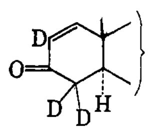

V

These results furnish indirect evidence for the operation of the addition–elimination mechanism in the previously reported[2] hydrogen–deuterium exchanges with acyclic α,β-unsaturated compounds such as chalcone.

Experimental[6]

β-Phenylindenone (II).—This compound was prepared by a new method involving dehydrogenation of β-phenylindanone through its dicarbanion.[7] The liquid product was characterized as its p-nitrophenylhydrazone, m.p. 266–267°, reported[8] m.p. 266–267°.

Deuteration of II to Form β-Phenylindenone-α-d_1 (III).—To 60 ml. of deuterioethanol (b.p. 79–79.5°)[9] was added 0.2 g. (0.0087 g.-atom) of sodium. The resulting solution was cooled to 0° and an ethereal solution of 1.8 g. (0.0087 mole) of freshly prepared β-phenylindenone (II) was added. After standing 50–90 hr. at 0°, the reaction mixture was treated with a wet ethanolic solution of p-nitrophenylhydrazine hydrochloride (containing a slight excess of hydrochloric acid) to yield 67–88% of the p-nitrophenylhydrazone of III, m.p. 266–267° after recrystallization from acetonitrile. Combustion analysis indicated that the material contained 6.69 atom % excess deuterium; calcd. for $C_{21}H_{14}N_3O_2D$, 6.67%, corresponding to approximately 1.0 D atom/molecule. The infrared spectrum showed bands at 1185, 1175, 1055, 1030, 922, 780, and 718 cm.$^{-1}$ while the undeuterated p-nitrophenylhydrazone had bands at 1210, 1130, 1048, 847, and 774 cm.$^{-1}$. The deuterated and the undeuterated compounds showed similar infrared N–H stretching bands at 3295 cm.$^{-1}$.

α,β-Diphenylindenone (IV).—A mixture of 12 g. (0.04 mole) of α,β,β-triphenylpropionic acid,[10] 14.3 g. (0.12 mole) of thionyl chloride, and a few drops of pyridine was warmed on the steam bath for 1 hr. The excess thionyl chloride was removed by distillation *in vacuo*, and the residue was dissolved in 40 ml. of benzene. The solution was cooled (ice bath), and 5.4 g. (0.04 mole) of aluminum chloride was added in small portions with stirring during 30 min. After standing at 0° for 1 hr., the reaction mixture was poured onto ice and acidified with dilute hydrochloric acid. The resulting mixture was extracted with ether, and the ethereal extract was dried over anhydrous magnesium sulfate. The solvent was removed, and the viscous oily residue was chromatographed on alumina to give, after recrystallization from cyclohexane, 6.8 g. (60%) of α,β-diphenylindanone, m.p. 99–100°, reported[11] m.p. 100–101°.

This compound was dehydrogenated with sulfur by the method of Koelsch[11] to give α,β-diphenylindenone (IV), m.p. 152–153°, reported[12] m.p. 150–151°.

Attempted Deuteration of α,β-Diphenylindenone (IV).—To a solution of 0.0013 mole of sodium ethoxide (prepared from 0.03 g., 0.0013 g.-atom, of sodium) in 16 ml. of deuterioethanol at 0° was added an ethereal solution of 0.36 g. (0.0013 mole) of α,β-diphenylindenone (IV). After standing 100 hr. at 0°, the reaction mixture was neutralized with glacial acetic acid and the solvent was removed under reduced pressure. Recrystallization of the residue gave 0.16 g. (89%) of recovered α,β-diphenylindenone, m.p. 151.5–153°. A mixture m.p. with authentic material was undepressed and no alterations were observed in the infrared spectrum. Combustion analysis indicated that the ketone contained 0.31 atom % excess deuterium, corresponding to only 0.04 D atom/molecule.

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(6) Melting points were determined with a Mel-Temp capillary melting point apparatus and are uncorrected. Infrared spectra were determined with a Perkin–Elmer Infracord by the potassium bromide pellet method. Deuterium analyses were by Dr. Josef Nemeth, Urbana, Ill.

(7) The details of this and related reactions will be published soon.

(8) K. von Auwers and R. Hugel, *J. prakt. Chem.*, **143**, 157 (1935).

(9) V. J. Shiner, Jr., and M. L. Smith, *J. Am. Chem. Soc.*, **83**, 593 (1961).

