TABLE IV

ACTIVATION PARAMETERS IN TOSYLATE SOLVOLYSIS

	Substituent									
	p-No$_2$		p-Cl		H		p-F		p-CH$_3$	
Solvent[a]	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$
96.2 A	19.4	31.2	18.9	21.8	19.1	23.8	18.9	23.2	19.1	18.4
90.9 A	19.6	23.8	18.9	21.5	19.4	19.1	18.3	21.8	19.8	12.4
83.3 A	18.3	22.1	18.9	19.1	19.8	15.1	19.1	16.1	20.0	8.4
76.9 D	18.5	23.8			18.9	15.4	23.1	13.4	18.9	9.4
66.7 D	19.1	20.1	19.1	13.7	18.5	14.4	21.5	16.4	18.3[b]	8.4
55.6 D	20.4	14.4	17.8	15.6	18.3	12.8			17.8[b]	6.7

[a] Numbers refer to volume per cent. of cosolvent; A indicates acetone and D indicates dioxane. [b] Using 45° rate extrapolated from slower solvents.

TABLE V

FIRST-ORDER RATE CONSTANTS FOR SOLVOLYSIS OF BENZYL TOSYLATES IN AQUEOUS SOLVENT MIXTURES

	$\log k_s + 8$													
	p-CH$_3$			p-F		H			p-Cl			p-NO$_2$		
Solvent[a]	25°	35°	45°	25°	45°	25°	35°	45°	25°	35°	45°	25°	35°	45°
96.2 A	5.26		4.35	1.87	2.77	1.61		3.52	1.50		2.44	0.55		1.42
90.9 A	3.54	4.02	4.48	2.63	3.50	2.39	2.85	3.31	2.24	2.74	3.14	1.24		2.17
83.3 A	4.28	4.78	5.23	3.26	4.17	2.95	3.41	3.89	2.78	3.26	3.68	1.70		2.62
76.9 D	4.88	5.31	5.78	3.85	4.76	3.57	4.02	3.47				2.02		2.90
66.7 D	5.55	5.95		4.40		4.05	4.51	4.93	3.76	4.23	4.67	2.38	2.87	3.39
55.6 D	6.24	6.65		5.04	5.83	4.60	5.03	5.47	4.33	4.76	4.18	2.68	3.21	3.65

[a] Number refers to volume per cent. of cosolvent; A refers to acetone and D to dioxane.

different workers with entirely new preparations and reconstructed apparatus gave rate constants which agreed to 4% or better after correction of a numerical error. All rate constants in reference 1 should be multiplied by a factor of 2.303. Our new data are summarized in Table V.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

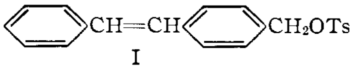
Benzyl Tosylates. VI. The Effects of Phenyl as a Substituent

BY GEORGE S. HAMMOND AND CHARLES E. REEDER

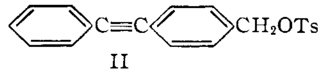
RECEIVED AUGUST 14, 1957

The isomeric *m*- and *p*-biphenylcarbinyl tosylates have been prepared and solvolyzed. The results are compared with those of an earlier study of the influences of β-styryl and phenylethynyl as substituents. There is a strong qualitative similarity between β-styryl and phenyl, although the former provides the greater resonance effects. Phenylethynyl is a unique group in that the values of σ^+ and σ_R apparently have different signs. The entropy of activation in the solvolysis of *p*-biphenylcarbinyl tosylate is less negative than usual.

We have continued our application of benzyl tosylate solvolysis rates to the study of the conjugative effects of unsaturated, all-carbon substituents. We previously showed[1] that the *p*-β-styryl substituent in I accelerated the solvolysis rate far more than would have been anticipated by consideration of the Hammett σ-constant for the group. The effect of the *p*-phenylethynyl group in II was qualitatively of the same sort but was quantitatively much reduced. The reactivity of the corresponding *m*-substituted compounds was adequately correlated by the unmodified Hammett equation. The different results were attributed to the firmer binding of electrons by carbon atoms in the sp state of hybridization than by sp^2 carbon atoms. Such considerations lead to the expectation that phenyl as a substituent should resemble β-styryl rather than phenylethynyl. Consequently, we now have made measurements with compounds III and IV.



