TABLE I

SULFATOALKYL AMINES

Name (formula)	M.p., °C.	Nitrogen, %		Sulfur, %		Potassium, %		Chloride, %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
Sulfatoalkyl ethylenediamine hydrochloride ($HO_3SOCH_2CH_2NHCH_2CH_2NH_2 \cdot HCl$)	192	12.70	13.19	14.53	14.20			16.07	16.18
2-Sulfato 1,3-diaminopropane hydrochloride [$H_2NCH_2CH(OSO_3H)CH_2NH_2 \cdot HCl$]	270	13.56	13.71	15.52	15.00			17.17	17.20
Potassium (disulfatoethyl)-amine monohydrate ($KO_3SOCH_2CH_2NHCH_2CH_2OSO_3H \cdot H_2O$)	127.5	4.37	4.36	19.90	19.73	12.17	12.16		
1-Sulfato-2-diethylaminopropane [$HO_3SOCH_2CH(CH_3)N(C_2H_5)_2$]	228.5	6.60	6.61	15.08	14.85				
2-(2-Sulfatoethyl)-pyridine ($HO_3SOCH_2CH_2NC_5H_4$)	167	6.90	6.73	15.76	15.31				
2-Sulfatoethyldimethylamine hemihydrate [$HO_3SOCH_2CH_2N(CH_3)_2 \cdot {}^1/_2H_2O$]	Anh. 253	7.90	7.90	18.05	18.15				
3-Sulfatopropylamine ($HO_3SOCH_2CH_2CH_2NH_2$)	230.5	9.03	8.97	20.65	20.71				

either ethylenimine or substituted ethylenimines by the method of Wenker[3] or similar methods.[4] Saunders[5] prepared a number of sulfuric acid esters of the simple monohydroxyethylarylamines. Aminized cotton is produced by allowing 2-aminoethylsulfuric acid to react with cotton in the presence of sodium hydroxide.[6] A number of other sulfatoalkyl amines, some of which have not previously been reported, were made (see Table I) for use in determining their reactivity with cotton and evaluating the chemically modified cottons produced by such reactions.

In each case the sulfates were prepared from the corresponding aminoalkyl alcohol by allowing the alcohol to react with chlorosulfonic acid in carbon tetrachloride. With carbon tetrachloride as the solvent or as the suspending agent the solution or the mixture is stirred and maintained near 0°. A cooled mixture of chlorosulfonic acid in carbon tetrachloride is initially added dropwise and later aliquot additions are increased as the reaction becomes less vigorous. Under these conditions there is no charring, and the product separates out either as a viscous liquid or a granular mass. The monosulfato monoamines may be obtained as inner salts, and the monosulfato diamines are easily isolated as hydrochlorides, whereas the disulfato monoamines are readily crystallized as monosodium or potassium salts. These crystalline products generally contain some free sulfate ion, but this contamination can easily be removed by crystallizing from an appropriate aqueous ethanol solution. When the hydrochloride is to be crystallized, the ethanol solution should be acidified with hydrochloric acid.

Since the sulfation of each alcohol was carried out under similar conditions, only one typical preparation will be described.

Experimental

Potassium Acid Disulfatoethyl Amine.—Diethanolamine (210 g.) suspended in 270 ml. of carbon tetrachloride was cooled to near 0° in an ice-salt-bath. Chlorosulfonic acid (466 g.) was added to the cool diol while stirring. At first the addition of chlorosulfonic acid was dropwise and slow; the later additions were larger and more rapid. After all the chlorosulfonic acid had been added, the mixture was removed from the cooling bath and stirred until the contents reached about room temperature. Much of the liberated hydrochloric acid had been removed at this stage. The crude granular disulfato compound separated out as an extremely deliquescent material. The neutral potassium salt was made by dissolving the acid in 500 ml. of water, then adding 30% potassium hydroxide in 50% ethanol until the solution had a *p*H of 7–8. Three liters of 95% ethanol was stirred in and when cooled, 550 g. (86% yield) of potassium acid disulfatoethyl amine separated. To get a highly purified sample, a portion of the above material was dissolved in a minimum of hot 67.5% ethanol and allowed to crystallize slowly.

Acknowledgment.—The authors wish to express their appreciation to the following members of this Laboratory: Lawrence E. Brown and Samuel M. Stark, Jr., for sulfur determinations; Vidabelle O. Cirino for nitrogen determinations; and Alva F. Cucullu for potassium determinations.