(10) W. R. Dunnavant and C. R. Hauser, *Org. Syn.*, **40**, 38 (1960).

(11) C. F. Koelsch, *J. Am. Chem. Soc.*, **56**, 1337 (1934).

(12) G. Heyl and V. Meyer, *Ber.*, **28**, 2776 (1895).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY, TECHNOLOGY CENTER, CHICAGO 16, ILL.]

A New Method of Evaluating *ortho* σ-Constants

BY IRVINE J. SOLOMON[1,2] AND ROBERT FILLER

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A method for evaluating *ortho* σ-constants by using ionization constants and rate of esterification with diphenyldiazomethane of substituted phenylpropiolic acids is described. Values for chloro, fluoro, trifluoromethyl, and nitro groups have been determined. The reduced acidities relative to the p-isomers of acids substituted in the o-position with negative substituents are ascribed to a field effect. A related dipolar field effect is revealed by the infrared and ultraviolet spectra of the acids.

Introduction

In recent years acetylenic compounds have been studied for the purpose of correlating rate and/or equilibrium data with Hammett σ-values for substituents on the aromatic nucleus. Newman and Merrill[3] measured the ionization constants and the rates of esterification of o-, m-, and p-chloro-, methoxy-, and nitrophenylpropiolic acids, and Roberts and Carboni[4] made other measurements of reactivities on some of these compounds. More recently, Dessy and his coworkers[5] examined the effect of various substituents on the rates of deuterium exchange of substituted phenylacetylenes.

A linear free-energy relationship similar to the Hammett equation but applicable to aliphatic and o-substituted aromatic compounds has been proposed by Taft.[6,7] This relationship is valid only for a restricted number of reaction series, and among the o-substituents, fluorine, the amino group, and hydrogen are not included.

We were interested in extending knowledge in this area by obtaining additional data for the o-, m-, and p-fluoro- and trifluoromethyl-substituted phenylpropiolic acids. On the basis of these data and the data of Newman and Merrill[3] and Roberts and Carboni,[4] *ortho* σ-constants for the fluoro, trifluoromethyl, chloro, nitro, and methoxy groups have been defined.

Results and Discussion

The ionization constants and the rates of various reactions of several substituted phenylpropiolic acids have previously been studied by two groups of workers.[3,4] The phenylpropiolic acid system was chosen because the acetylenic bond is linear and should eliminate steric effects of o-substituents more than any other group capable of joining the carboxyl group to the benzene ring. Also, the unsaturated bond should be capable of transmitting polar effects to the reaction site.

The apparent ionization constants of the trifluoromethyl- and fluoro-substituted phenylpropiolic acids[8]

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(1) Abstracted from the Ph. D. thesis of I. J. Solomon, January, 1962.

(2) Part of this work was supported by IIT Research Institute (formerly Armour Research Foundation).

(3) M. S. Newman and S. H. Merrill, *J. Am. Chem. Soc.*, **77**, 5552 (1955).

(4) J. D. Roberts and R. A. Carboni, *ibid.*, **77**, 5554 (1955).

(5) R. E. Dessy, Y. Okazumi, and A. Chen, *ibid.*, **84**, 2899 (1962).

(6) R. W. Taft, Jr., *ibid.*, **74**, 2729 (1952).

(7) R. W. Taft, Jr., *ibid.*, **74**, 3120 (1952).

(8) See Experimental.

were determined in a solution containing 35% by weight of dioxane in water. These results are shown in Table I along with the results of Newman and Merrill,[3] who determined apparent ionization constants of the corresponding nitro-, chloro-, and methoxy-substituted acids. These p*K* values plotted against the Hammett σ-constants, Fig. 1, resulted in a ρ-constant of 0.80. This constant was then used for calculations of the *ortho* σ-constants given in Table I. It should be pointed out that Newman and Merrill[3] found a ρ-constant of 0.81, and that the addition of the points measured in this investigation did not appreciably change this value.

