

The infrared spectrum of II (in Nujol) contained a P=O band at 1152 cm^{-1} and the C-F heptad at 998, 1100, — (masked), 1214, 1242 and 1260 (doublet), 1295, and 1348 cm^{-1} .

The acid was converted to its dianilinium salt by adding aniline dropwise to a portion of the acid in acetone; mp 267° dec, after recrystallization from ethanol.

Anal. Calcd for $\text{C}_{17}\text{H}_{18}\text{F}_6\text{N}_2\text{O}_6\text{P}_2$: C, 39.09; H, 3.47; N, 5.36. Found: C, 38.83; H, 3.34; N, 5.47.

The infrared spectrum of this salt (in Nujol) contained a P=O band at 1154 cm^{-1} , a P-OH band at 2645 cm^{-1} , and the C-F heptad at 998, 1095, — (masked), 1180, 1246 and 1256 (doublet), 1293, and 1343 cm^{-1} .

3,3,4,4,5,5-Hexafluoro-1-cyclopenten-1,2-ylenediphosphonic Tetrachloride (III).—A solution of 114.0 g (0.34 mole) of II in 500 ml of phosphorus oxychloride was treated with 298.0 g (1.43 mole) of phosphorus pentachloride in portions over a 30-min period at 30–40°. Gas evolution was brisk. The temperature was then raised gradually to 76°, and when the gas evolution subsided (3.5 hr) the solvent was stripped off under vacuum. The pot temperature was not allowed to rise above 70° during the stripping. The residue, 139.5 g, which was partly solid, gave on distillation 11.6 g of a fraction, bp 52–55° (1.3 mm), 16.6 g of an intermediate fraction, bp 53–58° (1.3–0.8 mm), n_D^{20} 1.4313, and 90.2 g of a fraction, bp 89–90° (0.45 mm). The low-boiling fraction, bp 52–55° (1.3 mm), n_D^{20} 1.4281, was identified by analysis and by its infrared spectrum as IV (25% yield).

Anal. Calcd for $\text{C}_5\text{Cl}_3\text{F}_6\text{OP}$: Cl (t), 32.5; Cl (h), 21.7. Found: Cl (t), 32.0; Cl (h), 22.6.

The high-boiling fraction, bp 89–90° (0.45 mm), was the desired III (65% yield). It crystallized on cooling: mp 78.5–81.5°.

Anal. Calcd for $\text{C}_5\text{Cl}_4\text{F}_6\text{O}_2\text{P}_2$: Cl, 34.6; P, 15.1. Found: Cl (t), 33.2; Cl (h), 33.3; P, 15.2.

The infrared spectrum of this product (in carbon tetrachloride) contained a P=O band at 1303 cm^{-1} and the C-F heptad at 1007, 1096, 1168, 1213, 1246 and 1272 (doublet), — (masked), and 1332 and 1342 (doublet) cm^{-1} .

Tetrakis(2,2,2-trifluoroethyl) 3,3,4,4,5,5-Hexafluoro-1-cyclopenten-1,2-ylenediphosphonate (Ic).—A solution of 29.8 g (0.073 mole) of III in 100 ml of benzene was treated dropwise with 29.1 g (0.291 mole) of trifluoroethanol over a 24-min period at room temperature. Hydrogen chloride began to evolve during the addition and subsided after 7 hr of stirring at room tempera-

ture. The solvent was stripped off under vacuum, leaving 43.1 g of residue which gave on distillation a small forecut, 2.2 g, followed by 24.6 g (51%) of Ic: bp 84–86° (0.1 mm), n_D^{20} 1.3591, fp –28°. The undistilled residue was substantial.

Anal. Calcd for $\text{C}_{13}\text{H}_5\text{F}_{18}\text{O}_6\text{P}_2$: Cl, nil; P, 9.3. Found: Cl (t), 1.6; P, 9.2.

