

at 210 $m\mu$ (ϵ 9300), 245 $m\mu$ (ϵ 345), 267 $m\mu$ (ϵ 260), 276 $m\mu$ (ϵ 224). Analysis of a small sample by means of vapor phase chromatography on a column containing silicone oil on fire-brick indicated that the sample was composed of three components in the ratio of 7:2:1.

Anal. Calcd. for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 83.51; H, 10.74.

Aromatization of the Diol XV.—To 84 mg. (0.50 mmole) of diol, m.p. 133–133.5°, was added 5 ml. of 20% (by volume) sulfuric acid, and the mixture was heated under reflux for 10 minutes. After cooling to 25° the mixture was worked up according to the procedure used for the aromatization of the diol XVI above. Distillation of the ether eluate in a Hickman column afforded 30 mg. of oil. Infrared spectrum (carbon disulfide solution): identical with that of product obtained in aromatization of diol XVI, except for minor differences in intensities of peaks in the 1000–1150 cm^{-1} region. A small sample was passed through a silicone-on-fire-brick column in the vapor phase at 200°, and the main component (70%) was collected in a small receiver in a Dry Ice trap. The chromatographed sample was taken up in ether and distilled in a small Hickman column at 190°, 1 atm., and the distillate was taken up in ethanol. Ultraviolet spectrum (concentration not determined): peaks at 247, 253, 259, 263, 265, 270 and 276 $m\mu$.

Aromatization of Mixture of Diols XV and XVI.—To 559 mg. (3.30 mmoles) of diols XV and XVI, m.p. 82–101°, was added 6 ml. of 20% (by volume) sulfuric acid, and the mixture was heated under reflux for 2 hr. The mixture was worked up according to the procedure used for the aromatization of the diol XVI above. Infrared spectrum (carbon disulfide solution): identical with that of 1,3-dimethyl-4-ethylbenzene, except for intensities of peaks in the 1000–1150 cm^{-1} region.

The chromatographed sample was passed through the column in the vapor phase for a second time, as above. Distillation of the product in a small Hickman column afforded a sample of 1,3-dimethyl-4-ethylbenzene. Infrared spectrum (carbon disulfide solution): identical with that of 1,3-dimethyl-4-ethylbenzene described below.

Anal. Calcd. for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 88.79; H, 10.56.

To 55 mg. of material from the vapor phase chromatogram was added 0.5 ml. of concentrated sulfuric acid and

dropwise, 0.5 ml. of fuming nitric acid. The mixture was heated on a steam-bath for 10 minutes and poured over 5 g. of ice. The yellow precipitate (90 mg.) was recrystallized from ethanol (fine needles) to constant m.p. 126.8–129°; no depression in m.p. after mixing with a synthetic sample of the trinitro compound described below.

One drop of hydrocarbon was added to one drop of synthetic 1,3-dimethyl-4-ethylbenzene. Analysis of the mixture by means of vapor phase chromatography on a column containing silicone oil on fire-brick indicated that only one molecular species was present.

1,3-Dimethyl-4-ethylbenzene (XXVI).—A solution of *m*-xylene in carbon disulfide was treated with aluminum chloride and acetic anhydride according to the procedure of Adams and Noller.²⁶ The 2,4-dimethylacetophenone was reduced by means of amalgamated zinc in hydrochloric acid according to the procedure of Martin.²⁷ A small quantity of the crude product was passed through a column of silica gel. The material eluted with petroleum ether was distilled in a Hickman column at 195°, 1 atm., affording a pure sample of 1,3-dimethyl-4-ethylbenzene, n_D^{20} 1.5008, the infrared spectrum of which was identical with Infrared Spectrum No. 736, American Petroleum Institute. Infrared spectrum (carbon disulfide solution): 690, 725, 734, 772, 784, 814, 871, 922, 940, 962, 975(sh), 1015, 1030, 1059, 1113, 1155, 1207, 1227, 1280, 1305, 1318, 1336, 1375, 1428, 1613, 1684, 1737, 1811, 1880, 2380, 2720, 2880, 2930, 2960, 3000(sh) and 3120 cm^{-1} .

A small amount of the synthetic material was nitrated as described above. The crystalline material was recrystallized from ethanol (small needles) to constant m.p. 127.4–129.5° (lit.²⁸ for trinitro derivative of 1,3-dimethyl-4-ethylbenzene).

Acknowledgments.—We are indebted to the National Institutes of Health for a fellowship to I. M. Goldman and to Mr. Monroe Evans for the high resolution infrared spectra.

CAMBRIDGE 39, MASS.

(26) R. Adams and C. R. Noller, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 109.

(27) E. L. Martin, *ibid.*, Coll. Vol. II, 1943, p. 499.

(28) J. Stahl, *Ber.*, **23**, 989 (1890).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF BARNARD COLLEGE]

Dissociation Constants of Acids and Rates of Alkaline Hydrolysis of Esters in the Benzylidenepyruvic Acid Series

BY EMMA DIETZ STECHER, FRANCES DUNN AND ERNESTINE GELBLUM

RECEIVED MARCH 1, 1957

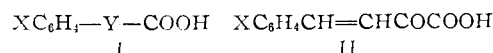
The dissociation constants of *m*- and *p*-substituted benzylidenepyruvic acids (pK_0 2.58) have been determined in 48 volume per cent. methanol–0.2 *M* lithium chloride and compared with those of substituted benzoic acids in the same solvent (pK_0 4.99). The ρ -value for the former is +0.106, for benzoic acids $\rho = +1.260$. The first-order rates of hydrolysis of substituted methyl benzylidenepyruvates have been determined spectroscopically at 24.8° in 11.8 volume per cent. methanolic buffers and compared with those of substituted methyl benzoates. The ρ -value for methyl benzylidenepyruvates is +0.484; for methyl benzoates it is +1.672. The rate for methyl benzylidenepyruvate is estimated as 47,400 times that of methyl benzoate. Data are included for *o*-methoxy- and *o*-nitrobenzylidenepyruvic acids and esters. Taft's polar substituent constant, σ^* , for $C_6H_5CH=CHCO$ relative to CH_3 is estimated as +1.9 (or +1.6) depending on the method of calculation.