TABLE I

IONIZATION CONSTANTS AND RELATED DATA FOR SUBSTITUTED PHENYLPROPIOLIC ACIDS IN A SOLUTION OF 35% DIOXANE IN WATER AT 25°

Number[a]	Substituent	$K \times 10^4$	p*K*	σ[b]
1	H	5.75	3.24	. .
2	*o*-Cl	8.32	3.08	0.24
3	*m*-Cl	10.00	3.00	. .
4	*p*-Cl	8.51	3.07	. .
5	*o*-NO_2	15.0	2.83	0.55
6	*m*-NO_2	19.0	2.73	. .
7	*p*-NO_2	27.0	2.57	. .
8	*o*-OCH_3	4.27	3.37	−0.13
9	*m*-OCH_3	6.15	3.21	. .
10	*p*-OCH_3	3.57	3.44	. .
11	H	5.37	3.27	. .
12	*o*-F	6.76	3.17	0.13
13	*m*-F	7.94	3.10	. .
14	*p*-F	5.75	3.24	. .
15	*o*-CF_3	7.94	3.10	0.21
16	*m*-CF_3	8.32	3.08	. .
17	*p*-CF_3	9.55	3.02	. .

[a] The data given in numbers 1 through 10 were determined by Newman and Merrill,[3] and those in numbers 11 through 17 were determined in the present investigation. [b] A ρ-constant of 0.80 (see Fig. 1) was used to calculate the *ortho* σ-constants. The pK_0 used was 3.27.

TABLE II

IONIZATION CONSTANTS AND RELATED DATA FOR SUBSTITUTED PHENYLPROPIOLIC ACIDS IN A 50% ETHANOL–WATER SOLUTION AT 25°

Number[a]	Substituent	$K \times 10^4$	p*K*	σ[b]
1	H	2.63	3.58	. .
2	*o*-Cl	3.09	3.51	0.21
3	*m*-Cl	3.72	3.43	. .
4	*p*-Cl	3.39	3.47	. .
5	*o*-NO_2	4.07	3.39	0.48
6	*m*-NO_2	5.25	3.28	. .
7	*p*-NO_2	5.50	3.26	. .
8	H	2.51	3.60	. .
9	*o*-F	3.31	3.48	0.27
10	*m*-F	3.16	3.50	. .
11	*p*-F	3.02	3.52	. .
12	*o*-CF_3	3.23	3.49	0.25
13	*m*-CF_3	4.37	3.36	. .
14	*p*-CF_3	4.68	3.33	. .

[a] The data given in numbers 1 through 7 were determined by Roberts and Carboni,[4] and those in numbers 8 through 14 were determined in the present investigation. [b] A ρ-constant of 0.44 was used to calculate the *ortho* σ-constants. The value of pK_0 used was 3.60.

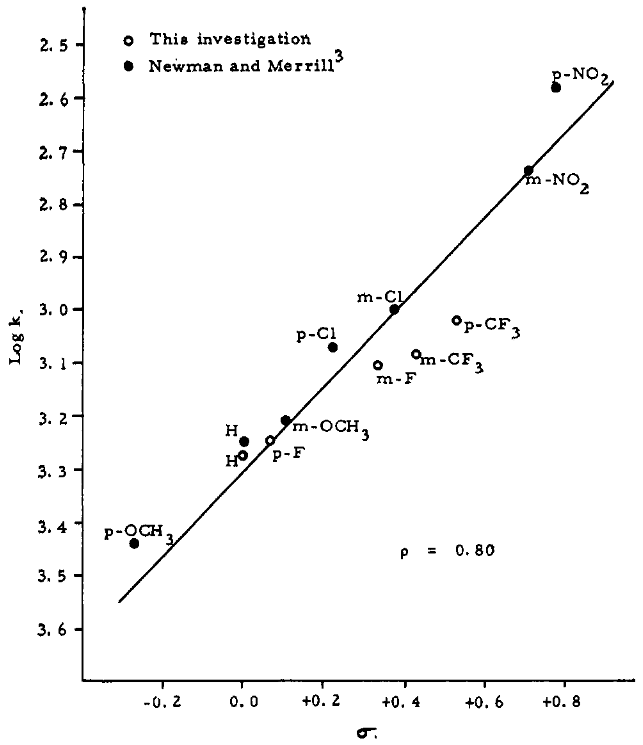

Fig. 1.—Hammett σ-constants *vs.* log ionization constants of substituted phenylpropiolic acids in a solution of 35% dioxane in water at 25°.

