene is not even the cyclopropyl analog of a conjugated diene, it appears likely that these reactions do not represent true Diels–Alder additions to a cyclopropyl system.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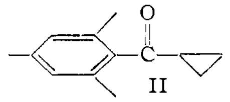
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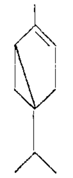
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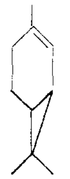
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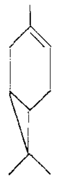
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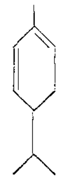
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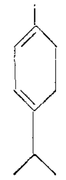
VII

The situation relative to transmission of conjugation has led to conflicting reports. Eastman, on the basis of the study of the ultraviolet spectra of umbellulone (VIII), dihydroumbellulone (IX) and 1-methyl-4-isopropyltricyclo[4,1,0^{1,6},0^{2,4}]heptanon-5 (X), concluded that the three-membered ring is capable of extending conjugation but is incapable of transmitting it.[3c] He also showed that the spectrum of umbellulone is not made peculiar as a result of the substituents present by obtaining the same absorption curve from the analogous compound in which the positions of the methyl and isopropyl had been interchanged.[3d] He also found that α-hydroxyumbellulone (XI) does not have the enhanced acidity which one would expect if it were the conjugative analog of a 2-hydroxycyclopentadienone and could delocalize the electron density of the conjugate base as indicated in XII.[12] In further support of this argument, Eastman synthesized 1-acetyl-2,2-dimethyl-3-(2-methyl-1-propenyl)-cyclopropane (XIII) and showed that its ultraviolet spectrum does not agree with that calculated for a similarly substituted conjugated dienone.[13] Earlier, Smith and Rogier had arrived at the same conclusion from the study of phenylcyclopropane (XIV) and 2-phenylbicyclopropyl (XV).[5a] On the other hand, Mohrbacher and Cromwell arrived at the opposite conclusion from study of the ultraviolet and infrared spectra of some *trans*-2-phenylcyclopropyl aryl ketones (XVI).[7] Also, it has been reported that malonic ester anion adds to ethyl 2-vinylcyclopropane-1,1-dicarboxylate (XVII) in both the 1,4- and, to a lesser extent, 1,6-manner.[9c] This is indicative of conjugative transmission through the cyclopropane ring since malonic ester anion does not ordinarily add to either an olefin or a vinylcyclopropane.

In view of these conflicting reports, it was decided to study the problem from a different approach, *i. e.*, by comparing the relative abilities of various *m*- and *p*-substituents to affect the acidity of the carboxyl group in *trans*-cinnamic acid (XVIII), *trans*-2-phenylcyclopropanecarboxylic acid (XIX) and β-phenylpropionic acid (XX).

For this purpose, one makes use of the well-known Hammett equation 1

$$\log K/K_0 = \sigma\rho \qquad (1)$$

which relates the relative equilibrium (or rate)

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[2] (a) A. D. Walsh, *Nature*, **159**, 164 (1947); (b) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949); (c) T. M. Sugden, *Nature*, **160**, 367 (1947); (d) C. A. Coulson and W. E. Moffitt, *J. Chem. Phys.*, **15**, 151 (1947); (e) C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, **40**, 1 (1949).

[3] (a) J. D. Roberts and C. Green, THIS JOURNAL, **68**, 214 (1946); (b) M. T. Rogers, *ibid.*, **69**, 2544 (1947); (c) R. H. Eastman, *ibid.*, **76**, 4115 (1954); (d) H. E. Smith and R. H. Eastman, *ibid.*, **79**, 5500 (1957); but see also (e) R. P. Mariella and R. R. Raube, *ibid.*, **74**, 518, 521 (1952).

[4] I. R. Klotz, *ibid.*, **66**, 88 (1944).

[5] (a) L. I. Smith and E. R. Rogier, *ibid.*, **73**, 3840 (1951); (b) R. P. Mariella, L. F. A. Peterson and R. C. Ferris, *ibid.*, **70**, 1494 (1948).

[6] M. T. Rogers and J. D. Roberts, *ibid.*, **68**, 843 (1946).

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

[8] R. van Volkenburgh, K. W. Greenlee, J. M. Derfer and C. E. Boord, *ibid.*, **71**, 172, 3595 (1949).

