

TABLE III

ANALYSIS OF COPOLYMERS

Monomer	Calcd. for homopolymer, %		Calcd. for copolymer, %		Found, %		
	C	H	C	H	C	H	N
I	78.26	4.38	73.15	7.37	72.44	6.64	..
II	79.97	6.67	74.97	8.39	73.95	7.99	1.00
III	28.84	0.80	37.30	3.13	35.98	2.16	..

TABLE IV

ULTRAVIOLET SPECTRA OF POLYMERS AND MODEL COMPOUNDS^a

Compound	λ_{\max} , m μ	log ϵ
Poly-(1,4-phenylene oxide)	295	2.93 ^b
Anisole	277	3.15
Diphenyl ether	278	3.26
4-Hydroxydiphenyl ether	281	3.48
4-Methoxydiphenyl ether	280	3.43
Poly-(2,6-dimethyl-1,4-phenylene oxide)	287	2.84 ^b
2,6-Dimethylanisole	265	2.78

^a In chloroform. ^b Extinction coefficient calculated on the basis of a 1:1 copolymer.

tetramethyltetrahydrofuran³¹ at 0° afforded 0.16 g. (25%) of yellow polymer, 74% of which was soluble in benzene and had an intrinsic viscosity of 0.059. Subjecting 2,6-dimethyl-*p*-benzoquinone diazide to similar treatment afforded only a trace of

(31) L. Henry, *Compt. rend.*, **143**, 496 (1906).

TABLE V

RATE OF PHOTODECOMPOSITION OF A 3.108×10^{-4} M SOLUTION OF 2,6-DIMETHYLBENZOQUINONE-4-DIAZIDE

Time $\times 10^{-2}$, sec.	ln (C_0/C)	Time $\times 10^{-2}$, sec.	ln (C_0/C)
2.1	0.193	9.0	0.982
3.9	.367	11.4	1.344
5.7	.510	13.8	2.064
7.2	.677		

polymer. Thermal decomposition of 0.5% solutions of the two monomers at reflux temperature (111.0°) produced only traces of polymer.

D. In Tetrahydrofuran.—Summarized in Table II are the results of decompositions in tetrahydrofuran. Tables III and IV give analytical and ultraviolet spectral data, respectively. The products from *p*-benzoquinone diazide are slightly yellow and those from 2,6-dimethyl-*p*-benzoquinone diazide are white. Polymer samples prepared from the hydrated monomers only showed weak bands at 1695 cm.⁻¹ (C=O str., conj.) in the infra-red region while all polymers showed maxima at 1195–1200 cm.⁻¹ (C–O–C str.).

Kinetics.—Tetrahydrofuran solutions 2.325×10^{-3} M (Fig. 1) and 3.108×10^{-4} M (Table V) in 2,6-dimethyl-*p*-benzoquinone diazide were placed in a flask equipped with a mechanical stirrer, and blanketed by an atmosphere of nitrogen. This apparatus was partially immersed in a bath maintained at 0°. During irradiation with a G.E. AH-4 mercury vapor lamp, 1-ml. aliquots were withdrawn, diluted to 10 ml. in the dark and placed in a Beckman DU spectrophotometer at 0° to determine optical density at 357 m μ . The quantum yield was obtained by using both uranyl nitrate and oxalic acid as standards.

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The Acid Dissociation Constants of Some 1,2-Cyclopropanedicarboxylic Acids. Some Comments Concerning Acid Dissociation Constants of Dicarboxylic Acids¹

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The acid dissociation constants of twenty-three substituted 1,2-cyclopropanedicarboxylic acids are reported. Some of the trends in the relationships between structure and dissociation constants are pointed out and discussed. A general discussion of some problems connected with acid dissociation constants, especially for dicarboxylic acids, is given.