The ionization constants of the trifluoromethyl- and fluorosubstituted phenylpropiolic acids were also determined in a 50% ethanol–water solution. The results are given in Table II along with the results of Roberts and Carboni,[4] who determined the ionization constants of chloro- and nitro-substituted phenylpropiolic acids. These p*K* values plotted against the Hammett σ-constants for the *m*- and *p*-compounds resulted in a ρ-constant of 0.48. This ρ-constant was then used to calculate the *ortho* σ-constants shown in Table II. This new ρ-constant compares favorably with the value of 0.44 reported by Roberts and Carboni.[4]

Rates for the reactions of fluoro- and trifluoromethyl-substituted phenylpropiolic acids with diphenyldiazomethane in ethanol at 30° were determined. The results are shown in Table III along with those of Roberts and Carboni,[4] who determined the same rates for the chloro- and nitro-substituted acids. The logarithms of the rate constants were plotted against the Hammett σ-constants for the *m*- and *p*-substituted compounds. The resulting straight line had a slope (ρ-value) of 0.31,

TABLE III

RATE DATA FOR THE REACTION OF SUBSTITUTED PHENYLPROPIOLIC ACIDS WITH DIPHENYLDIAZOMETHANE IN ABSOLUTE ETHANOL AT 30°

Number[a]	Substituent	*k*, l. mole^{-1} min.$^{-1}$	log *k*	σ[b]
1	H	19.6	1.29	. .
2	*o*-Cl	23.4	1.37	0.26
3	*m*-Cl	25.6	1.41	. .
4	*p*-Cl	21.8	1.34	. .
5	*o*-NO_2	29.7	1.47	0.58
6	*m*-NO_2	33.3	1.52	. .
7	*p*-NO_2	32.5	1.51	. .
8	H	19.3 ± 0.1	1.29	. .
9	*o*-F	24.8 ± .2	1.39	0.32
10	*m*-F	23.2 ± .4	1.37	. .
11	*p*-F	22.8 ± .2	1.36	. .
12	*o*-CF_3	30.4 ± .4	1.48	0.61
13	*m*-CF_3	32.5 ± .3	1.51	. .
14	*p*-CF_3	31.7 ± .3	1.50	. .

[a] The data given in numbers 1 through 7 were determined by Roberts and Carboni,[4] and those in numbers 8 through 14 were determined in the present investigation. [b] A ρ-constant of 0.31 was used to calculate the *ortho* σ-constants. The value used for log k_0 was 1.29.

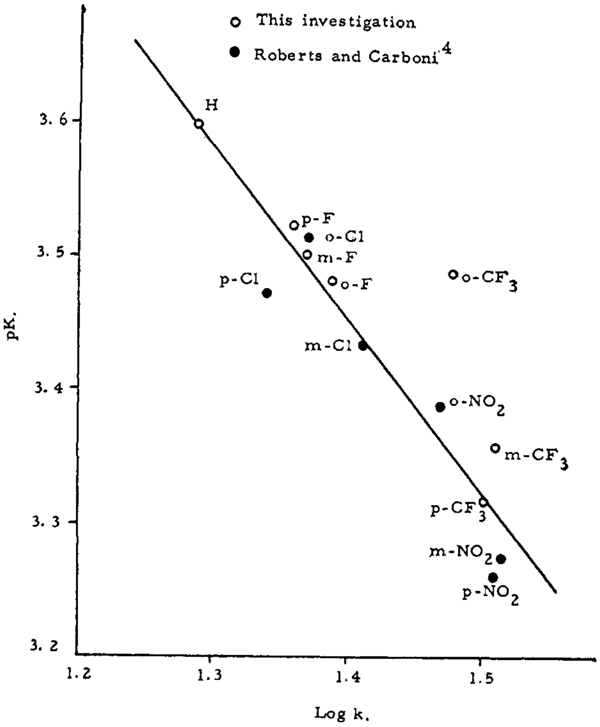

Fig. 2.—Log rate constants for reactions of substituted phenylpropiolic acids with diphenyldiazomethane in absolute ethanol at 30° *vs.* p*K* values for substituted phenylpropiolic acids in a 50% ethanol–water solution at 25°.

which is the same as that obtained by Roberts and Carboni.[4] This value of ρ was used for calculations of the *ortho* σ-constants given in Table III.

