[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF IOWA STATE COLLEGE]

Benzyl Tosylates. III. The Relative Conjugative Aptitudes of the Acetylenic and Ethylenic Bonds

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The characters of ethylenic and acetylenic units in conjugated systems have been compared. The groups β-styryl and phenylethynyl have been treated as meta and para substituents in the Hammett relationship. As para substituents both accelerate the solvolysis of benzyl tosylates more than would be predicted by examination of their "normal" σ-constants. The "normal" values, derived from the ionization constants of the benzoic acids and the saponification rates of ethyl benzoates, are: *p*-β-styryl, −0.05; *m*-β-styryl, 0.025; *m*-phenylethynyl, 0.16; *p*-phenylethynyl, 0.19. From these results it is concluded that acetylenic groups show a low conjugative aptitude toward electron deficient systems but may exhibit acceptor properties by interactions in addition to exerting a strong dipole influence.

The solvolysis of benzyl tosylates[1] and the saponification of ethyl benzoates[2] represent two reactions of opposed charge requirements. Whereas tosylate solvolysis is facilitated by electron-repelling substituents, the saponification of ethyl benzoates is retarded by these same groups. Tosylate solvolysis shows only a limited correlation with the Hammett relationship[3] in that donor substituents in the para position provide exceptionally large driving forces. However, this deviation has been taken as a measure of the ability of those substituents to donate a pair of electrons to the benzyl carbon atom in the transition state.

With this interpretation in mind we have sought to determine the relative conjugative aptitudes of the carbon–carbon double and triple bonds.

An early comparison of the electrostatic or inductive effects of these two unsaturated systems was made by Baker, Cooper and Ingold,[4] who analyzed the mixture of isomers resulting from the quantitative nitration of phenylpropiolic and cinnamic acids and their esters. On the basis of the isomer ratios, they attributed a greater electron-attracting power to the acetylenic bond. Dippy[5] reached similar conclusions by inspecting the ionization constants of various acetylenic and ethylenic acids. In the case of the rearrangement of unsaturated alcohols, which is aided by electron accession to the hydroxyl group, Braude and Jones[6] found that some vinylacetylenic carbinols rearranged at rates which were slower by as much as a factor of 3,000 than those of the corresponding divinylic compounds.

The relative rates of bromination of substituted acetylenes and ethylenes were utilized by Robertson and co-workers[7] for assigning a greater polarizability to the ethylenic bond than the acetylenic bond. Similar conclusions as to the relative polarizabilities of the double and triple bond can be deduced from the application of the reasoning used by Bordwell and Rohde[8] to the data of Baker, Cooper and Ingold.[4] Furthermore, the contribution of the "allenic" structures to solvolysis transition states does not appear to be of great importance if one compares the rate of solvolysis of 3-chloro-3-methyl-butyne-1[9] with those of its ethylenic analogs, 3-chlorobutene-1 and 1-chlorobutene-2,[10] under similar conditions.

Experimental

Preparation of 3- and 4-Carboxystilbene.—The 4-carboxystilbene was prepared by the method of Meerwein, Buchner and van Emster,[11] which involves the reaction of cinnamic acid with 4-carboxybenzenediazonium acetate. The yields, based on several attempts, were not as high as that reported in the literature[12]; yield 12%, m.p. 248.1–248.4°. *Anal.*[13] Calcd. for $C_{15}H_{12}O_2$: C, 80.33; H, 5.39; neut. equiv., 224. Found: C, 80.77; H, 5.29; neut. equiv., 226.

The corresponding 3-carboxy isomer was prepared in an analogous manner using the 3-carboxybenzenediazonium salt. The maximum yield from several attempts was 6%; m.p. 197.0–197.5°. *Anal.* Calcd. for $C_{15}H_{12}O_2$: C, 80.33; H, 5.39; neut. equiv., 224. Found: C, 78.83; H, 5.38; neut. equiv., 224.

Preparation of 3- and 4-Carboxytolane.—To a suspension of 1.6 g. of 3-carboxystilbene in 160 ml. of carbon tetrachloride, a solution of 1.5 ml. of bromine in 25 ml. of carbon tetrachloride was added dropwise. The solution was then warmed on a water-bath at 70° and allowed to react for 20 minutes, cooled and filtered. The resulting light yellow-colored solid was recrystallized from absolute ethanol. The colorless dibromide, obtained in 87% yield, melted at 246–248°.

To a solution of 60 g. of potassium hydroxide in 100 ml. of absolute ethanol was added 2.4 g. of 3-carboxystilbene dibromide, in order to effect dehydrobromination. After the solution was refluxed for 20 hours, it was poured into a slurry consisting of 200 g. of crushed ice and 500 ml. of water. Twenty per cent. hydrochloric acid was then slowly stirred in until the solution was acid to litmus. The crude 3-carboxytolane was recrystallized several times from aqueous ethanol; yield 78%, m.p. 160–161°. *Anal.* Calcd. for $C_{15}H_{10}O_2$: C, 81.06; H, 4.54; neut. equiv., 222. Found: C, 80.50; H, 4.66; neut. equiv., 224.

The preparation of 4-carboxytolane was carried out in a similar manner. Seventeen grams of 4-carboxystilbene was suspended in 500 ml. of carbon tetrachloride. A solution of 5.2 ml. of bromine in 200 ml. of carbon tetrachloride was then added slowly. The mixture was heated on a water-bath for one-half hour, cooled and filtered, and then washed twice with boiling ethanol. The white crystalline dibro-

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[1] J. K. Kochi and G. S. Hammond, THIS JOURNAL, **75**, 3445 (1953).

[2] N. B. S. Newling and C. N. Hinshelwood, *J. Chem. Soc.*, 1357 (1936).

[3] The Hammett equation frequently has been invoked to assess the electronic effects of substituent groups on aromatic systems. See, for example: J. D. Roberts, R. Clement and E. McElhill, THIS JOURNAL, **72**, 409 (1950); F. Bordwell and G. Cooper, *ibid.*, **74**, 1059 (1952); E. Berliner and E. A. Blommers, *ibid.*, **73**, 2479 (1951).