As a result of previous studies on the preparation of polysubstituted cyclopropanes,³⁻⁶ we have accumulated a number of sets of substituted isomeric 1,2-cyclopropanedicarboxylic acids. Many of the compounds were new, and others were not readily accessible previously. Earlier studies of the physical and chemical properties of substituted cyclopropanes often have been limited to readily available alkyl-substituted compounds. As the result of our work making cyclopropanes with carboxyl, ester, nitrile groups and halogen available, we have considered it desirable to investigate the physical properties of these cyclopropanes substituted with electron-withdrawing groups. The present report gives an initial survey of the acid dissociation constants of most of the 1,2-diacids available to us. Because our compounds comprise a rather heterogeneous group, we have not aimed for extremely refined results, but rather we have tried to obtain adequate data for the following purposes: (1) To observe any trends in the relationships between structure and acid dissociation constants, and if such trends were discernible to see if they matched similar trends in related succinic acids or maleic-fumaric acids. (2) To use

any empirical relationships observed in (1) to help assign configurations to some of the new diacids.

Experimental

Materials.—The diacids used are listed in Table I with references to their source. In all cases, the samples titrated were those for which analyses are reported in the references, or they are samples prepared in an identical manner. All of the acids titrated to better than 99% of theoretical equivalence.

Titrations.—These were carried out with type SBR 2/SBU/TTT 1 automatic titration equipment of the Radiometer Corporation, with Radiometer type G 202 B glass electrode and type K 4312 calomel electrode. A jacketed container of about 100-ml. capacity, the jacket connected to a temperature-controlled water-bath, which permitted temperature control at $20.0 \pm 0.1^\circ$, was used as the titration vessel. During each titration, the access of air (carbon dioxide) was prevented by maintaining a nitrogen blanket over the solution. Titrant, 0.100 N sodium hydroxide, was added by means of a 2.5-ml. syringe buret to 100.0 ml. of a 0.00100 M solution of the acid in carbon dioxide-free distilled water. Before each titration, the pH meter was standardized against buffer solutions (Fisher Scientific) over the range pH 3.00 to pH 6.50. At least two titrations were run on each acid, the first of which was automatically recorded, while during the second titration direct readings were taken from the micrometer arrangement of the syringe buret and from the pH meter. Automatically recorded data were found to be unsuitable for the desired evaluation because the chart could not be read with sufficient accuracy. Agreement between titrations of the acid was generally within 0.03 pH unit.

Determination of Acid Dissociation Constants.—The data were treated by the method of Speakman⁷ and by Ebersson's modification thereof.⁸ All *trans*-acids, where K_1/K_2 was about 50 or less, were treated according to Speakman's graphical

(1) Part of this report is taken from a senior honors project by G. W. Nachtigall.

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(3) L. L. McCoy, *J. Am. Chem. Soc.*, **80**, 6568 (1958).

(4) L. L. McCoy, *J. Org. Chem.*, **25**, 2078 (1960).

(5) L. L. McCoy, *J. Am. Chem. Soc.*, **84**, 2246 (1962).

(6) L. L. McCoy and G. W. Nachtigall, *J. Org. Chem.*, **27**, 4312 (1962).

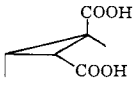
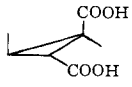
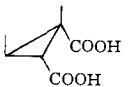
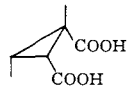
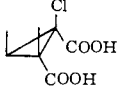
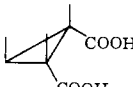
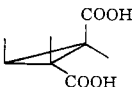
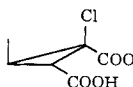
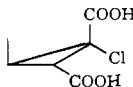
(7) J. C. Speakman, *J. Chem. Soc.*, 855 (1940).

(8) L. Ebersson, *Acta Chem. Scand.*, **13**, 211 (1959).