Rates for the reactions of fluoro- and trifluoromethyl-substituted phenylpropiolic acids with diphenyldiazomethane in dioxane at 30° were also measured; Table IV. The results of Roberts and Carboni,[4] who determined similar rates with the nitro- and chloro-substituted phenylpropiolic acids, are also given. A Hammett plot reveals a slope of 0.89 compared with the 0.95 reported by Roberts and Carboni.[4]

TABLE IV

RATE DATA FOR THE REACTION OF SUBSTITUTED PHENYLPROPIOLIC ACIDS WITH DIPHENYLDIAZOMETHANE IN DIOXANE AT 30°

Number[a]	Substituent	k, l. mole^{-1} min.$^{-1}$	log k	σ^b
1	H	3.32	0.52	. .
2	*o*-Cl	5.64	.75	0.27
3	*m*-Cl	6.34	.80	. .
4	*p*-Cl	5.25	.72	. .
5	*o*-NO_2	10.5	1.02	0.57
6	*m*-NO_2	14.0	1.15	. .
7	*p*-NO_2	18.9	1.28	. .
8	H	3.2 ± 0.1	0.51	. .
9	*o*-F	5.7 ± .1	.75	0.27
10	*m*-F	5.6 ± .2	.75	. .
11	*p*-F	4.7 ± .1	.67	. .
12	*o*-CF_3	6.5 ± .2	.82	0.35
13	*m*-CF_3	8.1 ± .1	.91	. .
14	*p*-CF_3	7.8 ± .2	.89	. .

[a] The data given in numbers 1 through 7 were determined by Roberts and Carboni,[4] and those in numbers 8 through 14 were determined in the present investigation. [b] A ρ-constant of 0.89 was used to calculate the *ortho* σ-constants. The value used for log k_0 was 0.51.

Thus, the use of known σ-constants for *m*- and *p*-substituted phenylpropiolic acids made it possible to calculate *ortho* σ-constants for the fluoro, trifluoromethyl, chloro, nitro, and methoxy groups. These constants, calculated from the data given in Tables I through IV, are summarized in Table V.

TABLE V

HAMMETT *ortho* σ-CONSTANTS

Group	σ	Method[a]	σ_{av}
Fluoro	0.13	1	0.25
	.27	2	
	.32	3	
	.27	4	
Trifluoromethyl	.21	1	0.33
	.25	2	
	.61	3	
	.35	4	
Chloro	.24	1	0.28
	.09	5	
	.21	2	
	.26	3	
	.27	4	
	.49	6	
	.28	7	
	.43	8	
Nitro	.55	1	0.54
	.25	5	
	.48	2	
	.58	3	
	.57	4	
	.63	6	
	.66	7	
	.60	8	
Methoxy	− .13	1	
	− .32	5	
Methyl	− .09	7	
	− .15	8	

[a] 1, Table I; 2, Table II; 3, Table III; 4, Table IV; 5, Table II; 6, p*K*'s of phenylacetic acids in water at 25°[9]; 7, p*K*'s of phenylpropionic acids in water at 25°[10]; 8, p*K*'s of cinnamic acids in water at 25°.[10]

To show the generality of the method, values for nitro, chloro, and methyl groups are also given. These values were calculated from the ionization constants of phenylacetic, phenylpropionic, and cinnamic acids (Table VI). For each group, one or two values do not seem to agree with the others, but in general the agreement is much better than that obtained from a similar treatment of benzoic acid data. More information for methyl- and methoxy-substituted compounds must be obtained before more clearly defined *ortho* σ-constants can be obtained for these groups.

TABLE VI

p*K* VALUES FOR NITRO-SUBSTITUTED ACIDS IN WATER AT 25°[9,10]

Acid	p*K* *ortho*	p*K* *meta*	p*K* *para*
Benzoic	2.17	3.49	3.42
Phenylacetic	4.00	3.97	3.85
Phenylpropionic	4.50	. .	4.47
Cinnamic	4.15	4.12	4.05
Phenylpropiolic	3.39	3.28	3.26

To illustrate the general applicability of the Hammett equation to these systems, Hammett plots are shown in Fig. 2 through 4. It should be pointed out that these data were taken from three different sources. In general, the agreement obtained for the *o*-substituted compounds was as good as that obtained for the *m*- and *p*-substituted acids.

The reduced acidity of the *o*-nitrophenylpropiolic acid relative to the *p*-isomer has been explained on the basis of a direct field effect between the negative ring substituent and the carboxyl –OH group.[4,11] This

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(9) J. F. J. Dippy and F. R. Williams, *J. Chem. Soc.*, 161 (1934).

(10) J. F. J. Dippy and J. E. Page, *ibid.*, 375 (1938).