[4] J. Baker, K. Cooper and C. K. Ingold, *J. Chem. Soc.*, 427 (1926).

[5] J. Dippy, *Chem. Revs.*, **25**, 179 (1939).

[6] E. A. Braude and B. Jones, *J. Chem. Soc.*, 129 (1946).

[7] P. Robertson, W. Dasent, P. Milburn and W. Oliver, *ibid.*, 628 (1950).

[8] F. Bordwell and K. Rohde, THIS JOURNAL, **70**, 1190 (1950).

[9] G. Hennion and D. Maloney, *ibid.*, **73**, 4735 (1951).

[10] W. G. Young and L. Andrews, *ibid.*, **66**, 421 (1944).

[11] H. Meerwein, E. Buchner and K. van Emster, *J. prakt. Chem.*, **152**, 237 (1937).

[12] F. Bell and D. H. Waring, *J. Chem. Soc.*, 1024 (1948).

[13] All carbon and hydrogen analyses were performed by Drs. Weiler and Strauss, Oxford, England.

mide, in the form of a fine powder, melted at 267–269°; yield 91%. To dehydrohalogenate the dibromide, 20 g. was treated with a solution of 80 g. of potassium hydroxide in 140 ml. of absolute ethanol and refluxed for 36 hours. The solution was then filtered and the filtrate acidified in the usual manner. The crude flocculent 4-carboxytolane, after recrystallization from ethanol twice, melted at 220.5–221.0°; yield 74%. *Anal.* Calcd. for $C_{15}H_{10}O_2$: C, 81.06; H, 4.54; neut. equiv., 222. Found: C, 80.80; H, 4.71; neut. equiv., 222.

Preparation of 3- and 4-Carbethoxystilbene.—The 4-carbethoxystilbene was prepared by the procedure given by Fuson and Cooke.[14] It involved the Meerwein reaction using 4-carbethoxybenzenediazonium acetate. The product was obtained in poor yields averaging 13.7%; m.p. 108.5–109.0°. *Anal.* Calcd. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39; sapon. equiv., 252. Found: C, 80.44; H, 6.36; sapon. equiv., 251.

The preparation of 3-carbethoxystilbene was not successful using the method described above. This compound was prepared by the Fischer esterification of 3-carboxystilbene. Five and two-tenths grams of 3-carboxystilbene was dissolved in 50 ml. of absolute ethanol. One ml. of concentrated sulfuric acid was added and the solution was refluxed for 72 hours. The hot solution was then poured quickly into 900 ml. of water, and the oily suspension was extracted successively with 500 ml. and 200 ml. of ether. The combined ethereal extracts were then washed with 5% sodium bicarbonate until the wash solution gave no precipitate on acidification. The combined weight of the recovered acid was 0.5 g.

The ethereal solution was washed twice with water and then dried with Drierite. The residue from the evaporation of the ether was a slightly colored oil. The short path distillation of this oil *in vacuo* gave a colorless liquid which solidified on cooling. The solid was crystallized twice from petroleum ether. The melting point of the ester, compound I, was 63.2–64.0°. When the combined mother liquors were chilled in a Dry Ice–acetone-bath, a second crop of crystals, compound II, was obtained. This compound, however, melted when it warmed to room temperature. Evaporation of the solvent from the resulting mother liquor led to a third material, fraction III. In appearance it was a yellow solid of no definite melting point. It appears to be a mixture of the first two compounds mentioned, and it probably represents a mixture of the *cis* and *trans* isomers. The yield of the ester melting at 63° was 2.0 g. *Anal.* Calcd. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39; sapon. equiv., 252. Found: C, 81.29; H, 6.14; sapon. equiv., 253.

Preparation of 3- and 4-Carbethoxytolane.—The 3-carbethoxytolane was prepared by Fischer esterification of the acid. Five and six-tenths grams of 3-carboxytolane was dissolved in 75 ml. of absolute ethanol containing 2 ml. of concentrated sulfuric acid and the solution was then refluxed for 75 hours. The subsequent treatment of the solution was the same as that for the dihydro compound. The combined weight of the recovered acid was 0.4 g. The evaporation of the ether left a yellow-colored oil. The micro-distillation of this oil could not be effected satisfactorily. At a pressure of 1.2 mm. and bath temperature of 230° the viscous liquid could not be distilled without flooding the column. A partial separation into six fractions was obtained. The corrected refractive indices at 29° were as follows.

Fraction	Vol. of distillate, ml.	Refractive index
I	0.3	1.6108
II	.3	....
III	.2	1.6122
IV	.4	....
V	.2	....
VI	.1	1.6125

Subsequent studies on the saponification rate of the esters showed that fractions III through VI were the same compound. *Anal.* Calcd. for $C_{17}H_{14}O_2$: C, 81.58; H, 5.63; sapon. equiv., 250. Found: C, 81.41; H, 5.63; sapon. equiv., 255.

The esterification of 4.0 g. of 4-carboxytolane was carried out in 75 ml. of absolute ethanol and 1.8 ml. of concentrated sulfuric acid. The solution was refluxed for 80 hours. It was treated in a manner similar to the previous synthesis. The recovered tolanecarboxylic acid amounted to 0.5 g. A light yellow solid was obtained from the ethereal solution after the solvent was evaporated. Recrystallization of the crude 4-carbethoxytolane yielded 3.0 g. of ester melting at 83.5–84.0°. *Anal.* Calcd. for $C_{17}H_{14}O_2$: C, 81.58; H, 5.63; sapon. equiv., 250. Found: C, 81.55; H, 5.60; sapon. equiv., 250.