In a series of substituted benzoic acids the inductive and resonance effects of the substituent groups are reflected in a predictable manner in the ionization constants of the acids. These group effects have been generalized and treated quantitatively by Hammett¹ and more recently by Jaffe.²

(1) (a) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter VI; (b) *Chem. Revs.*, **17**, 125 (1935); (c) *THIS JOURNAL*, **59**, 96 (1937).

(2) (a) H. H. Jaffe, *Chem. Revs.*, **53**, 191 (1953); (b) **53**, 253 (1953); (c) *J. Chem. Phys.*, **21**, 415 (1953).

Any grouping (Y in formula I) intervening between the benzene ring and the carboxyl group re-



duces the electronic effect of a substituent X—less however, if the group is unsaturated and conjugated with the ring. Thus β -phenylpropionic acids show smaller group effects than cinnamic acids, though in both cases Y contains two atoms.

In a previous paper³ data were reported on ionization constants for five substituted benzylidenepyruvic acids (II). In these keto acids Y is a 3-carbon system ($-\text{CH}=\text{CH}-\text{CO}-$) conjugated with the benzene ring; furthermore the ketone group is cross-conjugated with the carboxyl group. In water solution, group effects were too small to be detected by our experimental method (ρ is close to zero). In 48 volume % aqueous methanol-0.2 M lithium chloride as a solvent, effects were very small but measurable.

The present paper reports dissociation constants for two *o*-substituted and six additional *m*- and *p*-substituted benzylidenepyruvic acids in the same 48% methanol-lithium chloride solvent. For purposes of comparison, *pK*'s of five substituted benzoic acids were also determined in the same medium. The relative *pK*' values measured by *pH* titration and not corrected for activities are listed in Table I.

TABLE I
DISSOCIATION CONSTANTS^a OF BENZOIC ACIDS AND OF BENZYLIDENEPYRUVIC ACIDS IN 48% AQUEOUS METHANOL-0.2 M LiCl

Substituent	Benzoic acids <i>pK</i> ' ₂₅ ^b	Benzylidenepyruvic acids, <i>pK</i> ' ₂₅ ^c
2-OCH ₃		2.70
4-OCH ₃	5.30	2.60 ^d
4-OC ₂ H ₅		2.64
4-CH ₃	5.21	2.62 ^d
H	5.02 ^e	2.52 ^{d,f}
3-OCH ₃		2.57
4-Br		2.58
3-Br		2.52
3-NO ₂	4.04	2.51
4-NO ₂	4.05	2.51
2-NO ₂		2.54 ^g

^a *pK*' values were obtained by substituting *pH* values as given by the glass electrode and have only relative validity. ^b Two determinations were made; average deviation for the series ± 0.01 *pK*' unit. ^c Two to four determinations were made; average deviation for the series ± 0.025 *pK*' unit. ^d Our previous values were slightly lower (see Experimental section). ^e *pK*'₀ = 4.99 calculated from the least squares slope $\rho = +1.260 \pm 0.025$, $r = 0.999$ (see Jaffé^{2a} for method of calculation). A. L. Bacarella, E. Grunwald, H. P. Marshall and E. L. Purlee, *J. Org. Chem.*, 20, 747 (1955), report a *pK* value in 50 volume % methanol of 5.25 (interpolated). ^f *pK*'₀ calcd. = 2.58, $\rho = 0.106 \pm 0.027$, $r = 0.827$. ^g 2-OCH₃ and 2-NO₂ values were not used in determining ρ , but they fit the line well if Taft σ^* -values are used (-0.39 and $+0.80$).⁶

It will be noted that group effects are roughly in the same direction in both series of compounds, although they are much larger in the benzoic acids because of the shorter distance between substituent group and site of dissociation. In actual acid strength, however, benzoic acid (*pK*' 5.02) is much weaker than benzylidenepyruvic acid (*pK*' 2.52). This high degree of ionization is attributable to the electron-withdrawing effect of the carbonyl group (*pK* for pyruvic acid in water is 2.49⁴; for benzylidenepyruvic acid in water at 25° it is 1.97⁵).

Figure 1 is a plot of the *pK*' values in Table I referred to Hammett σ -values. Linear relationships are observed for both benzoic acids and *m*-

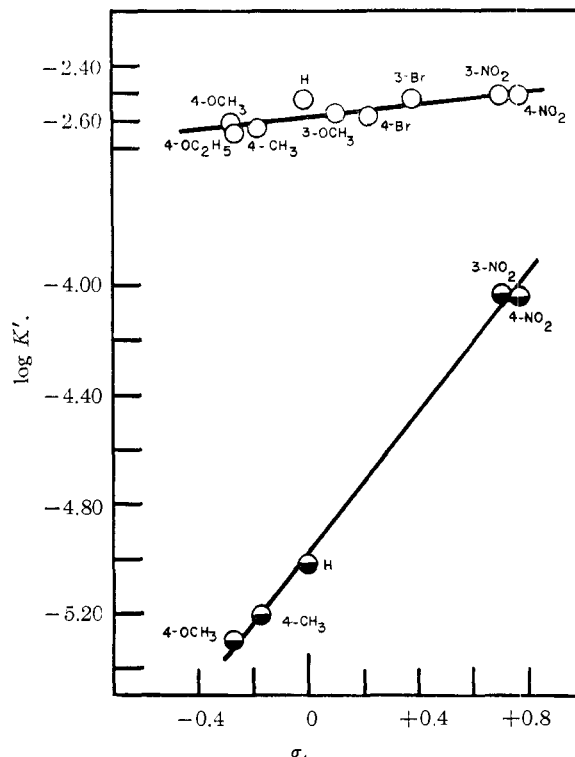


Fig. 1.—Plot of log dissociation constants against Hammett's σ -values in 48% methanol-0.2 M lithium chloride: O, benzylidenepyruvic acids; ●, benzoic acids.

and *p*-substituted benzylidenepyruvic acids, but the slopes of the lines (ρ -values) are quite different. ρ for the dissociation of the benzoic acids in this medium is $+1.260$ with an average deviation from the least square line of ± 0.025 and a correlation coefficient (r) of 0.999.^{2b} This agrees well with the value of 1.241 calculated by Grunwald and Berkowitz^{5a} from the data of Kuhn and Wasserman^{5b} determined in 50% methanol. Grunwald has derived a quantitative relationship between ρ -values for substituted benzoic acids in different solvents.

$$\rho = \rho^w + 0.628Y_-$$

where ρ is the reaction constant in a given solvent and ρ^w is the reaction constant in water (1.00), Y_- is an activity function characteristic of carboxylate-carboxylic acid equilibria in a given solvent. Substituting our ρ -value (1.260) in this equation we calculate $Y_- = 0.414$ for our solvent (48 volume % methanol-0.2 M lithium chloride).