TABLE I
 DISSOCIATION CONSTANTS OF 1,2-CYCLOPROPANEDICARBOXYLIC ACIDS AT 20°

Substituent	Section A					Section A				
	Source ^a	pK_1	pK_2	ΔpK	K_1/K_2	Source ^a	pK_1	pK_2	ΔpK	K_1/K_2
None	A	3.80	5.08	1.28	19.4	A	3.56	6.65	3.09	1210
1-Methyl	A	3.93	5.30	1.37	23.4	A	3.67	6.47	2.80	638
1-Phenyl	C	3.72	5.14	1.42	26.3	C	3.48	6.08	2.60	396
1,2-Diethyl	C	3.53	5.03	1.50	31.8	C	4.16	6.58	2.42	264
1,2-Dimethyl	A, B	3.70	5.24	1.54	34.3	A, B	4.06	6.56	2.50	312
1-Methyl-2-chloro	B, C	2.72	4.27	1.55	35.0	B, C	2.95	5.25	2.30	198
1-Methyl-2-phenyl	C	3.61	5.33	1.72	53.1	B, C	3.84	6.28	2.44	281
None ^b		3.65	5.13	1.48	33		3.33	6.47	3.14	1380
3,3-Dimethyl ^c (caronic acids)		3.82	5.32	1.50	31.8		2.34	8.31	5.97	929,000

Section B^d

					
pK_1	4.23	3.93	3.69	3.09	2.91
pK_2	5.65	5.51	6.82	7.91	5.41
ΔpK	1.42	1.58	3.13	4.82	2.50
K_1/K_2	26.1	38.2	1,345	66,700	316
					
pK_1	4.23	3.77	2.66	2.61	
pK_2	6.74	5.42	5.41	4.46	
ΔpK	2.51	1.65	2.75	1.85	
K_1/K_2	321	45.2	552	71.2	

^a A, ref. 3; B, ref. 4; C, ref. 5. ^b Ref. 9; the *trans* values are at 24° and the *cis* values are K_1 at 24° and K_2 at 25°. ^c Ref. 10; values for both isomers at 25°. ^d Ref. 6.

method,⁷ while the *cis*-acids were treated by the simple expressions given by Ebersson.⁸ Volume corrections for the added titrant were insignificant. Corrections for liquid junction potentials and salt errors were not attempted.

The titration technique and calculation method (graphical evaluation) were tested by titrating succinic acid under identical experimental conditions. The result was pK_1 4.29 and pK_2 5.72 as compared to 4.22 and 5.67, respectively, reported by Speakman.⁷ On the basis of this observation and of statements made by Speakman⁷ and Ebersson⁸ regarding the accuracy of their methods, it is estimated that the accuracy of the thermodynamic dissociation constants reported in Table I is about ± 0.1 pK unit. It appears justified, however, to assume that a higher degree of accuracy, possibly ± 0.03 – 0.05 pK unit, is reflected in the relative differences of the reported values, and it is this aspect of the measurements that primarily has been made use of in the following discussion.

Discussion

Prior to the present work, apparently the only dissociation constants of 1,2-cyclopropanedicarboxylic acids that had been reported are those of the unsubstituted *cis*–*trans* pair⁹ and those of *cis*- and *trans*-caronic acids (the 3,3-dimethyl derivatives).¹⁰ These values are shown at the end of Section A, Table I, for comparison with our values.

Section A of Table I shows a number of interesting relationships and trends in the relationships between structure and dissociation constants. Three of the more obvious ones are: (1) The K_1/K_2 ratio for the *cis* isomers decreases with increasing size of the substituents. (2) The K_1/K_2 ratio for the *trans* isomers (one exception) increases with increasing size of the substituents. (3) The value of K_1 for about half of the *trans* isomers is greater than for the corresponding *cis* isomers. Because of the rather heterogeneous nature of this group of acids, it is somewhat difficult to draw clear-cut conclusions as to the basis for these results. We have no doubt that all of these results can be "ex-

plained," but for reasons discussed below we do not wish to present any such "explanations" at this time with the exception of a suggestion concerning the decreasing values of K_1/K_2 for the *cis* isomers.