Preparation of 3- and 4-Hydroxymethylstilbene.—To 3.8 g. of powdered lithium aluminum hydride suspended in 175 ml. of absolute ether in a three-neck round-bottom flask attached with a Trubore stirrer, condenser and graduated dropping funnel, was added dropwise a solution of 2.4 g. of 4-carboxystilbene in 50 ml. of absolute ether. The reduction was then carried out in the usual manner.[15] Evaporation of the ether left 4-hydroxymethylstilbene which after two recrystallizations from ligroin melted at 170.0–170.5°; yield 3.0 g. The sodium bicarbonate extracts did not yield any acid on acidification. *Anal.* Calcd. for $C_{15}H_{14}O$: C, 85.68; H, 6.70. Found: C, 85.83; H, 6.66.

In a manner similar to the previous synthesis, 3.1 g. of 3-carboxystilbene was reduced with 2.0 g. of lithium aluminum hydride. The evaporation of the ether solution *in vacuo* yielded a light yellow solid. This crude 3-hydroxymethylstilbene was recrystallized three times from ligroin, yielding colorless platelets melting at 97.8–98.5°. Acidification of the bicarbonate extracts gave no acid. The yield of the alcohol was 2.5 g. *Anal.* Calcd. for $C_{15}H_{14}O$: C, 85.68; H, 6.79. Found: C, 86.43; H, 6.67.

Preparation of 3- and 4-Hydroxymethyltolane.—The reduction of 4-carboxytolane (10.5 g.) with 5.0 g. of lithium aluminum hydride was effected in the usual manner. Three recrystallizations of the crude 4-hydroxymethyltolane yielded colorless platelets melting at 125.8–126.5°; yield 9.2 g. *Anal.* Calcd. for $C_{15}H_{12}O$: C, 86.50; H, 5.81. Found: C, 86.59; H, 5.89.

The 3-carboxytolane was treated similarly. The reduction of 14.1 g. of acid with 4.0 g. of lithium aluminum hydride produced 10.1 g. of 3-hydroxymethyltolane which, recrystallized twice from ligroin produced 9.1 g. of colorless platelets melting at 47.5–48.5°. *Anal.* Calcd. for $C_{15}H_{12}O$: C, 86.50; H, 5.81. Found: C, 86.47; H, 5.77.

Preparation of Benzyl Tosylates.—The tosylates of the unsaturated alcohols were prepared by the method previously described.[16] The tosylate of 4-hydroxymethylstilbene was always contaminated with the alcohol and could only be isolated 85% pure. The partial purification procedure for this compound consisted of dissolving the solid obtained from the chilled ether solution (−70°) in anhydrous benzene (approximately 5 ml. of benzene for 2 g. of crude solid). The solution was filtered to remove the unreacted alcohol. The clear benzene solution was then evaporated under vacuum, without heating. The residual solid was then washed twice with ligroin and used as such. The sole contaminant of the tosylate was the alcohol. This was determined by hydrolyzing the tosylate in a medium consisting of 50 volume per cent. aqueous acetone. The solution was then titrated with standard base to assay the tosylate. The acetone was evaporated and the resulting aqueous mixture treated with ether. The ether solution was washed with water and the ether removed *in vacuo*. A melting point of the residual solid was in all cases, regardless of the assay of the tosylate (which was sometimes as low as 35%), within a few degrees of 4-hydroxymethylstilbene. The melting point was not depressed by mixture with the authentic alcohol. Solvolysis rates on these crude samples also gave constant values for the rate constant.

The pertinent data for the preparation of the tosylates are given in Table I. In Table II are listed some of the physical constants of these tosylates.

Materials.—Reagent grade acetone was treated with potassium permanganate and Drierite for two days at room temperature. The liquid was filtered and then distilled through a five-foot, helix-packed, vacuum jacketed still. A two hundred milliliter forerun was rejected; 2.5 liters boiling at 55.1° was collected.

Carbonate-free Sodium Hydroxide.—A concentrated solution of sodium hydroxide in water (56% weight water)

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[14] R. Fuson and H. Cooke, THIS JOURNAL, **62**, 1180 (1940).

[15] W. G. Brown, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 469.

[16] J. K. Kochi and G. S. Hammond, THIS JOURNAL, **75**, 3443 (1953).

TABLE I

PREPARATION OF SUBSTITUTED BENZYL TOSYLATES

Alcohol	Time reaction with NaH, hr.	Reaction TsCl with alkoxide Mix Temp., °C.	Mix Time, hr.	Stir Temp., °C.	Stir Time, hr.	Wt. alcohol, g.
4-Hydroxy methyl-	60	−60	1	15	2	1.8
3-Hydroxy stilbene	36	−30	2	25	3	2.1
4-Hydroxy methyl-	38	−30	1	20	3	1.7
3-Hydroxy tolane	26	−30	1	30	3	2.1

TABLE II

PHYSICAL CONSTANTS OF SOME SUBSTITUTED BENZYL TOSYLATES

Tosylate	Mol. wt.	Yield, %	M.p., °C.	Sulfur[a] analyses Calcd.	Found	S.E.[b]
m-β Styryl-	364.5	44	104.0–104.5	8.80	8.67	362
p-β benzyl	364.5	30	>150	8.80	..	...
m- Phenyl-	362.4	57	79.0– 79.5	8.85	9.45	358
ethynyl-						
p- benzyl	362.4	61	115.2–115.9	8.85	9.38	362

[a] Parr Instrumental Manual No. 121, Parr Instrument Co., Moline, Illinois. [b] Solvolysis equivalent.

was filtered through a fine grade sintered glass crucible. Five and six-tenths milliliters of this solution was added to two liters of carbon dioxide-free water in a paraffin-lined bottle. The normality of this solution did not change noticeably throughout the experiments.

Indicator.—Cresol red solution was made by dissolving 0.04 g. of cresol red in 0.7 ml. of 0.15 *N* sodium hydroxide solution and 10 ml. of water. The resulting solution was diluted to 100 ml.