The ρ -value calculated for the *m*- and *p*-benzylidenepyruvic acids in the same solvent is $+0.106 \pm 0.027$, $r = 0.827$. This ρ -value is less than one-tenth that for the substituted benzoic acids. Since ρ is a measure of the degree of transmission of electronic group effects through the molecule to the carboxyl group, it follows that the $-\text{CH}=\text{CH}-\text{CO}-$ group is a very weak transmitter of such effects.

Table I includes *pK*' values for *o*-methoxy- and *o*-nitrobenzylidene-pyruvic acids. Both acids are

(3) E. D. Stecher and H. F. Ryder, *THIS JOURNAL*, 74, 4392 (1952).
(4) E. G. Clair and K. Wiesner, *Nature*, 165, 202 (1950).

(5) (a) E. Grunwald and B. J. Berkowitz, *THIS JOURNAL*, 73, 4939 (1951); (b) R. Kuhn and A. Wasserman, *Helv. Chim. Acta*, 11, 1, 31, 44 (1928).

a little weaker than the *para* substituted compounds. In this they resemble the cinnamic acids rather than the benzoic acids, which show very large *ortho* substituent effects.

If the pK' values for the two *o*-acids are plotted against Taft σ^* -values,⁶ they fall on the line for the *m*- and *p*-acids; ρ for the ionization of *ortho* cinnamic, phenylacetic and phenylpropionic acids also seems to be the same as that for the *m*- and *p*-derivatives. But as Taft has pointed out,⁶ ρ for the ionization of *o*-substituted benzoic acids in water at 25° is +1.787 as compared with 1.000 for the *m*- and *p*-substituted acids.

The second part of this investigation is concerned with the determination of hydrolysis rates of substituted methyl benzylidenepyruvates. In a previous paper³ we reported very small group effects in the acid-catalyzed hydrolysis of these esters in 50% dioxane ($\rho + 0.049$, calculated by Jaffé^{2b}). It is known that hydrolysis rates in alkali show much greater differences due to structure but the methyl benzylidenepyruvates hydrolyze too rapidly in alkali to permit measurement of rates by the usual titration procedure. However, a spectroscopic method has now been worked out using a 0.2 *M* phosphate buffer of pH 7.72 prepared in 11.8 volume per cent. of aqueous methanol. This involved reading on a spectrophotometer (provided with a thermostated cell compartment) the change in absorbancy with time. This change was measured at a single wave length chosen at a point where there is a considerable difference between the absorption of acid and ester (see Fig. 2). Since

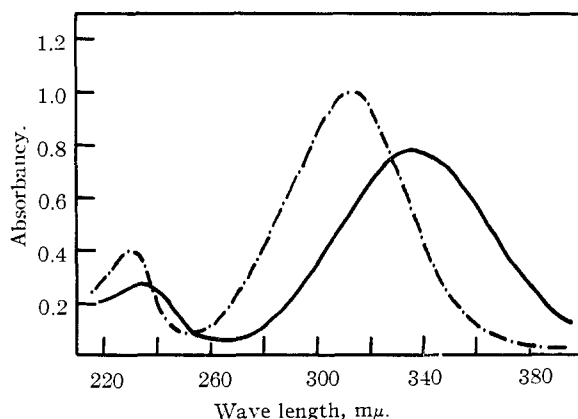


Fig. 2.—Absorption spectra in 11.8% methanol: ——— *p*-methylbenzylidenepyruvic acid in pH 7.7 buffer; - - - - - methyl ester in 4.0 buffer.

the buffer provides a constant hydroxyl ion concentration, the normally second-order hydrolysis becomes first order. Very good linear relationships were obtained, from the slopes of which rate constants were calculated. These constants (k') are equal to the product of the familiar bimolecular rate constant (k) and the hydroxyl ion concentration.

$$k' = k(\text{OH}^-) \quad (1)$$

(6) (a) R. W. Taft, Jr., *THIS JOURNAL*, **74**, 2729, 3116 (1952); **75**, 4231 (1953); (b) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chap. 13.

In Table II are listed specific first-order rate

TABLE II
SPECIFIC RATES OF HYDROLYSIS OF SUBSTITUTED METHYL BENZYLIDENEPYRUVATES IN 11.8% METHANOL AT pH 7.72^a

Substituent	$k' \times 10^3$, sec. ⁻¹	
	24.8°	34.6°
2-OCH ₃	1.66 ± 0.07 ^b	
4-OCH ₃	1.26 ± .05	3.63 ± 0.08 ^c
4-OC ₂ H ₅	1.33 ± .03	
4-CH ₃	1.80 ± .02	4.85 ± 0.13
H ^d	2.23 ± .11	
3-OCH ₃	2.31 ± .06	
4-Br	2.55 ± .07	7.08 ± 0.10
3-Br	2.97 ± .07	
3-NO ₂	3.97 ± .07	
4-NO ₂	4.68 ± .21	
2-NO ₂	4.61 ± .07	

^a Na₂HPO₄-KH₂PO₄ at an ionic strength of 0.6. ^b Four to ten determinations were made at 24.8°. ^c Four determinations were made for each acid at 34.6°. ^d $\log k'_0 = -2.71$, calcd. from the least squares slope; $\rho = 0.484 \pm 0.015$, $r = 0.978$; 2-OCH₃ and 2-NO₂ values were not used in determining ρ , but they fit the line well if Taft σ^* -values are used (-0.39 and +0.80).⁶

constants at 24.8° for the hydrolysis of ten methyl benzylidenepyruvates in an 11.8 volume % methanolic phosphate buffer of measured pH 7.72. Using the same spectroscopic method, the rates of hydrolysis of five substituted methyl benzoates were determined. Since the benzoic esters hydrolyze much more slowly, a more alkaline 11.8% methanolic phosphate buffer (pH 11.04) of about the same ionic strength was used to produce convenient reaction speeds. Table III lists the first-