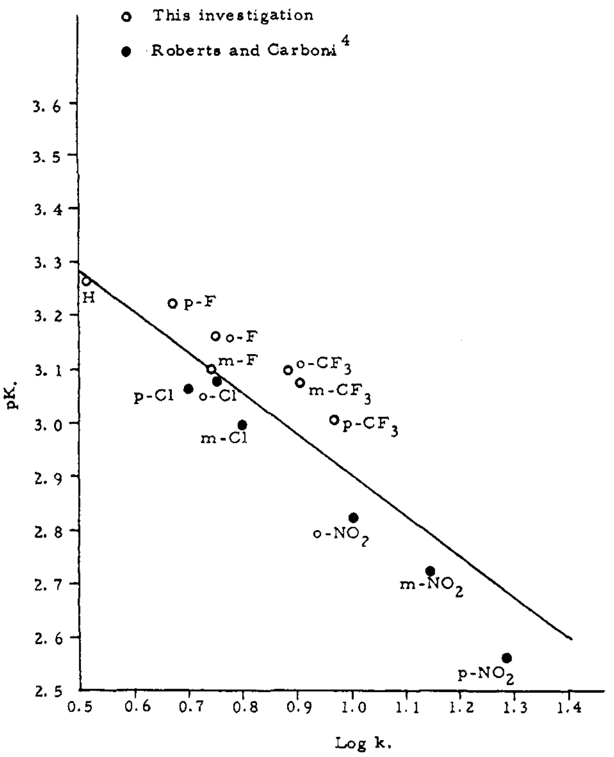

Fig. 3.—Log rate constants for reactions of substituted phenylpropiolic acids with diphenyldiazomethane in dioxane at 30° *vs.* p*K* values for substituted phenylpropiolic acids in a 50% ethanol-water solution at 25°.

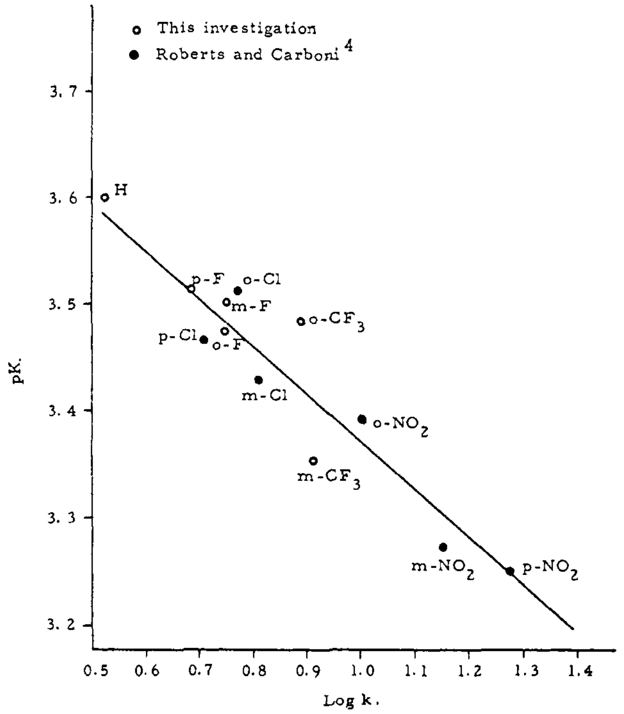

Fig. 4.—Log rate constants for reactions of substituted phenylpropiolic acids with diphenyldiazomethane in dioxane at 30° *vs.* p*K* values for substituted phenylpropiolic acids in a solution of 35% dioxane in water at 25°.

interaction more than balances the inductive effect, which alone would give the reverse result.

The trifluoromethyl group provides a second example of this effect. Examination of molecular models shows that both the $-NO_2$ and $-CF_3$ groups are in sufficiently close proximity to the carboxyl function for this interaction to be very significant. The slightly smaller chloro group still exerts sufficient influence to just outweigh a purely inductive effect, which however is operative to the extent that the *o*-Cl compound is stronger than phenylpropiolic acid itself. With the very small fluorine atom, however, this proximity effect is no longer of much consequence, and the *o*-acid is slightly stronger than its *m*- and *p*-isomers.

While such interactions may also play a role in the saturated acids, it should not be of importance in the rigid *trans*-cinnamic acid structure. More data are obviously necessary before adequate explanations in terms of field effects can be advanced.