Ethyl benzoate (Eastman Kodak Co., white label) was distilled at 20 mm. pressure through a short path column. Material boiling at 99.0–100.0° was collected.

Ethyl *m*-bromobenzoate was prepared by the Fischer esterification of *m*-bromobenzoic acid. Material boiling at 100.0–100.5° at 7 mm. was used.

The Determination of Apparent Ionization Constants of Substituted Benzoic Acids.—The titrations were performed with a Beckman Model G *p*H meter. All acid solutions were prepared to approximately the same molar concentration by weighing out the required amount of acid. This precaution was necessitated by the sensitivity of the *p*H meter to the ionic strength and the ionization constants of the acids to the concentration of the solutions. It was found that a 10% difference in the acid concentration (at 0.008 *M*) did not affect the *p*H appreciably at the midpoint of the titration.

A weighed amount of acid was transferred quantitatively to a 100-ml. volumetric flask and washed down with a small amount of ethanol. Twenty-five milliliters of bicarbonate-free water was pipetted into the flask and ethanol added to the mark. The solutions were allowed to equilibrate overnight and the levels readjusted.

Fifty milliliters of the acid solution was pipetted into the titration cell and the cell was attached to the air-driven stirrer and electrode assembly. A five-milliliter capacity microburet, calibrated in 0.01-ml. units, was then inserted through the stopper. The contents were, in this way, exposed to a minimum amount of atmosphere. The whole assembly was immersed in a thermostated bath maintained at 25.3 ± 0.1° and the potentiometric titration carried out within one-half hour. The titrant was 0.1 *N* carbonate-free sodium hydroxide solution in approximately 25 volume per cent. aqueous ethanol. In all cases the *p*H meter maintained a steady balance throughout the titration. The end-point was ascertained to within 0.07%; the *p*H readings, moreover, should be acceptable to 0.02 *p*H unit.

The titration curves were plotted for each acid in the usual manner, the end-points being determined by means of the familiar graphical differential method. The apparent pK_a's of the various acids were obtained with the aid of the Henderson equation,[17]

$$pH = pK_a + \log\left(\frac{[\text{salt}] + [H^+]}{[\text{acid}] - [H^+]}\right) - A(\mu)^{1/2} + C\mu$$

where *A* is a constant. *C* is a function of the particular anion and μ is the ionic strength. In the first approximation for dilute solutions, such as were used in these titrations, the low ionic strength may justify elimination of the activity coefficient terms. Secondly, the hydrogen ion terms (H^+) may be dropped altogether in comparison with the concentration of the salt and undissociated acid for acids with *pK*'s approximately equal to 10^{-5} in water. Thus

$$pH = pK_a + \log(\text{salt})/(\text{acid})$$

That these approximations are valid is apparent from the constancy of the pK_a values calculated at points of one-third, one-half and two-third neutralization. For all the acids the values were within the accuracy of the *p*H readings.

The Saponification Rates of the Esters.—The procedure used here is essentially that of Hinshelwood and Tommila.[18] One hundred milliliters of approximately 0.04 *N* sodium hydroxide was pipetted into a 250-ml. volumetric flask. Acetone was added to the mark with swirling and the solution allowed to equilibrate overnight. The volume was readjusted with acetone and the flask put into a constant temperature bath maintained at 25.3°. The ester was weighed carefully into a 250-ml. standard taper round bottom flask attached with a female "Trubore" assembly. One hundred milliliters of stock sodium hydroxide solution was then quickly pipetted into the flask, the flask corked and then immersed in the bath. Four runs were made simultaneously. Eight points were taken and recorded in the usual manner.

A 10-ml. aliquot was pipetted out of the flask at the designated time, quenched with 5 ml. of hydrochloric acid and then back titrated with 0.01 *N* sodium hydroxide. In the case of the unsaturated esters it was found necessary to add a slight amount of acetone to the quenched solution in order to effect solution of the precipitated acid and/or ester.

An infinite-time titer was obtained by transferring the flask, after the "Trubore" attachment was replaced by a standard taper stopper suitably tied down, to a bath at 55°.

TABLE III

RATE CONSTANTS FOR SAPONIFICATION OF THE ESTERS

Ester	Mol. wt. Calcd.	Mol. wt. Found	Infinite titer, %	10^4k, l./mole-sec.
Ethyl benzoate	150.2	150	100	31.3
			100	30.6
			100	31.8
			Av.	31.2 ± 0.6
Ethyl *m*-bromobenzoate	229.0	229	100	192
			100	192
			Av.	192
Ethyl 3-carbethoxystilbene	252.3	253	91.7	34.6
			97.2	37.0
			100	34.1
			100[a]	40.2
			Av.	35.2 ± 1.1
Ethyl 4-carbethoxystilbene	252.3	251	103	27.1
			100	27.0
			Av.	27.1 ± 0.1
Ethyl 3-carbethoxytolane	250.3	255[b]	99.4[c]	80.2
			98.4[d]	80.7
			Av.	80.4 ± 0.3
Ethyl 4-carbethoxytolane	250.3	250	97.6	107.8
			97.5	106.8
			Av.	107.3 ± 0.5

[a] Fraction III. [b] Fraction IV. [c] Fraction V. [d] Fraction II.

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(17) S. Glasstone, "Introduction to Electrochemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1940.

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

Twelve hours was sufficient to hydrolyze the esters completely. The stock solutions were titrated before and after each run in order to be sure that no change in titer occurred.

The alkaline solutions were titrated before and after each run with standard solutions of potassium acid phthalate (Baker and Adamson C.P., assay 99.9%). The hydrochloric acid solution was in turn standardized with the sodium hydroxide solutions. All titrations were reproducible to within 0.1%. The volumetric glassware used in the experiments was within the limits of acceptable tolerance (0.1%). Saponification equivalents were found in the usual manner. The rate constants for the saponification of the esters are listed in Table III.