The infrared spectrum of this product (neat) contained a P=O band at 1280 cm^{-1} , a much-displaced P-O-(C) band at 1070 cm^{-1} , and the C-F heptad at 1012, 1102, 1166–1200 (not resolved), 1243 and 1260 sh (doublet), 1300, and 1348 cm^{-1} .

sym Diethyl Dihydrogen 3,3,4,4,5,5-Hexafluoro-1-cyclopenten-1,2-ylenediphosphonate (VII).—A solution of 44.8 g (0.1 mole) of Ia¹ in 750 ml of anhydrous ethanol was heated to reflux in a distillation apparatus. Distillate was drawn off only as required to maintain the vapor temperature at 78°. When no further depression in the vapor temperature was observed (72 hr), the remainder of the ethanol was stripped off under vacuum, leaving 40.5 g (calcd 39.2 g) of VII as a slightly yellow, viscous liquid.

Anal. Calcd for $\text{C}_9\text{H}_{12}\text{F}_6\text{O}_6\text{P}_2$: P, 15.8; mol wt, 392. Found: P, 15.2; neut equiv, 416.

The infrared spectrum of this product (neat) contained a P=O band at 1157 cm^{-1} , three broad, shallow P-OH bands at 1600, 2200, and 2650 cm^{-1} , and the C-F heptad at 1010, 1100, — (masked), 1205, 1239–1252 (not resolved), 1295, and 1343 cm^{-1} .

The acid ester was converted to its bis(dicyclohexylammonium) salt by adding dicyclohexylamine to a portion of VII in acetone. No immediate reaction was observed, but crystals separated on standing overnight: mp 221–222° after one recrystallization from ethanol.

Anal. Calcd for $\text{C}_{33}\text{H}_{58}\text{F}_6\text{N}_2\text{O}_6\text{P}_2$: N, 3.71; P, 8.21. Found: N, 4.15; P, 8.09.

The infrared spectrum of this salt (in Nujol) contained a P=O band at 1215 cm^{-1} and the C-F heptad at 1006, 1100 sh, 1132, 1145 sh, 1200 sh, 1242, 1292, and 1340 cm^{-1} .

Acknowledgment.—The author is indebted to Mr. Leon A. Zengierski for capable technical assistance, and to Dr. Charles F. Baranauckas for his guidance and encouragement.

Rates of Alkaline Hydrolysis of *meta*- and *para*-Substituted Ethyl β -Phenylpropionates and Correlation with σ^0 ¹

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Received November 1, 1965

A series of twenty *meta*- and *para*-substituted ethyl β -phenylpropionates have been prepared, and the rates of alkaline hydrolysis in 87.8% ethanol at 30° have been measured. The rates generally follow the σ^0 values for the substituents estimated from other reactivities and from F¹⁹ nmr shielding in similar solvents. The unexpectedly high rate of the *m*-(CH₃)₃N⁺ compound may be due to a direct, short-range electrostatic interaction in the transition state for hydroxide ion attack of the ester.

Although the rates of alkaline hydrolysis of several *meta*- and *para*-substituted ethyl β -phenylpropionates had previously been reported,^{2,3} the present, more extensive study was carried out with the following objectives: (1) to furnish an extensive group of σ^0 data (appropriate to benzene derivatives lacking direct resonance interactions between substituent and functional group⁴) based on a single reactivity series in one solvent, for comparison with values obtained from

assorted reactivities⁴ and from F¹⁹ nmr shifts,⁵ (2) to establish σ^0 values for certain disubstitutions (3,4-methylenedioxy- and 3,4-dichloro-) which give readily purified, crystalline derivatives in a number of series; and (3) to determine the σ^0 values for the charged substituents *m*- and *p*-(CH₃)₃N⁺.⁶ The results are given in Table I.

The value of ρ is +0.63. This is based on six *meta* substituents having nearly invariant σ values.⁷ The original value³ of 0.591, based on *meta* and *para* sub-

(1) The support of this work by the Robert A. Welch Foundation under Grant E-136 is gratefully acknowledged.