Recent work by Ebersson⁸ has shown that as the size of substituents is increased in racemic dialkylsuccinic acids, the K_1/K_2 ratio increases enormously until with the racemic di-*t*-butylsuccinic acid is obtained the largest K_1/K_2 ratio ever observed; the *meso* isomers show no such changes. Ebersson has suggested "the main cause of an anomalously high K_1/K_2 ratio appears to be steric in origin. If the steric properties of a dibasic acid are such as to permit a close approach of the carboxyl groups, the pure electrostatic effect transmitted through the solvent and the molecule itself will increase. Besides, formation of an intramolecular hydrogen bond will be possible, which further magnifies the K_1/K_2 ratio."⁸ Such hydrogen bonding would make K_1 larger, K_2 smaller and, consequently, K_1/K_2 much larger. For other diacids, similar suggestions, including not only permissive close approach of carboxyl groups but also the actual forcing together of such groups, have been made often.¹¹ This close approach and forcing together of carboxyl groups might have been expected to occur in the 1,2-dialkyl-*cis*-1,2-cyclopropanedicarboxylic acids. That such an effect does occur is indicated by the ease of anhydride formation for these acids. Whereas the unsubstituted compound shows no anhydride formation on recrystallization from a variety of solvents, the diethyl compound is converted partially to the anhydride on recrystallization from nitromethane,⁵ and the diisopropyl derivative gives a mixture of acid and anhydride on recrystallization even from water.¹² The trend, decreasing K_1/K_2 ratio with

(11) H. C. Brown, D. H. McDaniel and O. Häfner, in "Determination of Organic Structures by Physical Methods," Vol. I, E. A. Braude and F. C. Nachod, Ed., Academic Press, Inc., New York, N. Y., 1955, p. 567. References to earlier similar suggestions may be found here, pp. 628–634.

(9) A. Wassermann, *Helv. Chim. Acta*, **13**, 207, 223 (1930).

(10) J. Jones and F. G. Soper, *J. Chem. Soc.*, 133 (1936).

increasing size of substituents for the *cis* isomers (Section A, Table I), then, is contrary to observations in other systems and is unexpected.

We would like to suggest that the hydrogen bond required for explanation of the values in these systems will have optimum stability with some specific geometry of the carboxyl groups. We do not know what that specific geometry is, and it is not particularly critical to the following discussion, but it is not unreasonable to assume that it would approximate a linear O—H . . . O grouping with the two carboxyl groups approaching coplanarity.¹³ Models suggest that even in the unsubstituted *cis*-1,2-cyclopropanedicarboxylic acid, the carboxyl groups in the assumed arrangement are too close together, *i.e.*, the O—H . . . O distance would be about 1.6 Å. (Dreiding models) as compared to 2.4 Å., a minimal distance observed in hydrogen bonding between carboxyl groups.¹³ To be accommodated on the cyclopropane ring, models (Stuart-Brigleb) suggest that the two carboxyl groups cannot be coplanar, that their rotation is markedly hindered, and that there is appreciable crowding between the two groups. Additional squeezing brought about by bulky 1,2-substituents will cause further crowding and quite possibly the crowding will reach a stage where a hydrogen bond is either not possible or very weak. On the other hand, the *cis*-3-methyl group of the *cis*-caronic acid may cause a spreading of the *cis*-carboxyl groups, thereby allowing them to come closer to the optimum hydrogen bond distance and arrangement. That is, due to the crowding of the three *cis* substituents, we would expect all three groups to be bent away from an axis perpendicular to the plane of the three-membered ring, and, consequently, to result in a spreading of the carboxyl groups.¹⁴ We suggest then a rationalization of the general trend observed for the K_1/K_2 ratio of *cis*-1,2-cyclopropanedicarboxylic acids: Assuming hydrogen bonding to be a major factor in determining the K_1/K_2 ratio, the degree of hydrogen bonding will depend on the spacing of the two carboxyl groups, and the spacing in turn will depend on the squeezing or spreading effect of substituents in various positions on the cyclopropane ring. That is, groups in the 1- and 2-positions will squeeze while a *cis*-3 group will spread the *cis*-carboxyl groups, and a *trans*-3 group will be innocuous or exert a buttressing effect on other substituents. The trend observed and the rationalization suggested indicate that a hydrogen bond of maximum stability would probably occur when the carboxyl groups are spread apart slightly more than what we have suggested for the *cis*-caronic acid. We hope to be able to test this possibility. We want to emphasize that in the general case substituents will affect hydrogen bonding by how they force carboxyl groups together or how they spread them apart *and* by how they constrain carboxyl groups to a position favorable for hydrogen bonding. The first involves distortion of bond angles while the second involves a hindrance to rotation. The two effects in most cases are probably not independent, but one or the other often will predominate,