TABLE III
SPECIFIC RATES OF HYDROLYSIS OF SUBSTITUTED METHYL BENZOATES IN 11.8% METHANOLIC PHOSPHATE BUFFER AT pH 11.04^a

Substituent	$k \times 10^4$, sec. ⁻¹	
	24.8°	
4-OCH ₃	0.355 ± 0.02 ^b	
4-CH ₃	0.527 ± .001	
H ^c	1.02 ± .02	
3-NO ₂	14.7 ± .03	
4-NO ₂	21.1 ± .2	

^a Na₂HPO₄-NaOH at a total molarity of about 0.2 ($\mu = 0.69$). ^b At least two determinations were made for each acid. ^c $\log k'_0$ calcd. = -4.00, $\rho = 1.672 \pm 0.019$, $r = 0.998$.

order rate constants obtained. Although two different hydroxyl ion concentrations were used, it is valid to compare values within each series. It will be noted that the spread of rates due to group effects is much greater among the benzoic esters than in the benzylidenepyruvic series. As would be expected, the *p*-nitro esters hydrolyze most rapidly and the *p*-methoxy esters most slowly in both series.

Table II lists also the hydrolysis constants for three of the benzylidenepyruvic esters at 34.6° and pH 7.72. To calculate activation energies, k rather than the listed k' values (see equation 1) must be substituted in the Arrhenius equation. In order to estimate accurately the hydroxyl ion concentration of the hydrolysis buffers, it is necessary to know the ion product of water (K_w) in this solvent (11.8% aqueous methanol of ionic strength

0.6) at the two temperatures. Since these K_w values are not known, we have used first-order rates, k' to calculate activation energies which include the heat of ionization of the solvent.

The activation energies calculated in this way for the 4-methoxy-, 4-methyl- and 4-bromobenzylidenepyruvic esters are 19.7, 18.4 and 19.0 kcal., respectively. Values for the activation energies of second-order alkaline hydrolysis of substituted ethyl benzoates are 17 to 19 kcal. in 85% ethanol⁷ and 14,560 kcal. in 56% acetone.¹⁰

According to equation 1 the hydrolysis rate is proportional to the hydroxyl ion concentration. In order to test this, methyl *p*-bromobenzylidenepyruvate was hydrolyzed in three different phosphate buffers of measured *pH* 7.47, 7.72 and 8.06. When the resultant rates (see Table IV) were

TABLE IV

VARIATION OF HYDROLYSIS RATE OF METHYL *p*-BROMOBENZYLIDENEPYRUVATE WITH APPARENT HYDROXYL ION CONCENTRATION

<i>pH</i>	Apparent ^a (OH ⁻) × 10 ⁷	k' , sec. ⁻¹ × 10 ³
7.47 ^b	2.95	1.47 ± 0.02 ^c
7.72	5.25	2.55 ± .07
8.05	11.2	5.32 ± .06

^a Calculated from the ion product of water (pK_w 14.003 at 24.8°). ^b Na₂HPO₄-KH₂PO₄ buffers of ionic strength 0.6 in 11.8% methanol. ^c At least 4 determinations were made at each *pH*.

plotted against apparent hydroxyl ion concentration, an excellent linear relationship was obtained. The apparent hydroxyl ion concentration was calculated from the *pH* data and the ion-product of water (14.003 at 24.8°). Since the solvent is 11.8% methanol and not water, a small but apparently systematic error is involved in this procedure. An extrapolation of the line in Fig. 2 goes very close to the origin indicating that there is no significant hydrolysis catalyzed by water itself. The water rate read from the line is 0.10×10^{-3} sec.⁻¹ which is negligible compared with the observed rate of 2.55×10^{-3} sec.⁻¹ at *pH* 7.72 for the hydrolysis of the ester.

Assuming that the ester hydrolysis rates are all directly proportional to apparent hydroxyl ion concentration, one can calculate a rate for methyl benzylidenepyruvate at *pH* 11.04 for comparison with the rate observed for methyl benzoate at this *pH* (1.02×10^{-4} sec.⁻¹). The calculated value for the keto ester at *pH* 11.04 is 4.81 sec.⁻¹ or 47,400 times as fast as methyl benzoate. Since the two buffers differ in ionic strength ($\mu = 0.60$ for *pH* 7.72 and 0.69 for *pH* 11.04), these figures include a 3% increase in rate in accordance with our experimental determination of change of rate with ionic strength (see table in Experimental Section).

The α -carbonyl group appears to be much more important in determining the very high rate of hydrolysis of the benzylidenepyruvic esters than the rest of the molecule. The carbonyl group

(7) (a) C. K. Ingold and W. S. Nathan, *THIS JOURNAL*, 222 (1936); (b) D. P. Evans, J. J. Gordon and H. B. Watson, *J. Chem. Soc.*, 1430 (1937).

(8) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd ed., Reinhold Publishing Corp., New York, N. Y., 1950, Chapter 15.

induces an increased positive charge on the ester carbon atom, thus greatly facilitating nucleophilic attack at this point by the hydroxyl ion. Thus Skrabal⁹ found that the rate of alkaline hydrolysis of ethyl pyruvate is 16,500 times that of ethyl acetate.

The observed rate of hydrolysis (k') of methyl benzoate at *pH* 11.04 can be used to estimate a bimolecular rate constant (k) for comparison with that in the literature. Thus 1.02×10^{-4} sec.⁻¹ divided by 1.10×10^{-3} mole/l., the apparent hydroxyl ion concentration at *pH* 11.04, gives a rate of 9.33×10^{-2} l. mole⁻¹ sec.⁻¹. The value reported¹⁰ for methyl benzoate in 60% acetone at 25° is 8.41×10^{-3} l. mole⁻¹ sec.⁻¹. Our value is reasonable when one considers the difference in solvents and that the rate increases with dielectric constant of the solvent.