(2) K. Kindler, *Ann.*, **452**, 90 (1927).

(3) R. Fuchs and J. J. Bloomfield, *J. Org. Chem.*, **28**, 910 (1963).

(4) R. W. Taft, S. Ehrenson, I. C. Lewis, and R. E. Glick, *J. Am. Chem. Soc.*, **81**, 5352 (1959).

(5) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *ibid.*, **85**, 709, 3146 (1963).

(6) Values have been reported based on nmr data⁵ but not on reactivities, nor in the solvent 87.8% ethanol.

(7) R. W. Taft and I. C. Lewis, *J. Am. Chem. Soc.*, **81**, 5343 (1959).

TABLE I
RATES OF ALKALINE HYDROLYSIS OF *meta*- AND *para*-
SUBSTITUTED ETHYL β -PHENYLPROPIONATES IN
87.8% ETHANOL AT 30°

Phenyl substituent	k_{meta}^a	k_{para}^a
H	5.97, 5.98 (5.78) ^b (5.72) ^c	
(CH ₃) ₃ N ⁺	32.7	20.7
NO ₂	17.3, 17.3	19.2 (18.2, 18.0) ^b
Cl	10.4 (10.6, 10.6) ^b	9.20 (8.98, 9.08) ^b (8.60) ^c
F	9.50, 9.65	8.02
CH ₂ O	6.44	4.97 (5.17, 5.18) ^b (4.80) ^c
CH ₃	5.57	4.98 (4.95, 4.83) ^b
CH ₃ CH ₂ O	...	4.88, 4.85
NH ₂	4.40	3.65, 3.73
(CH ₃) ₂ N	4.77	4.12, 3.95
3,4-Cl ₂		14.2 (15.3, 15.3) ^b
3,4-CH ₂ O ₂		5.94 (5.48) ^c

^a Second-order rate constants (l. mole⁻¹ sec⁻¹) $\times 10^3$. At time of mixing [KOH] = 0.04 M, [ester] = 0.025 M. Stated temperature regulated to $\pm 0.02^\circ$. Solvent composition, ethanol-water (87.8:12.2 vol %). The kinetic procedure has been previously described: J. J. Bloomfield and R. Fuchs, *J. Org. Chem.*, **26**, 2991 (1961). ^b Values from ref 3. ^c Values from ref 2.

perimental value for p -N(CH₃)₃⁺ of +0.85 is within the range of about 0.8–0.9, usually given.¹⁰ Other experimental values are 3,4-dichloro, +0.59; 3,4-CH₂O₂, 0.01; CH₃CH₂O, -0.14; m -NH₂, -0.21 ($\sigma^0 = -0.14$); p -NH₂, -0.33 ($\sigma^0 = -0.38$); p -N(CH₃)₂, -0.27 ($\sigma^0 = 0.44$); and m -(CH₃)₂N⁺, +1.16 (various σ values,¹⁰ +0.85 to +0.90).

Discussion

The observed discrepancies in the rates of the p -NH₂ and p -N(CH₃)₂ compounds are probably due in considerable part to the decreased resonance contribution to σ^0 (previously noted⁵ in the F¹⁹ nmr shifts of substituted fluorobenzenes) accompanying a change from a "normal" nonprotonic solvent to aqueous alcohol. The cause of the deviation of the m -NH₂ compound is uncertain. Taft⁵ has found a variation of ± 0.08 in the inductive contribution (σ_I) to σ^0 in a series of rather closely related (weakly protonic) solvents. The unexpectedly high experimental substituent constant for m -(CH₃)₃N⁺ does not appear to be primarily a