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[3] Henry Wenker, THIS JOURNAL, **57**, 2328 (1935).

[4] H. Schlapfer and A. Margot, U. S. Patent 2,558,273 (1951).

[5] K. H. Saunders, *J. Chem. Soc.*, **121**, 2667 (1922).

[6] Wilson A. Reeves and John D. Guthrie, *Textile Research J.*, in press.

[7] One of the Laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

The Electrical Effect of the Trimethylsilyl Group. II.

BY JOHN D. ROBERTS AND CLARE M. REGAN

RECEIVED MARCH 25, 1953

In an earlier investigation,[1] we presented evidence based on Hammett[2] σ-constants that the trimethylsilyl [$(CH_3)_3Si$-] group is electron-donating in character as judged by the manner in which it influences the acidity of the carboxyl group in benzoic acid. Since the electrical influence of the group is not apparently clear-cut in other types of compounds[3] we have reinvestigated the reactivities of the trimethylsilyl substituted benzoic acids and have prepared the corresponding ethyl esters and determined their alkaline saponification rates.[4]

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[1] J. D. Roberts, E. A. McElhill and R. Armstrong, THIS JOURNAL, **71**, 2923 (1949).

[2] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chap. VII.

[3] H. Soffer and T. DeVries, THIS JOURNAL, **73**, 5817 (1951).

[4] We have confined our attention to the acids and esters since Dr. R. A. Benkeser of Purdue University has measured the reactivities of a number of amine derivatives. ADDED IN PROOF.—R. A. Benkeser and H. R. Krysiak, *ibid.*, **75**, 2421 (1953). The results of these investigators with benzoic acid derivatives are in good agreement with those given in Table II.

TABLE I

APPARENT IONIZATION CONSTANTS, DIPHENYLDIAZOMETHANE REACTIVITIES AND ETHYL ESTER SAPONIFICATION RATES OF SUBSTITUTED BENZOIC ACIDS

Substituent	Av. half-point[a,b]	K_A × 10^6[c]	Concn., moles/l.[d]	Half-life,[d] min.	Av. k_2[b,d] l./mole min.	k_2 × 10^4,[b,e] l./mole min.	k_2 × 10^3[b,f] l./mole min.
			0.0487	13.21			
None	5.80 ± 0.01	1.59	.0874	7.29	1.08 ± 0.01	28.7 ± 0.50	8.68 ± 0.50
	(5.75)[g]		.0967	6.22	(1.04)[g]		
			.0800	7.41			
p-$(CH_3)_3Si$–	5.80 ± 0.01	1.59	.0823	7.35	1.15 ± 0.01	23.3 ± 0.6	9.98 ± 0.44
	(5.85)[g]		.0440	13.71	(1.05)[g]		
			.0810	7.72			
m-$(CH_3)_3Si$–	6.00 ± 0.02	1.00	.0737	8.69	1.10 ± 0.01	12.6 ± 0.3	6.64 ± 0.08
	(6.01)[g]		.0474	13.22	(1.07)[g]		
p-CH_3–	6.00 ± 0.01	1.00	....	...	....	....	....
	(5.94)[g]						
p-CH_3O–	6.12 ± 0.02	0.76	....	...	....	....	....
	(6.07)[g]						

[a] Reading on *p*H scale of *p*H meter calibrated for aqueous buffer solutions at half-neutralization point using glass and saturated calomel electrodes without correction for liquid junction potentials in 50% water–50% ethanol (by volume) solutions at 25°. [b] Standard deviations are appended to the average values. [c] Calculated assuming unit activities and readings of *p*H meter scale equal to logarithm of reciprocal of hydrogen ion concentrations. [d] For reaction of benzoic acids with diphenyldiazomethane in absolute alcohol solution at 30°. [e] Rate constants for saponification of ethyl esters in 56% acetone (by weight) at 24.9°, see ref. 5b. [f] Rate constants for saponification of ethyl esters in 87.83% ethanol (by volume) at 30.0°, see ref. 5a. [g] Values obtained previously[1] with different apparatus and materials.

The procedures have been described earlier in detail.[1,5] The ethyl esters of *m*- and *p*-trimethylsilylbenzoic acids were prepared in 50–57% yields by heating the silver salts of the acids[1] with a slight excess of ethyl iodide in ether; ethyl *m*-trimethylsilylbenzoate, b.p. 90–91° (1.5 mm.). *Anal.* Calcd. for $C_{12}H_{18}O_2Si$: C, 64.54; H, 8.12. Found: C, 64.84; H, 8.10. Ethyl *p*-trimethylsilylbenzoate, b.p. 105–106° (2.7 mm.). *Anal.* Calcd. for $C_{12}H_{18}O_2Si$: C, 64.54; H, 8.12. Found: C, 64.70; H, 8.11.