When the logarithms of the rate constants in Table II for the hydrolysis of *m*- and *p*-substituted benzylidenepyruvic esters are plotted against Hammett σ -values, a straight line is obtained (Fig. 3) the slope of which is ρ ($+0.484 \pm 0.015$,

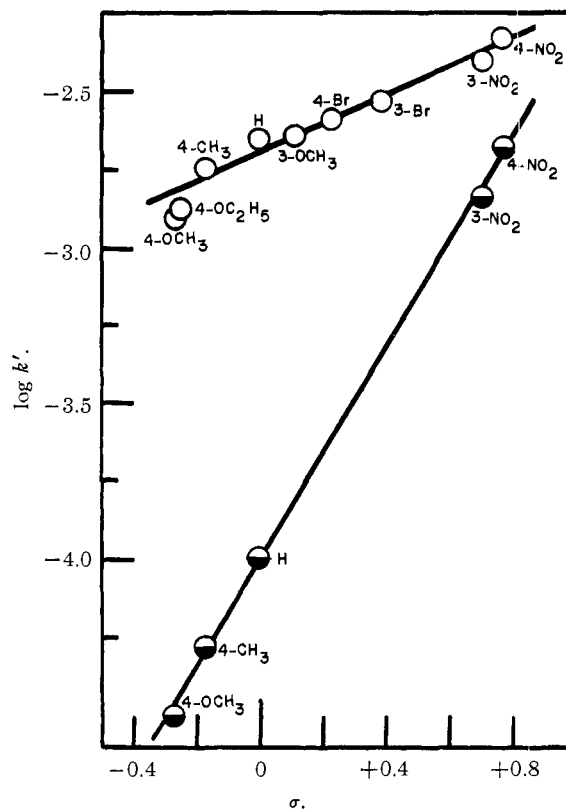


Fig. 3.—Plot of $\log k'$ (hydrolysis) against Hammett's σ -values in 11.8% methanolic buffer: O, methyl benzylidenepyruvates at *pH* 7.72; ●, methyl benzoates at *pH* 11.04.

$r = 0.978$). The lower line is a similar plot of the logarithms of the hydrolysis constants listed in Table III for the methyl benzoates; ρ in this case is $+1.672 \pm 0.019$, $r = 0.998$. A comparison of these two ρ -values indicates that the $-\text{CH}=\text{CH}-\text{CO}-$

(9) A. Skrabal, F. Pfaff and H. Airoldi, *Monatsh.*, 45, 148 (1924).

(10) E. Tommila and C. N. Hinshelwood, *J. Chem. Soc.*, 1801 (1938).

side chain in the benzylidenepyruvic acid esters reduces the transmission of group effects to 29% of that in the benzoic ester series.

The relative ρ -value (ρ/ρ^0) is a useful index for the comparison of the transmission of group effects in different molecules. It is the ratio of ρ for any given reaction for a series of compounds, compared to ρ for the same reaction in the same solvent for the benzoic series. Jaffé² believes this relation to be a constant independent of reaction type for a given side chain (Y in formula I) and has calculated its value by molecular orbital theory from atom-atom polarizabilities. Our relative ρ -value from acid dissociation is 0.084 and from alkaline hydrolysis of the methyl esters it is 0.289. Table V compares these results with values taken from

TABLE V

Acid	ρ/ρ^0 acid dissn.	ρ/ρ^0 ester hydrol.	ρ/ρ^0 calcd. by Jaffé
Phenylacetic	0.489	0.336	
Cinnamic	.466	.542	0.683
Biphenylcarboxylic	.341	.262	.177
Phenylpropionic	.212	.196	
Benzylidenepyruvic	.084	.289	-.010

Jaffé. The ratio 0.084 is lower than that observed for any other side chain, indicating that the transmission of polarity falls off rapidly with length of chain.

The relative ρ for ester hydrolysis, 0.289, is greater than would be expected and is close to the value 0.262 for biphenylcarboxylic esters. As in the case of cinnamic esters, the fact that the side chain is conjugated with the ring makes the relative ρ -value greater than that determined from ionization constants.

Also included in Table II are values for two o -substituted benzylidenepyruvic esters. Their rates of hydrolysis are very slightly higher than those of the corresponding p -substituted esters. This is in contrast to the large retarding effect of o -substituents on the rate of hydrolysis of ethyl benzoate,^{7b,11} where such substituents interfere with attack of the hydroxyl ion on the neighboring carbonyl group. Taft⁶ suggests that the ratio of the rates of o - and p -substituted derivatives is often a good measure of steric effects.

If our $\log k'$ values are plotted against Taft's σ^* -values^{6b} (-0.39 for o -OCH₃ and $+0.80$ for o -NO₂), they fit the line derived from the m - and p -substituted ester values as well as the other points. In the cinnamic ester series o -substituents have very little effect on the rate of hydrolysis.¹¹

It seems of interest to consider the polarity of the C₆H₅CH=CHCO— (cinnamoyl) group present in our compounds relative to the styryl (C₆H₅CH=CH—) and acetyl groups. Taft⁶ has introduced polar substituent constants, σ^* , which enable one to do this. σ^* -values are a measure of the polar nature of various groups, R, relative to methyl as a standard. They are widely applicable and additive in nature.

There follows a calculation of σ^* for the cinnamoyl group according to methods developed by Taft. The first uses the dissociation constant in

(11) K. Kindler, *Ann.*, **450**, 1 (1926); **452**, 90 (1927); **464**, 278 (1928).

water at 25° relative to that of acetic acid, according to the relationship

$$\log (K/K_0) = \sigma^* \rho^* + \psi \quad (2)$$

where ψ is a resonance parameter with a value of -0.5 . Substituting $\log K$ for benzylidenepyruvic acid = -1.97^3 and $\log K_0$ for acetic acid = -4.76 and $\rho^* = +1.721^6$, σ^* is found to be $+1.92$. Taft points out that unless ψ is used, this method of calculation leads to low values for benzoic, cinnamic and crotonic acids. These are all weaker than acetic acid, although the unsaturated groups are electron withdrawing and should make them stronger. Taft cites Branch and Calvin's explanation that resonance of the phenyl or other unsaturated group with the carboxyl stabilizes the free acid more effectively than it does the anion.