I



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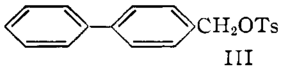

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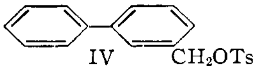

IV

Results and Discussion

The data for the rates of solvolysis of the biphenylcarbinyl tosylates are gathered in Table I. Data for styryl and phenylethynyl as substituents are included for comparative purposes.

The behavior of phenyl as a substituent is intermediate between β-styryl and phenylethynyl. The solvolysis rate of IV is correlated very well by the σ-constant for *m*-phenyl as determined by the ionization constant of *m*-biphenylcarboxylic acid[4] as was the case with the other two substituents.[1] The extra driving forces supplied by the three

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[1] J. K. Kochi and G. S. Hammond, THIS JOURNAL, **75**, 3454 (1953).

[2] G. S. Hammond, C. E. Reeder, F. T. Fang and J. K. Kochi, *ibid.*, **80**, 568 (1958).

[3] J. K. Kochi and G. S. Hammond, *ibid.*, **75**, 3445 (1953).

[4] N. N. Lichtin and H. P. Leftin, *ibid.*, **74**, 4207 (1952).

TABLE I

RATES OF SOLVOLYSIS OF ALL-CARBON SUBSTITUTED BENZYL TOSYLATES

Solvent	T, °C.	$k \times 10^6$, sec.$^{-1}$					
		p-C_6H_5	m-C_6H_5	p-$C_6H_5CH{=}CH$	m-$C_6H_5CH{=}CH$	p-$C_6H_5C{\equiv}C$	m-$C_6H_5C{\equiv}C$
83.3% acetone	25	76	6.2	1720	8.73[a]	9.62[b]	5.0[a]
83.3% acetone	45	790	50				
55.6% dioxane	25	510	19				
66.7% dioxane	25	100	6.0				

[a] Estimated using $\rho = -1.61$.[2] [b] Estimated using the extrapolation procedure described in reference 3.

groups as p-substituents are reflected by the $\Delta\sigma$-values calculated from the equation, $\log k/k_0 = \rho(\sigma + \Delta\sigma)$. The values for 83.3% acetone–water are: p-C_6H_5, -0.62; p-$C_6H_5CH{=}CH$, -1.35; p-$C_6H_5C{\equiv}C$, -0.19. There is probably no need for any special explanation of the fact that phenyl does not respond as much as β-styryl to the demand for electrons. Comparison of the σ-constants, which are given in Table II, indicates that the inductive effects of both groups must be small as would be expected since both groups contain only sp^2 carbon atoms. In both cases σ_p is more negative than σ_m. A separation of inductive and resonance effects could, therefore, be made by the method of Taft.[5,6] Taft finds that the quantity $\sigma - \sigma_I$ is, on the average, about three times as large for p-substituents as it is for the corresponding m-substituents. This relationship allows one to use σ-constants themselves to estimate σ_R and σ_I by equating the values of σ_I for a given substituent in the m- and p-positions.

TABLE II

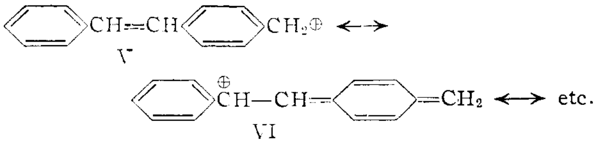
HAMMETT σ-CONSTANTS

Group	σ	Reference	σ_R	σ_I
p-C_6H_5	0.01	7	-0.07	0.08
m-C_6H_5	.06	4		
p-$C_6H_5CH{=}CH$	$-$ .05	1	$-$ .12	.07
m-$C_6H_5CH{=}CH$	.025	1		
p-$C_6H_5C{\equiv}C$	.190	1	.04	.15
m-$C_6H_5C{\equiv}C$	.160	1		