TABLE II
PHYSICAL CONSTANTS OF *meta*- AND *para*-SUBSTITUTED ETHYL β -PHENYLPROPIONATES

Phenyl substituent	n_D^{20} , [lit.]	Bp (mm) or mp, °C [lit.]	Calcd, %		Found, %	
			C	H	C	H
Unsubstituted	1.4905 ³⁰ [1.4951 ^{17,6}] ^a	66.5–66.8 (1) [127 (15)] ^a				
4- ⁺ N(CH ₃) ₃ I ^{-b}		176.4–176.8 dec	46.29	6.11 ^b	46.04	5.73
4-NO ₂ ^c		108 (0.02), 29.1–29.5 [33–34] ^d				
4-F	1.4746 ³⁰	126.5–127 (11)	67.33	6.68	67.21	6.91
4-Cl	1.5087 ²⁴	99 (0.4) [158–159 (15)] ^e				
4-CH ₃	1.4985 ²³	87 (0.4) [263–265] ^f				
4-NH ₂	1.5334 ³⁰	107 (0.03)	68.37	7.83 ^g	68.53	7.67
4-N(CH ₃) ₂	1.5241 ³⁰	103 (0.25)	70.56	8.65	70.89	8.61
4-OCH ₃	1.5011 ²⁵ [1.5016 ²⁵] ^h	99 (0.2), [103 (0.1)] ^h				
4-OCH ₂ CH ₃	1.4953 ³⁰	97 (0.2)	70.30	8.16	70.24	8.05
3,4-Cl	1.5220 ³⁰	92–93 (0.03)	53.68	4.92	53.78	4.90
3,4-CH ₂ O ₂	1.5120 ³⁰	100–103 (0.05) [182–183 (19)] ^e	64.85	6.35	64.85	6.34
3- ⁺ N(CH ₃) ₃		76–78 dec	46.29	6.11 ⁱ	45.41	6.09
3-NO ₂ ^c	1.5201 ³⁰	112 (0.04)	59.19	5.86	59.26	5.94
3-F	1.4758 ³⁰	121 (9)	67.33	6.68	67.40	6.57
3-Cl	1.5052 ³⁰	102 (0.5)	62.12	6.16	62.31	6.18
3-OCH ₃	1.5004 ³⁰ [1.5025 ²⁵] ^j	152.5–155.5 (9) [183–184 (17)] ⁱ	69.20	7.75	69.57	7.73
3-CH ₃	1.4911 ³⁰	128–129 (12)	74.96	8.39	75.38	8.41
3-N(CH ₃) ₂ ^k	1.5243 ³⁰	110 (0.6)	70.60	8.65	70.01	8.57
3-NH ₂ ^l	1.5330 ³⁰	102–103.5 (0.2)	68.37	7.83	68.42	7.79

^a A. Brochet and A. Cabaret, *Bull. Soc. Chim. France*, **17**, 57 (1915). ^b *Anal.* Calcd: I, 34.94. Found: I, 34.92. Methyl ester, mp 205.5–205.6° dec. *Anal.* Calcd: C, 44.75; H, 5.77; I, 36.30; N, 4.02. Found: C, 44.94; H, 5.68; I, 36.10; N, 3.80. ^c Prepared by the esterification of the corresponding acid: J. M. Gulland, R. D. Haworth, C. J. Virden, and R. K. Callow, *J. Chem. Soc.*, 1666 (1929). ^d F. K. Beilstein and A. Kuhlberg, *Ann.*, **163**, 133 (1872). ^e See ref 2. ^f C. Willgerodt and W. Hambrecht, *J. Prakt. Chem.*, **81**, 77 (1910). ^g *Anal.* Calcd: N, 7.25. Found: N, 7.87. ^h E. Bowden and H. Adkins, *J. Am. Chem. Soc.*, **62**, 2422 (1940). ⁱ *Anal.* Calcd: I, 34.94; N, 3.86. Found: I, 34.63; N, 3.58. Methyl ester, mp 143.8–146.2°. *Anal.* Calcd: C, 44.75; H, 5.77; I, 36.30; N, 4.02. Found: C, 44.35; H, 5.64; I, 36.20; N, 4.05. ^j W. S. Johnson, C. A. Erickson, and J. Ackerman, *J. Am. Chem. Soc.*, **74**, 2251 (1952). ^k m -Nitrobenzaldehyde was reductively methylated with a palladium catalyst and formaldehyde in aqueous ethanol to give m -dimethylaminobenzaldehyde [V. M. Ingram, *J. Chem. Soc.*, 2247 (1950)], which was converted to the product using the general procedure described above. ^l Prepared by the palladium-catalyzed hydrogenation of m -nitrocinnamic acid, followed by esterification.