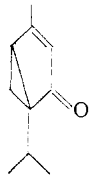
[9] (a) W. A. Bone and W. H. Perkin, *J. Chem. Soc.*, **67**, 108 (1895); (b) E. P. Kohler and J. B. Conant, THIS JOURNAL, **39**, 1404 (1917); (c) R. W. Kierstead, R. P. Linstead and B. C. L. Weedon, *J. Chem. Soc.*, 3616 (1952); but see also (d) R. C. Fuson and F. N. Baumgartner, THIS JOURNAL, **70**, 3255 (1952).

[10] (a) J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2509, 3542 (1951); (b) C. G. Bergstrom and S. Siegel, *ibid.*, **74**, 145 (1952).

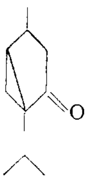
[11] R. M. Gascoigne, *J. Proc. Roy. Soc. N. S. Wales*, **74**, 359 (1940).

[12] R. H. Eastman and J. C. Selover, THIS JOURNAL, **76**, 4118 (1954).

[13] R. H. Eastman and S. K. Freeman, *ibid.*, **77**, 6642 (1955).



VIII



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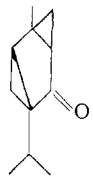

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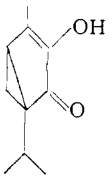

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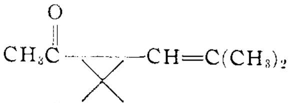

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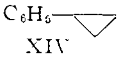

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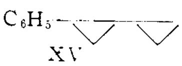

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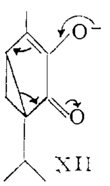

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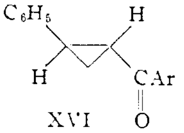

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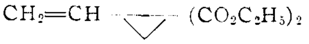
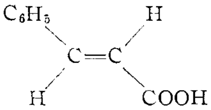
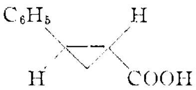


XVII

constants of a series of *m*- and *p*-substituted compounds to the parent, unsubstituted compound by the independent parameters σ and ρ where σ is characteristic of the nature of the given substituent and measures its electrical effect on a reaction and ρ is characteristic of the reaction, depending on the electrical demands of the reaction, the experimental conditions employed and the nature of the conjugative system between the various substituents and the site of the reaction.[14] Measurement of the *pK*'s of a series of such substituted compounds already has been made in the case of both *trans*-cinnamic acid and β-phenylpropionic acid,[15] and the values of ρ for the two cases calculated.[14b] It is our purpose to do the same for the *trans*-2-phenylcyclopropanecarboxylic acid system. Comparison of the three ρ-values should then permit an evaluation of the relative conjugative abilities of the double bond, the three-membered ring and the saturated dimethylene group.



XVIII



XIX

$C_6H_5CH_2CH_2COOH$

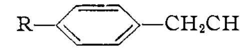
XX

Experimental

***m*- and *p*-Substituted *trans*-2-Phenylcyclopropanecarboxylic Acids.**—The syntheses and proofs of stereochemistry of *trans*-2-phenylcyclopropanecarboxylic acid substituted with *p*-nitro, *m*-nitro, *p*-chloro, *m*-chloro, *p*-hydrogen, *p*-acetamido, *p*-methyl and *p*-methoxy groups is reported in the accompanying paper.[16]

Substituted β-Phenylpropionic Acids.—Several *p*-substituted β-phenylpropionic acids were either purchased or synthesized following standard procedures in the literature. They are listed in Table I along with pertinent characterization data.

TABLE I



R—C₆H₄—$CH_2CH_2CO_2H$

R	Melting point, °C.[a] Found	Lit.	Analyses,[b] % Calcd.	Found
H	48.5–49.5	48–49[c]	......	...
NO_2	166–167	168[d]	C, 55.38	55.26
			H, 4.65	4.68
			N, 7.18	7.35
Cl	122–123	126[e]	C, 58.55	58.71
		122[f]	H, 4.91	4.91
			Cl, 19.21	19.43
CH_3	116.5–117	122[e]	C, 73.14	73.26
		116[g]	H, 7.38	7.69
OCH_3	107–108	107[e]	......	...

[a] All melting points are corrected. [b] All elementary analyses were performed either by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., or by Micro-tech Laboratories, Skokie, Ill. [c] Purchased from Fisher Scientific Co. and recrystallized from 95% ethanol. [d] Made by the method of F. von Konek and E. Pacsu, *Ber.*, 51, 858 (1918). [e] Made by the method of Dippy, see ref. 15. [f] S. Gabriel and M. Herzberg, *Ber.*, 16, 2040 (1883). [g] W. von Miller, *ibid.*, 23, 1898 (1890).