$$\sigma = \sigma_I + \sigma_R$$

$$\sigma_p - \sigma_I = 3(\sigma_m - \sigma_I)$$

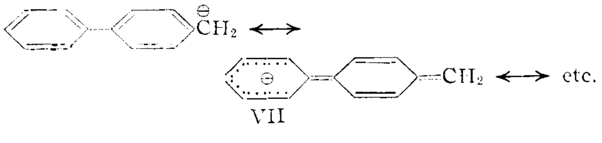
With σ-values so close to zero, one has little confidence in the absolute magnitude of the values of σ_I and σ_p obtained by application of the above equation. However, it is interesting that σ_R for the β-styryl group is larger than the value for phenyl since the same order holds for the $\Delta\sigma$-values. Taft[6] has found that the values of σ_R for electron-attracting groups are proportional to the values of σ^-_R, which are obtained by subtracting σ_I from the σ^- constants obtained by correlating the pK's of p-substituted anilines and phenols. Taft has observed[8] that there is no such regular relationship between the value of σ_R for electron donors and the values of σ_R^+ which are tabulated by Okamoto and Brown.[9] While there is some doubt[2,9] as to the applicability of σ^+-constants to benzyl tosylate solvolysis the constants are certainly related to $\Delta\sigma$ for tosylate solvolysis. Both σ_R and $\Delta\sigma$ indicate a higher conjugative aptitude for β-styryl than for phenyl. Quantitatively the ratios $\Delta\sigma/\sigma_R$ are much larger than Taft's value of σ^+_R/σ_R (1.72) but the differences *could* be attributed to a simple magnification of the uncertainty in σ_p. In order to account for the high conjugative aptitude of p-β-styryl one must assign a considerable weight to resonance structures such as VI in the derived benzyl cation.


V

VI

The same analysis of the effects of phenylethynyl as a substituent reveals a striking irregularity. Since σ_p is more positive than σ_m the value of σ_R *is necessarily positive. However,* $\Delta\sigma$ *is negative.* In this case the effects are large enough to lie well outside of experimental error. The fact is not intuitively disagreeable since one might expect the donor–acceptor properties of C–C π-bonds to adapt themselves to variations in electronic demands. The usual assumption that both allylic anions and cations are resonance stabilized amounts to the same hypothesis. The observation should serve as a caution against the indiscriminate assignment of immutable resonance influences to substituents; in agreement with the studies of Taft.[8]

Calculation of the activation parameters for the phenyl substituted tosylates in 83.3% dioxane gives the following values: p-C_6H_5, $\Delta H^{\ddagger} = 21.5$, $\Delta S^{\ddagger} = 5.4$; m-C_6H_5, $\Delta H^{\ddagger} = 19.1$, $\Delta S^{\ddagger} = 18.1$. The striking difference between the two isomers must reflect the fact that the spreading of the positive charge in the p-biphenylcarbinyl cation VII is reflected in an unusually small tendency for the ion to orient solvent (compare with reference 2).


VII

Experimental

4-Biphenylcarboxylic acid was prepared by a modification of the method of Fieser.[10] Sixty-six grams (0.5 mole) of anhydrous aluminum chloride (Baker and Adamson, reagent grade) was suspended in 75 ml. of tetrachloroethane in a 500-ml. flask which was equipped with a dropping funnel, reflux condenser and stirrer. A solution of 54 g. (0.35 mole) of biphenyl (Eastman Kodak Co., practical grade) and 27.4 ml. (0.385 mole) of acetyl chloride (Matheson, reagent grade) in 150 ml. of tetrachloroethane was added over

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(5) R. W. Taft in "Steric Effects in Organic Chemistry," M. S. Newman, Editor, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 595.

(6) R. W. Taft, THIS JOURNAL, **79**, 5075 (1957).

(7) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 188.

(8) R. W. Taft, private communication.

(9) Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).

(10) L. F. Fieser, *et al.*, THIS JOURNAL, **70**, 3186 (1948).

a one-hour period. The mixture was stirred at room temperature for one hour, at 80° for one hour, overnight without heating and, finally, for one hour at 105°. The mixture was poured into dilute hydrochloric acid and ice. The organic layer was separated and combined with additional tetrachloroethane extracts of the aqueous layer. The extract was washed with dilute, aqueous sodium hydroxide and with water and was dried with Drierite. The solvent was removed by vacuum distillation and the dark residue was recrystallized from ligroin (in which a tarry fraction was insoluble). The yield of 4-acetylbiphenyl, m.p. 115–117° (uncor.), was 43.5 g. (63.5%). Recrystallization of the material which was insoluble in ligroin from ethanol–ethyl acetate gave a material melting at 203–205° (uncor.) which we suspect to be a diacetylbiphenyl on the basis of its infrared spectrum.

4-Acetylbiphenyl was oxidized with sodium hypochlorite by the method of Newman and Holmes.[11] The yield of a crude acid was essentially quantitative. Sublimation gave a 76% yield of pure 4-biphenylcarboxylic acid, m.p. 226.0–226.5° (uncor.).