The infrared and ultraviolet spectra of the fluoro- and particularly the trifluoromethyl-substituted phenylpropiolic acids reveal another related proximity effect. Free rotation of the $C-CO_2H$ permits the existence of two rotational isomers with a very low energy barrier. In one, the carboxyl -OH lies *cis* to the *o*-substituent and this has been discussed in terms of acidity. In the other, the carbonyl group is in closer proximity to the substituent. Here, the dipolar field effect between the negative CF_3 group in the *o*-position and the carbonyl group of the acid[12] diminishes the carbonyl bond polarity and leads to an increase in frequency (Table VII). Such intramolecular field effects between carbonyls and *cis*-halogens have been examined by Bellamy,[13] Josien,[14] and Brown.[15] The smaller fluorine atom, much farther removed in space from the C=O, shows only a slight effect, and this may be due to induction.

TABLE VII

INFRARED ABSORPTION DATA FOR SUBSTITUTED PHENYLPROPIOLIC ACIDS[a]

Substituent	ν_{CO_2H}, cm.$^{-1}$
H	1685
o-F	1700
m F	1695
p-F	1698
o-CF_3	1712
m-CF_3	1688
p-CF_3	1695

[a] Potassium bromide pellets were used to obtain spectra.

TABLE VIII

ULTRAVIOLET ABSORPTION DATA FOR SUBSTITUTED PHENYLPROPIOLIC ACIDS[a]

Substituent	λ_{max}, mμ
H	251
o-F	243
m-F	248
p F	250
o-CF_3	240
m-CF_3	249
p-CF_3	253

[a] Spectra were obtained in 95% ethanol.

A further consequence of this dipolar interaction should be a decrease in the delocalization (resonance) energy of the conjugated system. This expectation is indeed confirmed by the ultraviolet spectra of the fluorinated phenylpropiolic acids (Table VIII), which show a pronounced hypsochromic shift in the maxima of the *o*-substituted acids.

Experimental

m-Trifluorophenylacetylene was prepared as follows: *m*-trifluoromethylphenylmethylcarbinol was prepared by the reaction of *m*-trifluoromethylphenylmagnesium bromide with acetaldehyde. The alcohol was dehydrated to *m*-trifluoromethylstyrene

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(11) J. Hine, "Physical Organic Chemistry," 2nd Edition, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 62.

(12) These spectra were measured with the acids as KBr pellets. It is recognized that under these conditions the acids are in the dimeric form. However, this should in no way alter the argument concerning the effects of ring substituents. Measurements with other solvents and of ester carbonyls are in progress. If there were a slow transition between rotamers, two C=O bands should become apparent. The observed band is probably an average. Another plausible explanation may be that the preferred conformation of the carbonyl is *cis* to the negative *o*-substituent, accounting for the one band actually observed. A direct consequence of the resulting diminution of the >C=O bond polarity would be a decrease in the acidity of the carboxylic acid, as found.

(13) L. J. Bellamy and R. L. Williams, *J. Chem. Soc.*, 4294 (1957).

(14) M. L. Josien and C. Castinel, *Bull. soc. chim. France*, 801 (1958).

(15) T. L. Brown, *Spectrochim. Acta*, **18**, 1615 (1962).