The second-order rate constants were obtained from the integrated equation

$$k_2(t_2 - t_1) = \frac{1}{a - b}\left[\ln\frac{(b - x_2)}{(b - x_1)} - \ln\frac{(a - x_2)}{(a - x_1)}\right]$$

where b and a are the initial concentrations of ester and sodium hydroxide, respectively. The subscripts 1 and 2 refer to two different points. In this manner, the rate constants were obtained between successive points. A representative run is given in Table IV.

TABLE IV

SAPONIFICATION RATE OF ETHYL BENZOATE AT 25.3°[b]

NaOH titer,[a] (0.01280 N), ml.	Time, min.	$\log\frac{(b - x_2)}{(b - x_1)} - \log\frac{(a - x_2)}{(a - x_1)}$
2.04		
3.22	00.0	
4.03	41.7	5.76
4.53	77.7	5.25
5.05	116.9	5.22
5.84	182.0	5.43
6.62	282.5	5.32
7.63	471.4	5.22
10.03	Infinite	
	Av.	5.29

[a] Initial base titer, 2.04 ml.; final base titer, 10.03 ml.; five milliliters of 0.0383 N HCl added to each aliquot; initial concentration of ester, 1.022 meq. per 100 ml. Initial concentration of NaOH, 1.639 meq. per 100 ml.
[b] k_2, 31.8 × 10^{-4} liter/mole-sec.

The Rate of Tosylate Solvolysis.—The kinetic method for the tosylate solvolysis has already been described.[1] The rate data for the unsaturated tosylates are tabulated in Table V.

TABLE V

SOLVOLYSIS OF SOME SUBSTITUTED BENZYL TOSYLATES

Tosylate	Wt. used, mg.	10^5k, sec.$^{-1}$	Reaction followed, %	Total reaction, %
m-β-Styrylbenzyl	113.2	5.33	81	97.8
	107.7	5.37	79	98.9
	108.1	5.38	83	97.2
p-β-Styrylbenzyl	54.4	75.3[a]	98	31.2
	112.9	74.5[a]	51	85.1
	89.9	74.2[a]	49	63.0
	32.0	71.4[a]	92	91.3
m-Phenylethynylbenzyl	96.2	1.65	85	97.3
	102.0	1.56	71	98.3
	119.1	1.46	73	96.9
p-Phenylethynylbenzyl	84.5	15.1	93	99.6
	108.2	14.7	92	98.4
	84.0	14.1	48	96.5
	100.4	14.6	88	95.0

[a] Values of the rate constants were determined in 44.8 mole per cent. aqueous acetone solutions.

The rate of reaction of *p*-β-styrylbenzyl tosylate, like *p*-methoxybenzyl tosylate, was too rapid to measure in the standard medium. We again resorted to the procedure utilized to obtain the rate constant for the latter compound. The variation in the rate constant with water concentration is listed in Table VI.

TABLE VI

RATE CONSTANTS FOR THE SOLVOLYSIS OF SOME SUBSTITUTED BENZYL TOSYLATES AS A FUNCTION OF THE WATER CONCENTRATION

Water, mole per cent.[a]	$k \times 10^5$, sec.$^{-1}$ *p*-β-Styrylbenzyl tosylate	$k \times 10^5$, sec.$^{-1}$ *p*-Phenylethynylbenzyl tosylate
44.8	74.7	...
55.0	189	...
62.0	356	2.38
71.1	...	6.66
74.1	...	10.1
76.6	...	14.7

[a] Solutions were at constant ionic strength (1.83 M $LiClO_4$).

Results

The apparent ionization constants of the substituted benzoic acids have been plotted against the respective σ-constants as shown in Fig. 1. The value for the ρ-constant obtained from the slope by the method of least squares was 1.60 with a probable error of 0.053 for seven points.

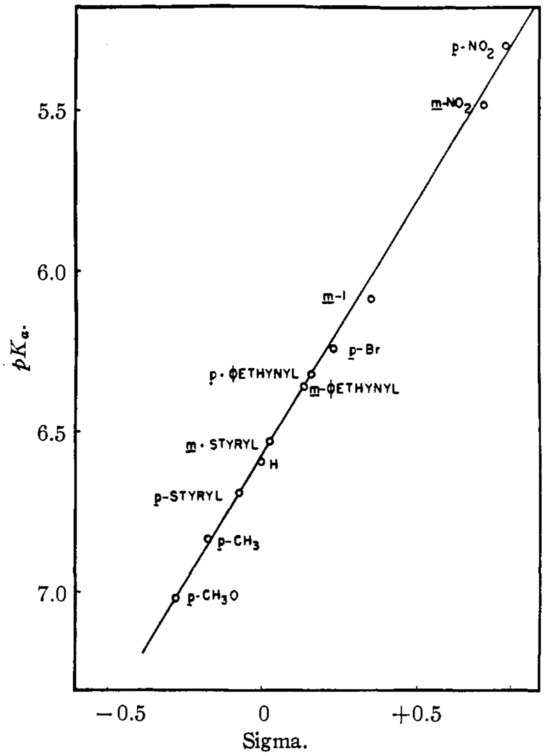

Fig. 1.—Hammett plot of apparent ionization constants of substituted benzoic acids.

A similar application of the data presented by Hinshelwood and Tommila[18] and Tommila[19] for the saponification of ethyl benzoates in aqueous acetone to the σ-constants gave ρ equal to 2.373, r = 0.049, n = 19 as shown in Fig. 2. This value is in striking agreement with the ρ equal to 2.373, r = 0.051, n = 7, obtained by Hammett[20] from a

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(19) E. Tommila, *Ann. Acad. Sci. Fennicae, Ser.* **A57**, No. 13, 3 (1941).

(20) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 191.

consideration of the data of Hinshelwood and Tommila alone.