(12) Unpublished data; the *cis* diisopropyl diacid has not yet been obtained free of the anhydride.

(13) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, pp. 236-238, 265-269.

(14) We wish to point out that the 3-*cis*-substituent possibly can contribute to the large K_1/K_2 ratio in other ways. (1) Owing to its bulk, the methyl group will constrain the somewhat spread carboxyl groups to lie more nearly in the same plane. This will not only help stabilize the monoanion (hydrogen bonded) as has been suggested before (see footnote 11 for references), but it will probably destabilize the dianion, the two carboxylate groups probably being most stable when they are facing each other, an arrangement not possible with the *cis*-methyl group present. (2) The methyl group may prevent or hinder solvation of one side of the carboxyl groups. Such hindrance to solvation might be more critical for a dianion with closely spaced charges than for a monoanion.

and both should be considered in any discussion of substituent effects on hydrogen bonding in dicarboxylic acids.

We do not wish to enter an explanation for the reason of the increase in K_1/K_2 ratio with increasing size of the substituent for the *trans* isomers; the differences are relatively small. However, considering the trends for both the *cis* and *trans* isomers, we will not be surprised to find with some combinations of substituents that the K_1/K_2 ratio for the *trans* isomer is larger than for the *cis* isomer.

As the second goal of this work, we hoped that the acid dissociation constants would be of some value in assigning configurations to more highly substituted compounds for which chemical methods of assignment would be difficult or impossible, the acids shown in Section B, Table I. The relative *cis* or *trans* configuration of all acids in Table I was readily established since only the *cis* isomers form monomeric cyclic anhydrides. The 1,3-dimethyl derivatives shown in Section B were assigned specific configurations primarily on the basis of n.m.r. data.⁶ At this point it was fairly obvious that dissociation constants for *trans* isomers are of no value in assigning configurations, but that the values for *cis* isomers are. For the two *cis* compounds with a third *cis* substituent, the ΔpK values 4.82 and 5.97 are much larger than for those compounds with a *trans*-3 substituent or no 3-substituent at all, in which cases ΔpK ranges from 2.50 to 3.13. We used these two ranges to make configurational assignments for the remaining *cis* isomers.⁶ We are planning to obtain more data which will substantiate, refute or clarify this apparent division into two classes of compounds with very different K_1/K_2 ratios.

General Discussion.¹⁵—In the course of trying to rationalize our results we have of necessity consulted the literature in this area. We have come across a number of peculiar situations with regard to the way our results fit in with previous work and interpretations, and with regard to the results already present in the literature. We wish here to comment on some of these.

The apparently anomalous values of the dissociation constants for the cyclobutane-1,3-dicarboxylic acids reported by Wassermann⁹ have been discussed in terms of orientation of dipoles¹⁶ and of micro-dielectric con-

(15) It should be noted that in much of the following discussion various examples are cited from different text and reference books. In most cases a variety of other sources could be given for the same examples, and those given are to be taken only as representatives of the class.

(16) (a) G. S. Hammond, "Steric Effects on Equilibrated Systems," p. 423, from "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 432.