The experimental results for the trimethylsilyl derivatives along with those for some reference compounds are given in Table I. A summary of available σ-constant data is presented in Table II. Reasonable experimental agreement was found with the earlier investigation[1] and from all of the results it is clear that the net electrical effect of the trimethylsilyl group on the reactivities of benzoic acids or esters is essentially negligible in the para-position but rather electron-donating in the meta-position. The spread of the meta-σ-values is large compared with what is customarily found[2] and may be related to the bulkiness of the group.[4,6]

TABLE II

σ-CONSTANTS FOR THE TRIMETHYLSILYL GROUP

Reaction[a]	(Meta)	(Para)
Ionization constants in 50% ethanol at 25°	−0.155 (−0.208)[b]	−0.020 (−0.060)[b]
Diphenyldiazomethane rates in absolute ethanol at 30.0°	+0.025 (−0.018)[b]	+0.002 (−0.022)[b]
Alkaline hydrolysis in 87.83% ethanol at 30.0°	−0.040	+0.027
Alkaline hydrolysis in 56% acetone at 24.9°	−0.150	−0.040
Average	−0.080 ± 0.042[c] (−0.113)[b]	−0.008 ± 0.014[c] (−0.041)[b]

[a] Data for log k_0 and ρ are given elsewhere.[1,2] [b] Ref. 1. [c] Standard deviations.

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(5) (a) K. Kindler, *Ann.*, **450**, 1 (1926); (b) E. Tommila and C. N. Hinshelwood, *J. Chem. Soc.*, 1801 (1936).

(6) *Cf.* ref. 5 of J. D. Roberts, R. A. Clement and J. J. Drysdale, THIS JOURNAL, **73**, 2181 (1951); C. C. Price and D. C. Lincoln, *ibid.*, **73**, 5836 (1951).

Direct Synthesis of Organotin Halides. I. Preparation of Dimethyltin Dichloride[1]

BY A. C. SMITH, JR.,[2] AND EUGENE G. ROCHOW

RECEIVED MAY 4, 1953

Organotin halides have been known for a hundred years,[3] and many compounds of the type R_aSnX_{4-a} have been synthesized. With the exception of two sealed-tube syntheses of iodides,[4,5] all preparations have been by indirect and often difficult methods.[6]

The direct synthesis of organosilicon and organogermanium halides[7] led to a study of the direct synthesis of organotin halides.[8] The effects of several metals as catalysts was studied by placing each metal over a thin film of evaporated tin on a microscope slide and heating the slide in an atmosphere of methyl chloride for one-half hour at 300°. Any unusual reactivity of the metallic couple was indicated by reaction and removal of the tin at the junction of the two metals. Copper proved to be the most promising catalyst, with some activity also exhibited by silver and gold. Mercury, iron, selenium, arsenic, titanium, antimony, tellurium, calcium, magnesium, zirconium, aluminum, chro-

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(1) From a thesis submitted by A. C. Smith, Jr., to the Graduate School of Arts and Sciences of Harvard University.

(2) Metal and Thermit Fellow at Harvard University 1949–1950.

(3) C. Lowig, *Ann.*, **84**, 309, 313 (1852).

(4) A. Cahours, *ibid.*, **114**, 373 (1860).

(5) Karantassis and Basileiados, *Compt. rend.*, **205**, 460 (1937).

(6) An extensive discussion is given in E. Krause and A. v. Grosse, "Die Chemie der metall-organischen Verbindungen," Chapt. V, Borntraeger, Berlin, 1937, pp. 311–372.

(7) E. G. Rochow, THIS JOURNAL, **67**, 963 (1945); **69**, 1729 (1947).

(8) The experiments reported herein were conducted in the period 1949 to 1951. After a full account had been prepared, U. S. Patent 2,625,559 in the same field, (Frederick A. Smith, assigned to Union Carbide and Carbon Corp.) appeared on Jan. 13, 1953. The present paper is a condensed version dealing almost entirely with those aspects of our work not touched upon by the F. A. Smith patent. Full details of our own work are available in the thesis of reference (1).