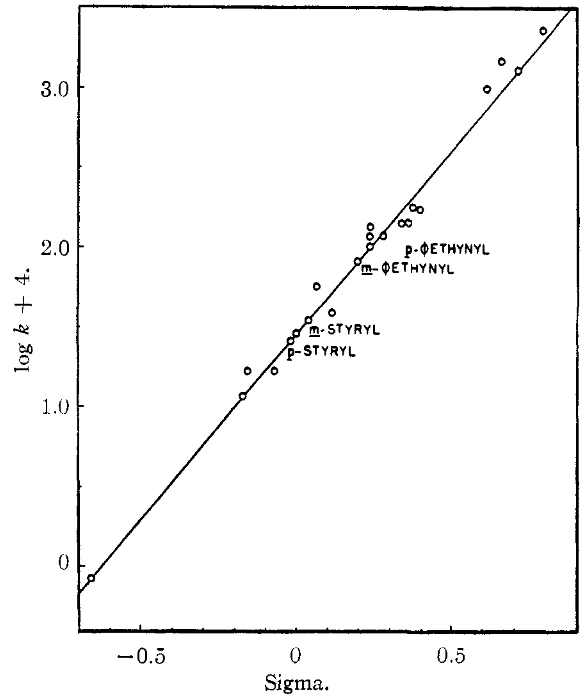


Fig. 2.—Hammett plot of rate constants for saponification of substituted ethyl benzoates.

The two determinations of the σ-values for *m*- and *p*-β-styryl and *m*- and *p*-phenylethynyl groups obtained from these graphs are listed in Table VII.

TABLE VII

SIGMA VALUES FOR β-STYRYL AND PHENYLETHYNYL

Substituent	σ_{ester}	σ_{pK}	$\sigma_{\text{av.}}$
m-$C_6H_5CH{=}CH$—	0.020	0.030	0.025 ± 0.005
p-$C_6H_5CH{=}CH$—	− .031	− .070	− .050 ± .020
m-$C_6H_5C{\equiv}C$—	.180	.140	.160 ± .020
p-$C_6H_5C{\equiv}C$—	.215	.165	.190 ± .025

The rate constant for the solvolysis of *p*-β-styrylbenzyl tosylate was obtained by the extrapolation procedure reported previously.[1] The *data have been* replotted in Fig. 3. The logarithms of the rate constants have been plotted against σ in Fig. 4. The slope of the line as determined previously coincided with that calculated using the new points. *p*-β-Styrylbenzyl tosylate was not included in the new calculations. The calculated value of ρ is, thus, −2.19, r = 0.27 and n = 9.

The $\Delta\sigma$ values for the two unsaturated substituents are given in Table VIII. The assignment of a value to the *p*-phenylethynyl group is somewhat uncertain. If one accepts the ρ-value given (*i.e.*, −2.20) then the value listed in Table VIII results. The ρ-value, −2.19, was, on the other hand, calculated on the basis that the *p*-phenylethynyl group behaved normally. In this case the $\Delta\sigma$-value of zero is proper for this substituent. If one examines the location of both *m*-styryl and *m*-phenylethynyl in Fig. 4, however, then the

TABLE VIII

DELTA SIGMA VALUES FOR SOME BENZYL TOSYLATES

Substituent	σ_{tosylate}	σ_{acid}	$\Delta\sigma$
p-β-Styryl	−1.0	−0.05	−1.0
p-Phenylethynyl	−0.03	.19	−0.22

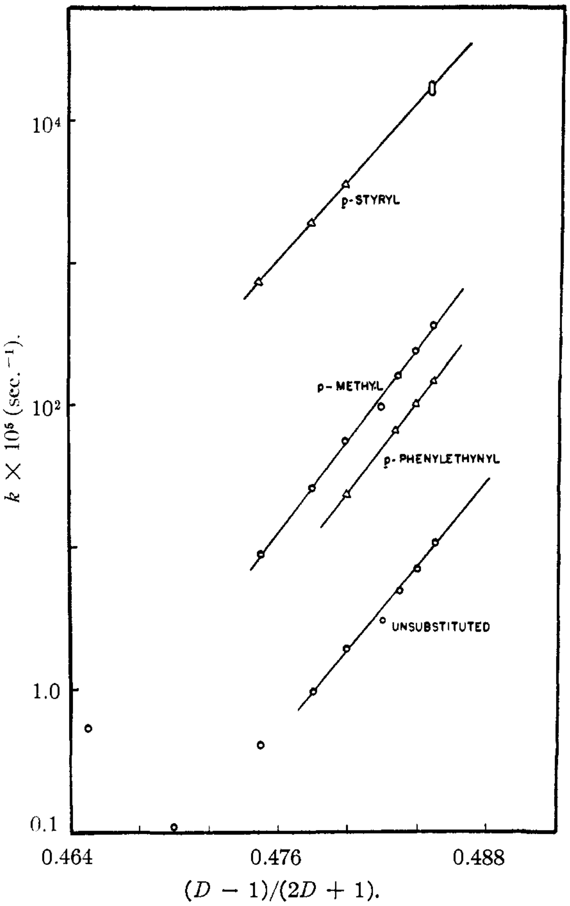


Fig. 3.—Variation of solvolysis rates as a function of the dielectric constant of the medium (rates on log scale).

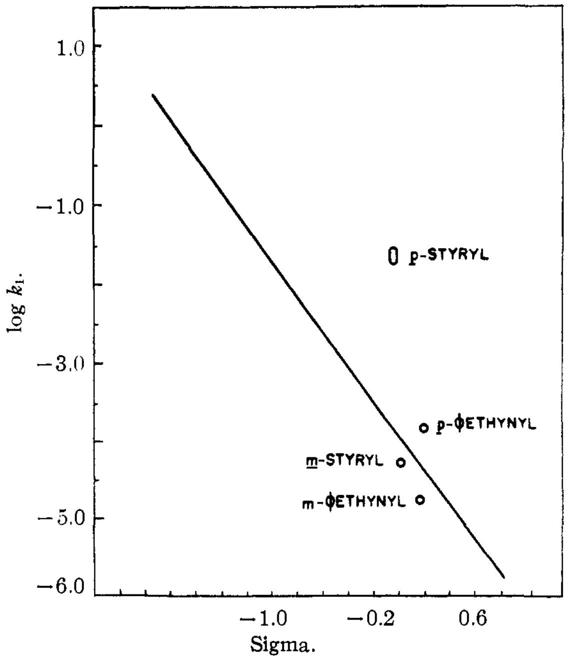
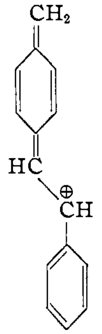


Fig. 4.—Hammett plot of rate constants for solvolysis of substituted benzyl tosylates.