Another method of calculation suggested by Taft avoids difficulties with resonance. In the expression

$$\log \left(\frac{k}{k_0} \right)_B - \log \left(\frac{k}{k_0} \right)_A = 2.48 \sigma^* \quad (3)$$

the relative rates are for acid- and base-catalyzed hydrolysis of the same ester referred to the corresponding acetate. From data in the present paper, $\log (k_{C_6H_5CH=CHCOOCH_3}/k_{C_6H_5COOCH_3})_B = +4.61$ determined in alkaline buffers containing 11.8 volume per cent. of methanol. Also $\log (k_{C_6H_5CH=CHCOOCH_3}/k_{CH_3COOC_2H_5})_A = -0.32$ determined in 50% dioxane.³ Adding $\log (k_{C_6H_5COOCH_3}/k_{CH_3COOCH_3})_B = -1.06$, to $+4.61$ and $\log (k_{CH_3COOC_2H_5}/k_{CH_3COOCH_3})_A = -0.09$ to -0.32 refers both rates to methyl acetate; and σ^* is found to be $+1.60$.

In a private communication Taft has expressed concern over the above substitution of our rates determined in highly aqueous solutions, when the 2.48 factor is based on ρ for basic hydrolysis in 60% acetone or 85% ethanol. A value smaller than 2.48 may apply here.^{11a}

Depending on the method of calculation two σ^* -values also are obtained for the acetyl group, based on measurements on pyruvic acid and ester. The preferred value is $+1.65$ calculated by Taft from equation 3. Another method uses equation 2 without the resonance factor, ψ . This leads to a value for σ^* of 1.3. This low substituent constant may be due either to a resonance effect or to enolization, both of which would weaken the acid strength. Indeed pyruvic acid (pK 2.49) is weaker than benzylidenepyruvic acid (pK 1.97) in water solution.

Experimental

Preparation of Compounds.—The benzoic acids and esters were Eastman Kodak Co. products purified if necessary. Table V lists the benzylidenepyruvic acids and esters synthesized, many of which have been described.^{3,12,13} Analyses are given for the six new compounds. All of the acids were prepared by the condensation of pyruvic acid with the

(11a) Unpublished data on the rates of alkaline hydrolysis of methyl benzylidenepyruvate and of methyl benzoate in 50% methanol, determined by a titration method and substituted in Equation 3, gave a σ^* value of $+1.9$.

(12) (a) M. Reimer, *THIS JOURNAL*, **46**, 785 (1924); (b) M. Reimer and E. Tobin, *ibid.*, **62**, 2518 (1940); (c) M. Reimer and M. Howard, *ibid.*, **50**, 2507 (1928); (d) M. Reimer and H. Kamerling, *ibid.*, **55**, 4645 (1933); (e) M. Reimer, *ibid.*, **48**, 2458 (1941); (f) M. Reimer and A. L. Morrison, *ibid.*, **63**, 236 (1941); (g) M. Reimer and E. Chase, *ibid.*, **60**, 2470 (1938).

(13) E. D. Stecher and A. Clements, *ibid.*, **76**, 503 (1954).

corresponding aldehyde, using an alkaline catalyst. Pyruvic acid and the nitro aldehydes were Eastman Kodak Co. products purified when indicated. The benzylidenepyruvic esters were prepared using diazomethane, or methanol with hydrogen chloride as catalyst.

TABLE V
BENZYLIDENEPYRUVIC ACIDS AND ESTERS^a
 $\text{XC}_6\text{H}_4\text{CH}=\text{CHCOCOOH}(\text{CH}_3)$

X	Acids		Esters	
	M.p., °C.	Lit. m.p., °C.	M.p., °C.	Lit. m.p., °C.
H	71-72 ^a	61-62 ^{12a}	73-74	73-74 ^{12a}
3-Br	103-104 ^b	...	127-128 ^c	...
4-Br	141-142	143 ^{12b}	122-122.8	122 ^{12b}
2-OCH ₃	132-133	131 ^{12c}	47	48 ^{12c}
3-OCH ₃	118-119	116-117 ^{12d}	55	57 ^{12d}
4-OCH ₃	131-132	131 ^{12e}	107-108	106 ^{12e}
4-OC ₂ H ₅	90	89-90 ^{12f}	79-80	79 ^{12f}
4-CH ₃	128-130	127 ^{12g}	82-83	81 ^{12g}
3-NO ₂	149-150 ^e	...	170-171 ^f	...
4-NO ₂	111(hydrate)	111(hydrate) ¹⁴	182.5-183.5 ^g	...
2-NO ₂	194 dec. ^d	...	97-98 ⁱ	...

All melting points are corrected.

^a The acids and esters were recrystallized from benzene-petroleum ether. The less soluble bromo and nitro compounds were recrystallized from acetone-petroleum ether. The acids solvate and hydrate readily. All were dried for 2 hr. at 5 mm. and 35° or 70°. The melting point of anhydrous benzylidenepyruvic acid falls 5 to 10° on exposure to air. ^b *Anal.* Calcd. for C₁₀H₇O₃Br: C, 47.08; H, 2.77; Br, 31.33. Found: C, 47.15; H, 2.93; Br, 31.53. ^c *Anal.* Calcd. for C₁₀H₇O₃N: C, 54.29; H, 3.19; N, 6.33. Found: C, 54.48; H, 3.16; N, 6.54. *Anal.* Calcd. for C₁₀H₇O₃N₂H₂O: C, 50.20; H, 3.79; N, 5.86. Found: C, 50.43; H, 3.74; N, 5.92. ^d *Anal.* Calcd. for C₁₀H₇O₃N: C, 54.29; H, 3.19; N, 6.33. Found: C, 54.42; H, 3.29; N, 6.23. ^e *Anal.* Calcd. for C₁₁H₉O₃Br: C, 49.08; H, 3.38; Br, 29.70. Found: C, 49.18; H, 3.65; Br, 30.05. ^f *Anal.* Calcd. for C₁₁H₉O₃N: C, 56.15; H, 3.86; N, 5.96. Found: C, 56.40; H, 3.65; N, 5.95. ^g *Anal.* Calcd. for C₁₁H₉O₃N: C, 56.15; H, 3.86; N, 5.96. Found: C, 56.31; H, 3.82; N, 6.09. ^h *Anal.* Calcd. for C₁₀H₇O₃N: C, 54.29; H, 3.19; N, 6.33. Found: C, 54.43; H, 3.23; N, 6.46. ⁱ *Anal.* Calcd. for C₁₁H₉O₃N: C, 56.15; H, 3.86; N, 5.96. Found: C, 56.30; H, 3.76; N, 6.01.