(b) This book, "Steric Effects in Organic Chemistry," is readily available and often quoted. We feel that it is important, therefore, to point out that the material from pp. 431-434 discussing dissociation constants of dibasic acids contains a number of errors, some of them serious, and consequently this section should be read with considerable caution. Although we have not checked all values, we have observed the following errors and inconsistencies: (1) In Table V, the values reported for cyclohexene-1,2-dicarboxylic acid are very probably incorrect. We have not been able to check the specific reference (a book by W. Hückel) given by Hammond, but a later edition (the eighth) of the same reference gives quite different values; the reference quoted in the eighth edition of Hückel's book is incorrectly cited. The original source for these data is W. Hückel and V. Lampert, *Ber. deut. chem. Ges.*, **67**, 1811 (1934), and the data given there are K_1 9.86 $\times 10^{-4}$, K_2 0.46 $\times 10^{-5}$ and K_1/K_2 212. (2) The values (Table V) for the *cis*- and *trans*-1,3-cyclobutanedicarboxylic acids and all discussion relating the values to these structures are meaningless as pointed out in our discussion in the present paper. (3) The comment on p. 432 that "The *cis*-acid is slightly stronger than the *trans* in the first dissociation [in the cyclopropane series], a phenomenon that is repeated with the 1,2-cyclobutane diacids . . ." is obviously inconsistent with the data of Table V. (4) The comment on p. 433 that "The value of K_1/K_2 is always smallest for the *cis*-acids," is inconsistent with values shown in Table V—quite obviously *cis* of this statement should be replaced by *trans*. (5) The value for K_2 for *trans*-1,2-cyclohexanedicarboxylic acid shown in Table VI is incorrect. It is too small by a factor of ten. This makes the value K_1/K_2 too small by a factor of ten, and this in turn invalidates a number of statements made in the following paragraphs.

stant effects.¹⁷ Unfortunately, neither of the acids on which Wassermann made his measurements is a cyclobutane derivative at all as it has been shown subsequently that the "trans" isomer is in fact 1-methyl-trans-1,2-cyclopropanedicarboxylic acid^{18,19} and the "cis" isomer is α -methylene-glutaric acid.²⁰

Similarly, the dissociation constants for *cis*-1,2-cyclobutanedicarboxylic acid reported by Kuhn and Wassermann²¹ are probably incorrect as pointed out by Bode.²² Bode determined the dissociation constants for the authentic *cis*-acid. In compilations of acid dissociation constants, this work²² seems to have been overlooked consistently.

As a more general case, a number of sources state or imply that in a *cis-trans* pair of 1,2-dicarboxylic acids, especially in rigid or moderately rigid systems such as ethylene or cyclopropane, the K_1 for the *cis*-acid will be larger than K_1 for the *trans*-acid.^{23,24} The usual "theoretical" explanation is either one that involves hydrogen bonding between the carboxyl groups in the *cis* isomer but not the *trans* isomer, or one that involves electrostatic and dipole effects between the carboxyl groups, the effects being greater in the *cis* isomer because the groups are closer together. Both effects presumably should increase K_1 , decrease K_2 , and increase K_1/K_2 for the *cis* isomer relative to the *trans*. Our work shows several exceptions (all of the 1,2-disubstituted-1,2-diacids) to this generality concerning K_1 and it is questionable whether other available data are adequate to support it. A rapid survey of all of the values for sets of *cis-trans* isomeric dicarboxylic acids listed by Kortüm, Vogel and Andrusow²⁵ indicates that there are more exceptions than there are followers of the rule. Consequently, we doubt that there is any validity of the "rule" that K_1 for a dicarboxylic acid is larger for the *cis* isomer of a *cis-trans* pair.

Conjugation of a cyclopropane ring with a carboxyl group is a possibility, and in so far as this can happen, an "explanation" of some of our results might be given as substituents hindering or aiding this conjugation. This would be based on similar proposals given to explain the increased acidity of *cis*- α,β -unsaturated acids relative to the corresponding *trans* isomer.²⁶ However, we have some doubts about the completeness of the arguments concerning steric inhibition of resonance in these systems. In Table II we have listed various

In spite of this error, the value of K_1/K_2 somehow has essentially the correct magnitude.

(17) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p. 243.

(18) D. H. Deutsch and E. R. Buchman, *Experientia*, **6**, 462 (1950).