stituents and ordinary σ values (benzoic reactivities) has been recalculated⁸ as 0.635, using the suggestion of Wepster.⁹ In addition to the substituents on which ρ is based (m -NO₂, m -Cl, m -F, m -OCH₃, H, and m -CH₃) agreement with σ^0 to within ± 0.03 is found for p -NO₂, p -Cl, p -F, p -CH₃, p -OCH₃, and m -N(CH₃)₂. The ex-

solvent effect, since the *para* isomer shows no unusual reactivity. Some question of the purity of the two compounds arose from earlier low values in the carbon-hydrogen analyses. These furnished the first indication that ester exchange occurred during recrystallization of the ethyl ester from hot methanol. Recrystallization of the *para* isomer from absolute ethanol (the presence of water prevents crystallization) gave a product with satisfactory carbon, hydrogen, and ionic

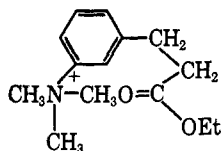
(8) K. Bowden, *Can. J. Chem.*, **41**, 2781 (1963).

(9) H. van Bekkum, P. E. Verkade, and B. M. Wepster [*Rec. Trav. Chim.*, **78**, 815 (1959)] concluded that certain σ values (which are best used in determining ρ) are relatively invariant, whereas others are highly variable. The major conclusions parallel those of Taft.⁷

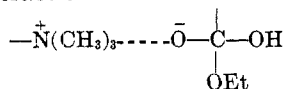
(10) P. R. Wells, *Chem. Rev.*, **63**, 182 (1963).

iodide analyses. Similar treatment of the *meta* compound gave a carbon analysis nearly 0.9% low, but satisfactory nitrogen and ionic iodide analyses. Both compounds decompose at the melting points [*p*-(CH₃)₃N⁺, 176.4–176.8°; *m*-(CH₃)₃N⁺, 76–78°] with evolution of methyl iodide. It appears that at the lower temperature, one-fourth to one-third fails to be oxidized to carbon dioxide during combustion analysis. Nitrogen and ionic iodide analyses are unaffected by this loss. A further indication of satisfactory purity was the consistency of the rate data for *m*- and *p*-ethyl and -methyl esters, corresponding with the reaction of at least 90% of the original ester in the kinetic solutions. Other physical constants are found in Table II.

The rate of alkaline hydrolysis of the *m*-(CH₃)₃N⁺ ester is considerably greater than can reasonably be attributed (by comparison with the *para* isomer) to a slightly shorter inductive path through the carbon skeleton. Molecular models indicate that, in an extreme conformation, the carbonyl group is essentially in contact with the *m*-(CH₃)₃N⁺ substituent



and a strong ion-dipole interaction (or, more probably, the ion-ion interaction



following addition of hydroxide ion to the carbonyl¹¹) should be possible. If an appreciable population of

the extreme conformation existed in solutions of the *meta*-substituted ester, significant differences in the carbonyl region of the infrared might be anticipated. No such differences were found. The observed rate enhancement by the *m*-(CH₃)₃N⁺ group would, however, be consistent with a very high reactivity of the relatively few molecules in the extreme conformation at a given time, due to the stabilization of the transition state for hydroxide ion attack.