Detailed directions for the preparation of the *p*-nitro compounds will be reported in another paper, which will include also tautomeric enol lactones in this series. Ciusa¹⁴ reported as pure keto acids compounds which we have shown to be *m*-nitro acid hydrate and *o*-nitro enol lactone. Our three keto acids are new compounds the structures of which have been substantiated by analysis, by infrared and ultraviolet absorption data, by dissociation constants and by the rapid hydrolysis rates of their methyl esters.

***m*-Bromobenzylidenepyruvic Acid.**—*m*-Bromobenzaldehyde,¹⁵ b.p. 104°, (17 mm.) was prepared from *m*-nitrobenzaldehyde. *m*-Bromobenzylidenepyruvic acid was prepared by the general procedure already described.³ The yield of yellow potassium salt was 86%. The acid is best recovered by acidifying the water solution of the salt with hydrochloric acid in the presence of ether, drying the ether solution with magnesium sulfate and concentrating. Benzene (300 ml.) was added and the solution was distilled at room temperature until no further water of hydration came off. After recrystallizing from benzene and from acetone-petroleum ether, the shiny yellow crystals of acid melted at 103-104°. The ester prepared from 5 g. of acid and 25 ml. of hot methanol containing about 5% of hydrogen chloride, crystallized immediately in 98% yield. Recrystallization from methanol yielded shiny yellow needles, m.p. 127-128°.

Dissociation Constants of the Acids.—The method of operation and calculation for both benzylidenepyruvic acids and benzoic acids was the same as that previously described in detail.³ For the less soluble nitro esters it was found convenient to dissolve the sample (0.001 mole) in 100 ml.

of purified methanol and then to add 100 ml. of 0.4 N aqueous lithium chloride solution. The total volume was 193 ml. at 25°. The alkali used for titration was 50% in methanol and 0.2 M in lithium chloride. This was prepared by mixing equal volumes of purified methanol and of carbon dioxide-free distilled water and adding a clear saturated solution of aqueous sodium hydroxide to produce a total normality of about 0.07. The required quantity of freshly dried solid lithium chloride (Merck reagent grade) was then added and the solution was standardized as usual.

The titration curves of the benzylidenepyruvic acids were determined with a Beckman model G pH meter, using outside glass and calomel electrodes. The curves were typical of strong acids with an end-point at about pH 7.25. The *pK'* values were found by the conventional method which takes into account the ionization of the acid.³ A blank titer of 0.02 ml. was obtained using solvent swept with nitrogen and from thymol blue as an indicator. Former data were recalculated on the basis of this new blank and of the shrinkage in volume to 193 ml. on mixing the solvents. The new *pK'* values are higher by about 0.03 to 0.10 unit than those previously reported.³ The *pK'*'s of the weaker benzoic acids were read directly from the mid-points of the titration curves.

Hydrolysis Rates of the Esters.—In an alkaline buffer of constant hydroxyl ion concentration, the normally second-order rate of hydrolysis of an ester becomes first order. The rate constant, *k'*, may be calculated from the familiar integrated form of the equation

$$k'(t_2 - t_1) = \ln(c_1/c_2) \quad (4)$$

in which *k'* is the rate constant and includes the hydroxyl ion concentration (see equation 1), *t*₁ and *t*₂ are time readings and *c*₁ and *c*₂ are the corresponding ester concentrations. Since the absorption curves of acid anion and ester are somewhat different, spectroscopy provides a convenient method for determining the ratio of ester concentrations. In a hydrolysis this ratio can be determined from absorbancy readings (*A*) at a single wave length. Equation 2 becomes

$$k' = \frac{2.303}{t_2 - t_1} \log \left(\frac{A_1 - A_\infty}{A_2 - A_\infty} \right) \quad (5)$$

The rate, *k'*, is the slope of log (*A* - *A*_∞) plotted against time, multiplied by 2.303, and is independent of the concentration of ester used.

Buffer Solutions.—pH values were all measured with a Beckman model G pH meter provided with outside glass and calomel electrodes (accuracy ±0.01 pH unit). Standard phthalate (pH₂₅ 4.01) and phosphate (pH₂₅ 7.00) buffers were used to set the pH meter. Our pH values are all "apparent" values since they include an error of unknown magnitude due to the liquid junction potential.

Stock solutions of buffers were prepared in 10% methanol. Solutions of (apparent) pH 7.45, 7.70 and 8.03 of constant ionic strength (0.6) were made from various mixtures of two solutions A and B. (For hydrolysis 2 ml. of methanol was added to 100 ml. of buffer, thus raising the pH by 0.02 unit and the methanol content to 11.8%.) Solution A, 0.2 M disodium hydrogen phosphate was prepared by dissolving the salt (anhydrous reagent grade) rapidly in 500 ml. of carbon dioxide-free distilled water at 60°, cooling and adding 100 ml. of purified methanol and then water to a total volume of one liter at 25°. Solution B, 0.6 M potassium dihydrogen phosphate, was similarly prepared in 10% methanol from anhydrous reagent grade salt. Solution B was added to A until the desired pH reading was reached. For example for the buffer of pH 7.70, 1.5 l. of A was mixed with 68 ml. of B; for pH 7.40, 2 l. of A was mixed with 153 ml. of B; and for pH 8.00, 1.95 l. of A was combined with 40 ml. of B. The buffer of pH 11.0 used for the benzoic ester hydrolysis was prepared from 1.65 l. of A and 246 ml. of 0.45 N sodium hydroxide prepared in 10% methanol (ionic strength 0.69). Insofar as possible enough of a given buffer was prepared for a complete series of hydrolyses; and the solutions were stable and clear for several months. Because of the good linear relationship between apparent hydroxyl ion concentration and hydrolysis rate, small adjustments were made in the rates to correspond to small differences in pH (±0.04) of successive batches of buffer. For hydrolysis at the higher temperature a buffer prepared from solutions A and B was adjusted to pH 7.72 at 34.6°. Standard aqueous buffers of pH 4 and 7 of known temperature coefficient were used to set the pH meter.

(14) R. Ciusa, *Gazz. chim. ital.*, **49**, I, 168 (1919).

(15) J. S. Buck and W. S. Ide, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 132.

The rate of hydrolysis varies somewhat with ionic strength of the buffer. This is shown by the following data on the hydrolysis of methyl benzylidenepyruvate in three phosphate buffers, all of pH 7.72 and 11.8% in methanol.