3-Biphenylcarboxylic acid was prepared by the carbonation of 3-bromobiphenyl which had been prepared by a modification of the method of Huber.[12] The published procedure for the preparation of 2-amino-5-bromobiphenyl was repeated without modification. Yields approached but did not equal those of the earlier workers. The deamination was done as follows: 50 ml. of concentrated hydrochloric acid and 250 ml. of water were placed in a flask equipped with a dropping funnel, thermometer and stirrer. The solution was heated to 60° and 48.6 g. (0.196 mole) of 2-amino-5-bromobiphenyl was added. A heavy precipitate was formed which all dissolved at 100° but was reprecipitated on cooling below 85°. The flask and contents were cooled to −5° and 15.0 g. (0.211 mole) of sodium nitrite in 36 ml. of water was added over a period of 50 minutes with cooling to keep the temperature between −8 and −3°. After 20 minutes additional stirring, 130 ml. of 50% hypophosphorous acid was added over a 40-minute period with the temperature at −5 to −2°. Stirring was continued for three hours and the flask was then transferred to a refrigerator for 40 hours. The aqueous layer was then decanted from the dark brown non-aqueous layer. The latter was dissolved in 300 ml. of benzene. The benzene solution was washed with 20% aqueous sodium hydroxide, water and warm 1:1 sulfuric acid (twice each). The benzene solution was finally washed thoroughly with distilled water and dried over anhydrous potassium carbonate. The solvent was removed by vacuum distillation. The residue was distilled at reduced pressure. Most of the material distilled as a colorless liquid at 177° at 4 mm.; yield 40.7 g. (89%).

The Grignard reagent was prepared according to the procedure of Vogel.[13] The Grignard solution was forced onto a slurry of Dry Ice in ether by means of a positive pressure of nitrogen. The light tan solid which formed became a gummy mass on warming to room temperature. Dilute hydrochloric acid was added and the ether layer was separated and extracted with 10% sodium hydroxide solution. The crude acid was precipitated by acidification of the basic extract with hydrochloric acid. The crude acid was recrystallized from acetone–petroleum ether to give white leaflets, m.p. 166.5–166.8° (uncor.). The average yield in three preparations was 60%.

4-Biphenylcarbinol.—The reduction of 4-biphenylcarboxylic acid with lithium aluminum hydride was carried out by the published method.[14] The crude product was recrystallized twice by dissolving it in acetone and pouring the acetone solution into petroleum ether; m.p. 100.5–101.0° (uncor.); yield in two preparations, 54 and 86%.

3-Biphenylcarbinol.—The crude product from lithium aluminum hydride reduction of 3-biphenylcarboxylic acid was recrystallized twice from ligroin. On cooling, the hot solutions first deposited an oil which was removed by decantation. White crystals, m.p. 51.2–51.5° (uncor.), were obtained by slow cooling of the residue; yield 44%.

Anal. Calcd.: C, 84.76; H, 6.56. Found: C, 84.67; H, 6.45.[15]

3- and 4-Biphenylcarbinyl Tosylates.—The tosylates were prepared by the previously described method.[14] The ether solutions from tosylation step were filtered, concentrated and cooled to Dry Ice temperature. The ether was separated through a filter stick with protection from atmospheric moisture. After the solids had been warmed to room temperature they were recrystallized three times from ether. The crystals were then dissolved in dry ether for storage. Samples were taken and the solvent was removed under reduced pressure as the compounds were needed for kinetic measurements. Because of their instability the compounds were not submitted for elementary analysis but solvolysis equivalents, calculated from the infinite titer after solvolysis of weighed samples, agreed with theoretical values with an accuracy of 1%. 3-Biphenylcarbinyl tosylate had m.p. 76–78° (uncor. dec.); 4-biphenylcarbinyl tosylate, m.p. 114° (uncor. dec.).

Kinetic measurements were made by methods previously described.[2,3]

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AMES, IOWA

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[11] M. S. Newman and H. L. Holmes, "Organic Syntheses," Coll. Vol. II, A. H. Blatt, editor, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 428.

[12] F. W. Huber, *et al.*, THIS JOURNAL, **68**, 1109 (1946).

[13] A. I. Vogel, "Practical Organic Chemistry," 2nd. ed., Longmans, Green and Co., London, 1951, p. 725.

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

[15] Microanalysis by H. Manser Laboratory, Zurich.