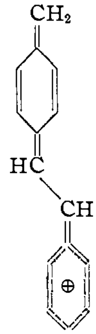
former assignment is not too objectionable. In either case the important point is the contrast between the two substituents.

Discussion

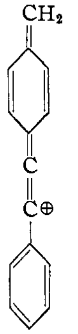
On the basis of the previous interpretation of solvolysis rates of benzyl tosylates, it appears, from an inspection of the σ-values, that *p*-β-styryl is a much better source of electrons than is the *p*-phenylethynyl function. In other words, the benzyl system which has attained much of the character of a carbonium ion in the transition state, is more stable when it is ethylenic than when it is acetylenic. Consequently one must assume that structures of the type I and II contribute more than the group represented by III and IV.



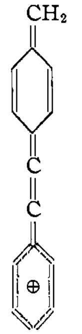
I



II

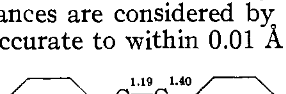


III

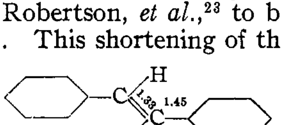


IV

That III might represent a relatively higher energy configuration than I was directly foreseen by reference to the study by Walsh[21] of the far ultraviolet spectra of acetylene and ethylene. Walsh assigned the values 11.41 and 10.50 e.v. to π^{-1} ionization potentials of acetylene and ethylene, respectively, and concluded, therefore, that the π electrons of the former are more firmly bound. This tighter binding may be discussed from two points of view. First, the large amount of s character in the σ-bond to an acetylenic carbon atom[22] results in a decrease in the "repulsions between σ and π electrons" relative to that felt in ethylenes. A second explanation, which probably implicitly overlaps the first, relates to the observed bond distances in acetylenes and olefins. The short carbon–carbon triple bond distance should lead to effective overlapping of *p*-orbitals. As is illustrated by the case of tolane and stilbene, the single bond distances in acetylenes are also reduced relative to those in ethylenes. The following distances are considered by Robertson, *et al.*,[23] to be accurate to within 0.01 Å. This shortening of the single bond distance also increases the overlap of a *p*-orbital of an acetylenic carbon atom with one on an adjacent atom. This effect should partially compensate for the shortening of the triple bond in determining the relative importance of II and IV. A more thorough analysis of this matter must wait upon comparable experiments with systems in which the ethylenic and acetylenic linkages are not flanked on both sides by unsaturated groups. At the present time we can only reiterate that acetylenes have a lower aptitude than ethylenes for conjugation with electron deficient systems. One should bear in mind, however, that the substitution of *p*-phenylethynyl for hydrogen in the benzyl tosylate system did effect an increase in the solvolysis rate indicating that electron migration from the group does occur either at the expense of the acetylenic or the phenyl function or both.



V



VI

The "normal" σ-constants of the unsaturated substituents are derived from the ionization constants of the benzoic acids and the saponification rates of the corresponding ethyl esters. The most striking result is that the two para substituents represent extremes with *p*-β-styryl being slightly acid-weakening (σ equals −0.050) and *p*-phenylethynyl being rather strongly acid-strengthening (σ equals 0.190). Since both meta substituents have positive values of σ we assume that the net result of the inductive effects is to decrease the electron density in the vicinity of the functional carboxyl groups. That the latter effect is more pronounced in the acetylenic compound is in line with the difference in the nature of the σ-bond between ring and the substituents in the two cases. The bonding orbital in the acetylene may be regarded as compounded from sp^2 and sp hybrid atomic orbitals and should, therefore, be markedly polar in the indicated sense. That β-styryl should also exert a negative inductive effect is not as obvious since in this case the bond is symmetrical ($sp^2 - sp^2$) in the first approximation. It would seem natural to call upon the analogy to the positive inductive effect usually attributed to phenyl group in accounting for the effect of *m*-styryl. The acid strengthening effect in phenylacetic and diphenylacetic acid[5] is well known and recently Lichtin and Glazer[24] have shown that whereas a *p*-phenyl substituent increases the ionization constant of triphenylchloromethane, *m*-phenyl slightly represses the ionization process. However, neither of these examples offers a truly analogous situation. In the acetic acids the bond to the aryl function is unsymmetrical ($sp^2 - sp^3$) and Streitwieser[25] has recently shown that the effect upon triarylmethyl halide ionization may be attributed to the inhibition of interannular resonance.[26] Furthermore, Keiffer and Rumpf[27] have measured the basicity constants of *m*- and *p*-biphenylamines and report that both are weaker[28] bases than aniline. Although the rate of saponification of ethyl *p*-phenylbenzoate[29] and the ionization

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[21] A. D. Walsh, *Ann. Reps. Progress Chem.*, **44**, 32 (1947).

[22] A. D. Walsh, *Discussions Faraday Soc.*, **2**, 19 (1947).

[23] J. M. Robertson, *Proc. Roy. Soc.* (*London*), **A164**, 436 (1938); L. O. Brockway and J. M. Robertson, *J. Chem. Soc.*, 1324 (1939); J. M. Robertson and I. Workmawn, *Proc. Roy. Soc.* (*London*), **A154**, 187 (1936).

[24] N. Lichtin and H. Glazer, THIS JOURNAL, **73**, 5537 (1951).