Experimental Section

If the appropriately substituted cinnamic acid was not commercially available, it was synthesized by refluxing the corresponding benzaldehyde overnight with a 20% excess of malonic acid and a small amount of a 50:50 piperidine-pyridine mixture in 1,2-dimethoxyethane as the solvent. The resulting mixture was acidified while still hot with dilute HCl; the product was allowed to crystallize and was then recrystallized. The cinnamic acid was hydrogenated in 95% ethanol solution using a palladium on barium sulfate catalyst, and an initial hydrogen pressure of about 2 atm. The resulting β -phenylpropionic acid was isolated and recrystallized, and then esterified in a mixture of absolute ethanol, benzene, and HCl or H₂SO₄, with continuous removal of water as the ethanol-benzene-water azeotrope.

m-(β -Carbethoxyethyl)phenyltrimethylammonium Iodide.—Ethyl β -(*m*-dimethylaminophenyl)propionate was dissolved in an excess of iodomethane. After several hours at room temperature the oily top layer was separated and taken up in absolute ethanol from which the product crystallized upon cooling. The crude crystals were recrystallized from acetone-heptane mixture. The somewhat hygroscopic ethyl ester appears to be converted by several recrystallizations from methanol to the methyl ester.

p-(β -Carbethoxyethyl)phenyltrimethylammonium Iodide.—Ethyl β -(*p*-dimethylaminophenyl)propionate was dissolved in absolute ethanol, and an excess of iodomethane was added. The precipitated product was removed by filtration and was recrystallized from absolute ethanol. Repeated recrystallizations from methanol gave the corresponding methyl ester.

(11) The authors are indebted to Professor E. S. Lewis for this suggestion.

Kinetics and Mechanism of Decomposition of the Trimethylsulfonium Cation

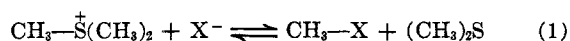
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Received December 17, 1965

The reactions (1) of the trimethylsulfonium cation with anions X⁻ (X = OEt, CN, I, SCN, N₃, Cl, F) to form dimethyl sulfide and CH₃X in ethanol and methanol at 100° are shown to be S_N2. Hydrolysis and methanolysis of (CH₃)₃S⁺ also proceed by the S_N2 mechanism and methanol and ethanol are more nucleophilic toward (CH₃)₃S⁺ than water. Ion association greatly influences the kinetics of (1) in ethanol. The equation $k_2^\mu = k_2^0\alpha^2$ (where α is the fraction of dissociated ions) fits the observed rates for (1) (X = Br), in ethanol at 100°, over a much larger range of ionic strength, μ , than does the Brønsted-Bjerrum equation. Nevertheless, the inclusion of formal activity coefficients leads to the conclusion that mechanisms involving separated ions (CH₃)₃S⁺ and X⁻ are indistinguishable in terms of kinetic rate law from the ones involving (CH₃)₃S⁺X⁻ pairs.

In bimolecular decompositions (1) of trimethylsulfonium salts charges are being partially destroyed in the transition state and reaction rates increase with decreasing capacity of the medium to solvate charges. Such decompositions are particularly suitable for an investigation of salt effects, influence of solvent, and the



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effect of X⁻, on the kinetics of anion-cation reactions. The present paper describes such an investigation.

There has been some controversy³⁻⁵ as to the mechanism of (1), but the reactions have been accepted as S_N2, by both Swain and Kaiser⁴ and by Hughes Ingold, and Pocker.⁶ The present work provides additional⁶ evidence that in ethanol, the solvent used by

(3) Y. Pocker, *Progr. Reaction Kinetics*, **1**, 224 (1961); cf. A. Strietweiser, Jr., *Chem. Rev.*, **56**, 610 (1956).

(4) C. G. Swain and L. E. Kaiser, *J. Am. Chem. Soc.*, **80**, 4089 (1958).

(5) J. L. Gleave, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 236 (1935).

(6) E. D. Hughes, C. K. Ingold, and Y. Pocker, *Chem. Ind. (London)*, 1282 (1959).