***pK* Measurements.**—The *pK*'s of the various substituted *trans*-2-phenylcyclopropanecarboxylic and β-phenylpropionic acids were determined potentiometrically in carbon dioxide-free water at 25.00 ± 0.05°. For the dissociation of an acid, HA (equation 2), the *pK* may be determined by neutralization with strong base, determination of the hydrogen ion concentration at half neutralization and use of equation 3[17]

$$HA = H^+ + A^- \quad (2)$$

$$pK = pH - \log([A^-]_{stoich} + [H^+])/([HA]_{stoich} - [H^+]) \quad (3)$$

where *pK* is the negative logarithm of the acid dissociation constant in terms of concentration, *pH* is the negative logarithm of the hydrogen ion concentration, $[H^+]$ represents the hydrogen ion concentration at half neutralization, $[HA]_{stoich} = [A^-]_{stoich}$ equals one-half the initial acid concentration, $[A^-]_{stoich} + [H^+]$ represents the real concentration of conjugate base at half neutralization and $[HA]_{stoich} - [H^+]$ represents the real concentration of undissociated acid at this point.[18] The frequently used simplification in which *pK* is set equal to *p*H at half neutralization cannot be employed when using solutions of high dilution, and the last term of equation 3, which represents the correction for self-ionization of the acid, must be incorporated.

The apparatus employed was a Beckman model GS *p*H meter with standard glass and calomel electrodes. The model GS *p*H meter is a modification of the model G and may be used either as a model G with rated precision of ±0.02 *p*H unit or as a model GS with rated precision of ±0.0025 *p*H unit. The latter rating was substantiated by observation of constancy of readings over a one-hour period and reproducibility of duplicate measurements. It was found, however, that one could take no readings at all due to excessive needle fluctuation unless the meter and all other apparatus in the immediate vicinity were grounded.

The titrations were carried out in a 500-ml. beaker tightly closed with a rubber stopper fitted with the two electrodes, a mechanically operated glass stirring rod, a microburet, nitrogen inlet and outlet and a glass rod curved at the bottom which served to transfer into the solution any droplets adhering to the buret tip. The microburet was of 5-ml. capacity and could be read to 0.003 ml. It was calibrated and found to be accurate to ±0.004 ml. All solutions were made using carbon dioxide-free water prepared by passing distilled water through Rohm and Haas Amberlite MB-3 resin, and all operations were performed in an atmosphere of prepurified nitrogen. The *p*H meter was standardized against a biphthalate buffer prepared by dissolving 10.211 g. of National Bureau of Standards potassium hydrogen phthalate in one liter of solution at 25.00 ± 0.05° (*p*H 4.005).[19] The base used in the titrations was 0.05 *N* sodium hydroxide.

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(14) (a) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 186; (b) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

(15) J. F. J. Dippy and J. E. Page, *J. Chem. Soc.*, 357 (1938).

(16) E. N. Trachtenberg and G. Odian, THIS JOURNAL, **80**, 4015 (1958).

(17) W. Rieman, J. D. Neuss and B. Naiman, "Quantitative Analysis," 3rd ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1951, p. 122.

(18) This equation is, of course, general and the various values cited could refer to any point during the titration.

(19) W. J. Hamer, G. D. Pinching and S. F. Acree, *J. Research Nat. Bur. Standards*, **36**, 47 (1946).

In the half neutralization range, *p*H measurements were made after addition of each 0.1 ml. of base using model GS operation. Operation of the meter as a model GS requires constant and frequent calibration, and this operation was only used in the critical half neutralization range. After passing this point, the *p*H meter was adjusted for model G operation and the titration continued, readings being taken after each 0.01-ml. addition of base as the equivalence point was neared. A plot of *p*H against ml. of standard base was made, a smooth curve drawn and the point of half neutralization graphically determined in the usual manner. A typical run is shown in Fig. 1.

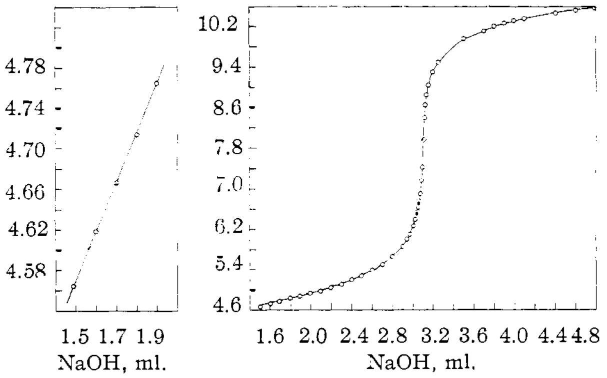

Fig. 1.—Potentiometric titration of an 8.41 × 10^{-4} molar aqueous solution of *trans*-2-*p*-tolylcyclopropanecarboxylic acid at 25.00°. The left curve (half neutralization range) was measured using model GS operation and the right curve using model G operation of the Beckman model GS *p*H meter.