TABLE IX

FLUORINE-CONTAINING PHENYLACETYLENES, PHENYLPROPIOLIC ACIDS, AND RELATED COMPOUNDS

Compound	Yield,[a] %	Physical properties			Analyses, %			
					Calcd.		Found	
		B.p., °C. (mm.)[b]	d^{25}_{25}	$n^{25}D$	C	H	C	H
o-$CF_3C_6H_4CHOHCH_3$	36	84–85 (20)[c]						
o-$CF_3C_6H_4CH{=}CH_2$	65	44–45 (11)						
o-$CF_3C_6H_4CH{=}CHBr$	38	65–66 (4)						
o-$CF_3C_6H_4C{\equiv}CH$	34	44–45 (8)	1.222	1.477	63.53	2.96	64.02	2.99
m-$CF_3C_6H_4CHOHCH_3$[d]	70	50–51 (20)						
m-$CF_3C_6H_4CH{=}CHBr$	44	62–63 (5)	1.420	1.492	43.05	2.41	42.81	2.64
m-$CF_3C_6H_4CH{=}CHOC_2H_5$	56	94–95 (8)	1.115	1.464	61.10	5.13	60.96	5.00
m-$CF_3C_6H_4C{\equiv}CH$	42	50–51 (20)	1.159	1.467	63.53	2.96	63.43	3.04
p-$CF_3C_6H_4CHOHCH_3$	69	72–74 (0.5)						
p-$CF_3C_6H_4CH{=}CH_2$	61	39–40 (7)						
p-$CF_3C_6H_4CH{=}CHBr$	39	65–67 (4)						
p-$CF_3C_6H_4C{\equiv}CH$	46	34–35 (6)	1.043	1.466	63.53	2.96	63.22	3.41
o-$FC_6H_4CHOHCH_3$	69	76–78 (7)						
o-$FC_6H_4CH{=}CH_2$	64	33–34 (7)						
o-$FC_6H_4CH{=}CHBr$	44	62–63 (5)						
o-$FC_6H_4C{\equiv}CH$	39	39–40 (12)	1.051	1.524	79.98	4.19	79.44	4.38
m-$FC_6H_4CHOHCH_3$	82	76–78 (7)						
m-$FC_6H_4CH{=}CH_2$	69	33–34 (7)						
m-$FC_6H_4CH{=}CHBr$	17	58–60 (1)						
m-$FC_6H_4C{\equiv}CH$	27	40–42 (11)	1.043	1.514	79.98	4.19	79.83	4.39
p-$FC_6H_4CHOHCH_3$	60	92–94 (11)						
p-$FC_6H_4CH{=}CH_2$	67	44–45 (15)						
p-$FC_6H_4CHBrCH_2Br$	96	67–69[e]			34.08	2.50	34.04	2.47
p-$FC_6H_4CH{=}CHBr$	43	69–70 (4)						
p-$FC_6H_4C{\equiv}CH$[f]	47	45–46 (20)	1.050	1.509	79.98	4.19	79.63	4.27

[a] Yield based on previous compound in reaction sequence. [b] Boiling points are uncorrected. [c] M.p. 32°, d^{25}_{25} 1.247. [d] C. S. Marvel, C. G. Overberger, R. E. Allen, and J. H. Saunders, *J. Am. Chem. Soc.*, **68,** 736 (1946). [e] All other dibromides were liquids and were used directly in the next step. [f] M. R. Tirpak, C. A. Hollingsworth, and J. H. Wotiz, *J. Org. Chem.*, **25,** 687 (1960).

with potassium bisulfate. The styrene was treated with bromine in an ether solution to give *m*-trifluoromethylstyrene dibromide. Evaporation of the ether gave the liquid styrene dibromide, which was slowly added to saturated alcoholic potassium hydroxide maintained at reflux temperature. The product was poured onto ice-water and extracted with ether. The ether was then evaporated and the product distilled. Upon analysis, it was found that the desired *m*-trifluoromethylphenylacetylene had not been obtained; instead, the elements of ethanol had added to the triple bond to result in the enol ether. When, however, *m*-trifluoromethylphenylstyrene dibromide was treated with molten potassium hydroxide, the monobromostyrene readily formed. This compound was recycled through the molten alkali to give *m*-trifluoromethylphenylacetylene.

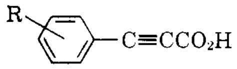
The *o*- and *p*-trifluoromethylphenylacetylenes were similarly obtained from *o*-chlorobenzotrifluoride and *p*-bromobenzotrifluoride.

The fluorophenylacetylenes were obtained in analogous fashion by starting with the bromofluorobenzenes. A slight modification was necessary for the *o*-isomer, because of difficulty in preparing the Grignard reagent of *o*-bromofluorobenzene, which was probably due to intervention of a "benzyne" intermediate. This problem was obviated by treating *o*-fluorobenzaldehyde with methylmagnesium bromide to give *o*-fluorophenylmethylcarbinol. The physical properties of the phenylacetylenes and their precursors are listed in Table IX.

The phenylacetylenes were converted to their lithium derivatives and carbonated to give the corresponding phenylpropiolic acids in 42–62% yields. The data for all of the acids prepared are given in Table X.

TABLE X

FLUORINE-CONTAINING PHENYLPROPIOLIC ACIDS



R	M.p., °C. (cor.)	Yield, %	Carbon, %		Hydrogen, %	
			Calcd.	Found	Calcd.	Found
o-CF_3	139.6–140.2	45	56.08	56.14	2.35	2.38
m-CF_3	86.5–87.5	62	56.08	56.37	2.35	2.44
p-CF_3	160.2–161.0	48	56.08	56.32	2.35	2.48
o-F	113.4–114.3	42	65.82	66.00	3.07	3.12
m-F	110.4–111.2	44	65.82	65.71	3.07	3.03
p-F	154.0–154.4	48	65.82	65.70	3.07	3.24