[25] A. Streitwieser, *ibid.*, **74**, 5288 (1952).

[26] Note that although the normal σ-constant for the *m*-styryl group correlates the solvolysis rate of the tosylate fairly well the observed rate is actually slightly lower than the predicted.

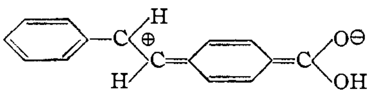
[27] F. Keiffer and P. Rumpf, *Compt. rend.*, **230**, 1874 (1950).

[28] It is interesting to note that this result for the meta base would probably not be predicted on the basis of Streitwieser's results since one would expect the maximum damping of inter-annular interaction in the free base rather than in the conjugate acid.

[29] K. Kindler, *Ann.*, **452**, 105 (1927).

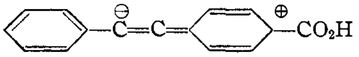
constant of the corresponding acid have been determined,[30] the corresponding data for the meta derivatives have not been reported. It is clear that more study of biphenyl derivatives with functional meta substituents is needed in order to establish whether or not the behavior of *m*-styryl indicates an important second-order dissymmetry of the σ-bond to the substituent. Experiments designed to provide the requisite information are in progress.

We will now return to the para substituents. It is clear that moving the substituent from the meta to the para position has an opposite effect upon the σ-constant in the two cases under consideration. Although the difference in, for example, the acidity constants is small in the case of the styrylbenzoic acids the fact that sign changes can only be accounted for by assuming that there is a small, direct interaction between a carboxyl function and the unsaturated substituent which is destroyed or inhibited in the reaction process. Structure VII illustrates the concept.



VII

That such an interaction should not be of importance in the acetylenic acid is implicit in our previous discussion. However, the geometry of the molecule will not permit the view that the effects responsible for the influence of *m*-phenylethynyl are alone sufficient to account for the large positive value of the para sigma constant. It is quite possible that the acetylenic function serves as an electron sink and actually exhibits a high conjugative aptitude toward donor systems. Structures such as VIII may account for the preferential stabilization of anions such as the substituted benzoate ion and the transition state for ester saponification.



VIII

An alternative to this explanation may be that the change in effective electronegativity of the carbon atom to which the ethynyl group is attached results in the development of a positive charge on the para position.[31]

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[30] E. Tommila, L. Brehmer and H. Elo, *Ann. Acad. Sci. Fennicae, Ser.* **A59**, No. 9, 3 (1942).

[31] This situation would be similar to that in pyridine in which a slight assymmetry is induced in the π electron density because of the high electron affinity of the hetero atom.[32] It is our opinion that such non-classical inductive effects are not sufficient to account for observed effects.

[32] J. Ploguin, *Compt. rend.*, **226**, 245, 339 (1948).

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF AGRICULTURAL CHEMISTRY, UNIVERSITY OF NEBRASKA COLLEGE OF AGRICULTURE, AND THE DEPARTMENT OF BIOLOGICAL CHEMISTRY, UNIVERSITY OF ILLINOIS COLLEGE OF MEDICINE]

Studies on Inulin. The Preparation and Properties of Inulobiose[1]

BY JOHN H. PAZUR AND ALAN L. GORDON[2]

RECEIVED FEBRUARY 23, 1953

Inulobiose, a reducing disaccharide with the probable structure 1-(β-D-fructofuranosyl)-D-fructose, has been isolated from a partial acid hydrolysate of inulin by paper chromatographic methods. The specific rotations of the new compound and of its octaacetyl derivative are −32.5° (*c* 2.6, water) and −6.5° (*c* 1.5, chloroform), respectively. The rate constant for the hydrolysis of inulobiose in 0.01 *N* hydrochloric acid at 70° is 0.042 min.$^{-1}$ and for the hydrolysis of sucrose under the same conditions it is 0.018 min.$^{-1}$.

The oligosaccharides produced enzymatically from sucrose[3] have been shown, by paper chromatographic procedures, to contain sucrosyl and inulobiosyl moieties. In order to establish the structure of these oligosaccharides with finality, it is necessary to have pure inulobiose available as a reference compound. Inulobiose can be prepared from inulin by controlled acid hydrolysis or from fructose and raffinose by enzymatic synthesis.[3] It is a reducing disaccharide consisting of two fructose residues united through a β-2,1′-D-fructosidic bond. The new disaccharide should prove to be an ideal substrate for the detection of β-D-fructofuranosidase activity[4] in enzyme preparations.

The methods for the preparation of inulobiose from inulin as well as the physical and chemical properties of the new compound are described in this paper. Preliminary experiments on the rate of hydrolysis of inulin in 0.01 *N* hydrochloric acid at 70° showed that the concentration of inulobiose attained a maximum in 30 minutes. The products in the neutralized hydrolysate consisted of fructose, inulobiose, inulotriose and the other homologous members of the inulin series[5] (Fig. 1). The first members of this series were resolved by descending paper chromatography. The inulobiose was extracted from the chromatograms with water, concentrated *in vacuo*, and precipitated with acetone. Details of the preparative procedures are presented in the experimental section.

Properties of Inulobiose.—From a hydrolysate of 10 g. of inulin, 0.42 g. of pure inulobiose was obtained. The disaccharide dissolves readily in

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[2] Research Fellow, University of Illinois, College of Medicine, Chicago, Illinois. The funds for this fellowship were made available through a grant to the University of Illinois College of Medicine from the National Fund for Medical Education.

[3] J. H. Pazur, *J. Biol. Chem.*, **199**, 217 (1952).

[4] C. Neuberg and I. Mandl, in J. B. Sumner and K. Myrbäck, "The Enzymes," Vol. 1, Part 1, Academic Press, Inc., New York, N. Y., 1950, p. 527.

[5] The small quantity of D-glucose present in inulin probably results in the formation of oligosaccharides of glucose and fructose residues. However, the concentration of these oligosaccharides is insignificant in comparison to the fructosyl series.