All of the acid solutions were made up to a concentration of as close to 8 × 10^{-4} molar as possible. This proved difficult in the cases of *trans*-2-(*m*-nitrophenyl)-cyclopropanecarboxylic acid and *trans*-2-(*p*-nitrophenyl)-cyclopropanecarboxylic acid whose solubility at 25° is less than that of the other compounds studied. To avoid this difficulty, solutions of these two acids were made up hot, neutralized with 40% of the calculated amount of base, cooled to 25° (no precipitation occurred) and then titrated in the usual manner. That no error was introduced by this technique was shown by applying the same method to the *p*- and *m*-chloro analogs and obtaining the same *pK*'s, respectively, as had been obtained using the standard procedure.

Results and Discussion

The *pK*'s of the various acids studied are listed in Tables II and III.

TABLE II

pK's OF *trans*-2-PHENYLCYCLOPROPANECARBOXYLIC ACIDS IN DILUTE AQUEOUS SOLUTION AT 25°

Substituent	pK_{25}	n^a	Mean dev.
m-NO_2	4.408	3	0.004
p-NO_2	4.448	3	.006
m-Cl	4.514	4	.005
p-Cl	4.529	4	.003
p-H	4.570	3	.002
p-$NHCOCH_3$	4.570	3	.002
p-CH_3	4.597	4	.003
p-OCH_3	4.617	3	.002

[a] *n* denotes the number of determinations.

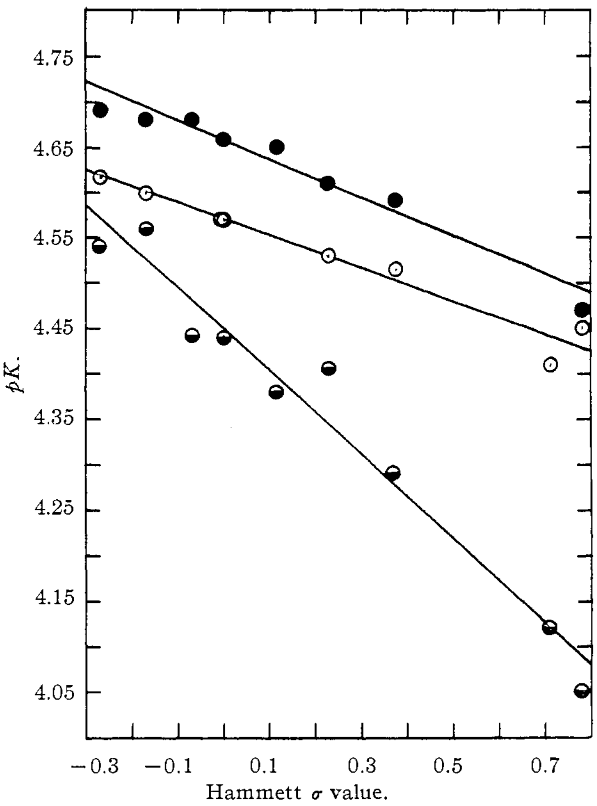

Fig. 2.—Plot of *pK*'s against Hammett σ values[14b]: ○, *trans*-2-arylcyclopropanecarboxylic acids; ◒, substituted *trans*-cinnamic acids; ●, β-arylpropionic acids. The latter two are taken from the data of Dippy[15] and are plotted for comparison purposes.

TABLE III

pK's OF β-PHENYLPROPIONIC ACIDS IN DILUTE AQUEOUS SOLUTION AT 25°

Substituent	pK_{25}	n^a	Mean dev.
p-NO_2	4.542	3	0.004
p-Cl	4.655	3	.002
p-H	4.709	3	.002
p-CH_3	4.737	3	.005
p-OCH_3	4.751	3	.003

[a] *n* denotes the number of determinations.

These *pK* values are plotted against the Hammett σ values[14b] as shown in Fig. 2. The ρ values were calculated by the method of least squares.[20] The use of the Hammett equation is shown to be valid by the linearity of the plots. Since the ρ of a reaction is a function not only of the reaction studied and the compound used but also of the experimental conditions, it is essential that these be constant for a given series. Thus, it is important to keep constant not only temperature but also solvent when determining the ρ for the dissociation of a series of acids. Although all measurements were made in the same solvent, water, at the same temperature, 25°, the control of ionic strength provided more of a problem.[21] All the acid solutions

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(20) W. J. Youden, "Statistical Methods for Chemists," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 40.