Soln. A Na_2HPO_4 , mole/l.	Soln. B K_2HPO_4 , mole/l.	Ionic strength, μ	$k' \times 10^3$, sec. ⁻¹
0.2	0.6	0.6	2.23
.15	.45	.45	2.06
.1	.3	.3	1.77

This relationship is not quite linear. Ionic strength was calculated from the expression $\mu = \frac{1}{2}cZ^2$ in which c is the concentration in moles per liter and z is the ionic charge. These results are subject to some uncertainty due to varying liquid junction potentials at different ionic strengths.

Kinetic Measurements.—A Beckman DU spectrophotometer was provided with four Beckman thermospacers through which water at $25 \pm 0.1^\circ$ was circulated from a thermostat, thus maintaining the cell compartment at $24.8 \pm 0.1^\circ$. In the summer the room temperature was kept close to 25° by means of an air conditioner. For the higher temperature the thermostat was held at $35 \pm 0.2^\circ$ and the cell temperature was $34.6 \pm 0.2^\circ$.

Spectra were taken of $4 \times 10^{-5} M$ solutions of acid in the alkaline hydrolysis buffer (where it exists as the anion) and the same concentration of ester in a buffer of pH 4 (0.2 M potassium dihydrogen phosphate-phosphoric acid). This weakly acidic buffer prevents any alkaline hydrolysis of the ester. From the plot of these spectra a wave length was then chosen where there was a difference of 0.2–0.4 absorbancy (optical density) unit and where the readings were in the more accurate part of the absorbancy scale (0.75–0). If the slope of the absorption curve of the acid anion is a minimum or is changing slowly, a more precise end-point can be reached (A_∞). Figure 2 shows spectra for benzylidenepyruvic acid and its methyl ester. Rates for this ester were measured at 345 $m\mu$ and a narrow slit width, 0.25 mm. Experiment showed that both acid and ester solutions followed Beer's law on dilution.

For the hydrolysis a methanol solution of the ester was added to the buffer in such a way as to minimize the temperature rise accompanying the addition of methanol (0.8° for 2 ml.). The ester solution was prepared from 2 or 4×10^{-4} mole dissolved in 50 ml. of purified methanol. In a stoppered 250-ml. erlenmeyer flask, 100 ml. of buffer and 1 ml. of methanol were brought to 24.5° . Then 1 ± 0.05

ml. of ester solution was dropped rapidly into the swirling buffer from a Mohr pipet with widened end, and a stop watch was started at the same time. As it does not enter the calculations, the exact concentration of ester is not critical and is determined by convenience. A 10-mm. stoppered, Beckman silica cell was filled as rapidly as possible, and the absorption was measured against the solvent cell filled with the same buffer. Readings were taken at 0.5 minute intervals at the start, later at longer intervals to determine the end value, A_∞ . The solution in the cell came to constant temperature in about two minutes.

Values of $\log(A - A_\infty)$ were plotted against time. The table lists typical data for the hydrolysis of methyl β -methylbenzylidenepyruvate and the slope of the line multiplied by 2.303 is equal to k' (see equation 5).

Time, min.	A	A - A ∞	Time, min.	A	A - A ∞
1.5	0.410	0.340	5.0	0.305	0.235
2.0	.395	.325	6.0	.281	.211
2.5	.376	.306	7.0	.261	.191
3.0	.361	.291	8.0	.242	.172
3.5	.345	.275	9.0	.225	.155
4.0	.331	.261	10.0	.209	.139
4.5	.317	.247	54.0	.070	.0

The rate obtained in this way is 0.108 min.⁻¹. The best line was drawn through the first nine points with a very good fit (standard deviation from $k' = 0.003$). Based on the first 14 points representing 89% hydrolysis the standard deviation is 0.008. From six to nine determinations were made on each of the benzylidenepyruvic esters and four determinations on each benzoic ester. After hydrolysis the pH of each rate solution was measured. An occasional check of the complete spectrum of the hydrolysis solution indicated that no decomposition had taken place.

Acknowledgment.—We gratefully acknowledge grants from the Research Corporation and from the National Science Foundation and wish to thank Dr. E. J. King for helpful advice on measurements. We also derived much benefit from conversations with Drs. L. P. Hammett, E. Grunwald and R. W. Taft, Jr.

NEW YORK 27, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

A Study of Organosilicon Free Radicals

BY JAY CURTICE,¹ HENRY GILMAN AND GEORGE S. HAMMOND

RECEIVED MARCH 11, 1957

Organosilicon free radicals have been studied as reactive intermediates in radical induced reactions of triphenylsilane, and as chain transfer agents in the thermal polymerization of styrene. Triphenylsilane was found to undergo a peroxide initiated oxidation to triphenylsilanol. The rates of oxidation of triphenylsilane initiated by azo-bis-isobutyronitrile were measured by following oxygen uptake. Evidence was found for the abstraction of chlorine from chlorobenzene by the triphenylsilyl radical; this reaction was studied under a variety of conditions.

Hexaaryldisilanes do not show any of the "unsaturated" properties characteristic of hexaphenylethane, nor do they show any other evidence of dissociation into triarylsilyl radicals at temperatures up to 130° .^{2,3} The apparently higher bond dissociation energy of the Si-Si bond in a hexaaryldisilane, as compared to the C-C bond in a

hexaarylethane, has been attributed to the lower reorganization energy of the triarylsilyl radicals, which can in turn be attributed to the lack of resonance energy of the triarylsilyl radicals, and the lack of steric strain in the hexaaryldisilane.^{3a}

Following the procedures developed by Kharasch and co-workers for the addition of chloroform, carbon tetrachloride, and a wide variety of other reagents to the double bond of terminal olefins,⁴ a

(1) Du Pont Predoctoral Fellow 1952–1953.

(2) W. Schlenk, J. Renning and G. Rackey, *Ber.*, **44**, 1178 (1911).

(3) (a) H. Gilman and G. E. Dunn, *THIS JOURNAL*, **73**, 5077 (1951);

(b) H. Gilman and T. C. Wu, *ibid.*, **76**, 3762 (1953).

(4) M. S. Kharasch, E. J. Jensen and W. H. Urry, *Science*, **102**, 128 (1945).