(19) The values of K_1 and K_2 reported for *trans*-1,3-cyclobutanedicarboxylic acid by Wassermann⁹ are 3.81 and 5.28, respectively, at 25° and these values agree moderately well with our values for 1-methyl-*trans*-1,2-cyclopropanedicarboxylic acid (Table I).

(20) E. R. Buchman, A. O. Reims and M. J. Schlatter, *J. Am. Chem. Soc.*, **64**, 2703 (1942).

(21) R. Kuhn and A. Wassermann, *Helv. Chim. Acta*, **11**, 600 (1928).

(22) H. Bode, *Ber.*, **67B**, 332 (1934).

(23) Reference 17, p. 211.

(24) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp. 187, 327-328.

(25) G. Kortüm, W. Vogel and K. Andrusow, "Dissociation Constants of Organic Acids in Aqueous Solution," Butterworths, London, 1961.

(26) (a) For discussion of this topic, see ref. 11, p. 583, ref. 24, pp. 328-329, and C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 744-745. (b) It should be noted that the maleic-fumaric acid system is used sometimes as an example. That is, the maleic-fumaric acid system is used to illustrate: (1) Hydrogen bonding in the *cis* but not the *trans* isomer; (2) the closer approach of carboxyl groups in *cis* as opposed to *trans* isomers so that electrostatic and dipole effects are larger in the *cis* case; and (3) the effect of a *cis* substituent on the conjugation of an α,β -unsaturated acid. Since all three effects presumably operate in the same direction to make K_1 for the *cis* isomer larger than K_1 for the *trans*, it is not easy to see how this system can be represented as a clear-cut example of any one of these effects as is commonly done.

cis-trans pairs normally used to illustrate this phenomenon, but we have also listed some additional compounds for comparison. In examining this list, we find some difficulties in correlating ΔpK values between acids and the differences in structure between the same acids. For example, it is not clear why a β -*cis*-methyl (*cis* to the carboxyl), which presumably will interfere with conjugation between the carboxyl group and the double bond, should show such different behavior when added to acrylic acid, *trans*-crotonic acid and methacrylic acid, the ΔpK values being +0.15, +0.43 and -0.37. In discussions^{26a} concerning the difference between *cis* and *trans* isomer of this type, no mention is ever made of the β,β -dialkyl-substituted acrylic acids (which also have *cis*-alkyl substituents). On the other hand, Branch and Calvin²⁷ have used the *trans* isomers and the β,β -dialkyl-substituted acrylic acids to show that the (inductive) effect of alkyl groups in the β -position of an α,β -unsaturated carboxylic acid is additive. Both the inhibition of resonance effect and the additive effect of β -groups can be "justified" by giving appropriate data, but neither explanation can accommodate all of the data in Table II without additional assumptions. Consequently, because these various arguments do not yet appear to be on firm ground, and because these effects are relatively small, we make no attempt to incorporate them into an explanation of our results.

TABLE II
DISSOCIATION CONSTANTS OF α,β -UNSATURATED MONOCARBOXYLIC ACIDS^a

Compound	$K \times 10^5$ pK	Compound	$K \times 10^5$ pK
	5.56(25°) 4.26		5.1(18°) 4.29
	1.95(18°) 4.71		1.1(18°) 4.96
	3.9(18°) 4.41		0.73(18°) 5.14
	2.2(18°) 4.66		0.74(25°) 5.13
	2.02(25°) 4.70		0.71(25°) 5.15

^a These values are from ref. 25, pp. 262-266.

Other factors such as solvation and inductive effects have been considered in connection with explaining acid dissociation constants, but most of these factors cannot be or have not been evaluated quantitatively at this time. Consequently, it is possible to weight arbitrarily the various factors so as to be able to "explain" almost any observed dissociation constant. Most of the data and interpretations presently available have been repeated so often, so clearly, and so logically that the topic has presented a picture of completion and order in which only details need be filled in. It should be obvious from the present discussion that this is not the case.

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(27) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1946, pp. 237-238.