(21) One possibility is to pack the solution with neutral salt and correct the observed *pK*'s to the *pK*'s in terms of activities by use of the Debye–Hückel relation (W. J. Moore, "Physical Chemistry," 2nd ed., Prentice-Hall, Inc., Englewood Cliffs, N. J., 1955, p. 462). Such procedure was deemed inadvisable in this case in that it would serve to increase solvating power and, therefore, ease of dissociation of the acids. This, in turn, would lead to a lower ρ, and since one is seeking to correlate the ρ's of three series of acids, two of which had previously been measured and found not to differ greatly, such a damping of the sensitivity of ρ would have been highly detrimental. A second possibility is to attempt a Debye–Hückel correction without packing with

were made up to as near the same concentration as was possible. This served to keep the ionic strength constant throughout the series save for the slight differences introduced by the fact that the acids vary slightly in dissociation constant. That this variation did not introduce any appreciable error was checked by recalculating ρ for each series of acids using the observed pK's of the strongest acid at the highest concentration (therefore having the highest ionic strength) and the weakest acid at the lowest concentration (therefore having the lowest ionic strength). It was found that this introduced an error in ρ of only 0.002, well within the experimental error.

The values of ρ for the three series are listed in Table IV.

TABLE IV

	Series	Hammett ρ^a	Standard deviation
I	*trans*-Cinnamic acid	0.466	0.040[15,14b]
II	*trans*-2-Phenylcyclopropanecarboxylic acid	.182	.014
III	β-Phenylpropionic acid	.212	.016[15,14b]
		.204	.007

[a] These ρ's are for a plot of log K's against σ and are the same as those plotted in Fig. 2 except for sign.

Since the ρ values for I and III had previously been determined by a conductometric method to yield the thermodynamic pK's, comparison of the potentiometrically determined ρ for II with these would not be valid unless one were certain that the results were correlatable. This was shown to be the case by repeating the measurements in series III by the potentiometric method. It is seen that the two values are in excellent agreement.

Since the values for the three series are all for the same reaction, dissociation of the acid, at the same temperature, 25°, in the same solvent, water, comparison of the ρ values gives the relative conjugative ability of the double bond, the cyclopropane ring and the saturated dimethylene group. Clearly, the cyclopropane ring approximates most closely in its behavior to the saturated dimethylene analog, and one thus concludes that it is incapable of transmitting conjugation. That the ρ value is actually slightly lower for II than it is for III is probably not important in that the difference is not significantly beyond the experimental error. In the event that the difference is real, this is, however, not altogether surprising. The enhanced electronegativity of the three-membered ring[2c] should and does (see Tables II and III) slightly enhance the acidity of correspondingly substituted members of series II over series III. This would lead to a slightly lower ρ for the former. That this effect is overcome by conjugation is clearly shown by series I which is similarly electronegative and possessed of enhanced acidity.

Our finding that the cyclopropane ring behaves like the saturated analog and differs markedly in its behavior from an olefin places us in agreement with the findings of Eastman[3c] and of Smith[5a] relative to conjugative transmission by cyclopropane. Cromwell's conclusion[7] that such conjugation does exist need not necessarily disagree with these results in that it is possible to have conjugation in an electronically excited state and not in the ground state. Such a situation would still produce the bathochromic shift which Mohrbacher and Cromwell observed. These results are also not necessarily in disagreement with the finding that ethyl 2-vinylcyclopropane-1,1-dicarboxylate adds malonic ester anion to a slight extent in the 1,6-manner.[9c] The latter does not necessarily imply conjugative transmission in the ground state. It is equally likely that such transmission occurs only in the transition state, *i. e.*, after bond breaking of the three-membered ring already has commenced.

In conclusion, it appears that cyclopropane is incapable of transmitting conjugation in the ground state although it is quite capable of extending conjugation and may be able to transmit it in some excited states. The explanation offered for this by Eastman[3c] based on the theoretical arguments of Roberts and Mazur[10a] denying to cyclopropane the role of an electron sink may well be valid.

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salt. This was tried and led to inconsistent results. This is not surprising in that one has to assume constancy in the activity coefficients of the un-ionized acids, an assumption which is not necessarily valid (F. A. Long and W. F. McDevit, *Chem. Revs.*, **51**, 119 (1952)).