Organosilicon Compounds. Part VIII.* The (Trimethylsilylmethyl)-benzoic Acids.

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The apparent ionisation constants in 50% water–ethanol and the absorption spectra of the three (trimethylsilylmethyl)benzoic acids are reported and discussed.

STUDIES of the electronic influence of the trimethylsilyl group attached directly to an aromatic nucleus have shown that an important $-E$ effect opposes the expected $+I$ effect of the group (Benkeser and Krysiak, *J. Amer. Chem. Soc.*, 1953, **75**, 2421; Speier, *ibid.*, p. 2930; Roberts and Regan, *ibid.*, p. 4102; Roberts, McElhill, and Armstrong, *ibid.*, 1949, **71**, 2923). With a methylene group between the silicon atom and the nucleus the $+I$ effect must be reduced, but the $-E$ effect is eliminated, and the strengths of the (trimethylsilylmethyl)benzoic acids reveal the overall result. The apparent ionization constants of these acids in 50% ethanol–water at 18° are shown in the following Table, along with those for benzoic acid and unsubstituted toluic acids determined with the same apparatus. The " pK_a " values listed are actually the values of the pH at half neutralization, and are subject to a standard deviation of ± 0.03.

R(in $R \cdot C_6H_4 \cdot CO_2H$)	H	$o\text{-}CH_3$	$o\text{-}Me_3Si\cdot CH_2$	$m\text{-}CH_3$	$m\text{-}Me_3Si\cdot CH_2$	$p\text{-}CH_3$	$p\text{-}Me_3Si\cdot CH_2$
pK_a	5·70	5·70	6·34	5·77	6·00	5·88	6·08
10^6K_a	2·00	2·00	0·457	1·70	1·00	1·32	0·832

The most striking features of the Table are: (i) the strong electron supply from the trimethylsilylmethyl group [use of Roberts, McElhill, and Armstrong's value (*loc. cit.*) of 1·464 for the Hammett rho constant for acid dissociation in the medium at 25° leads to σ_p and σ_m values for the group of -0.260 and -0.205 respectively—compare $\sigma_p = -0.268$ for the p-methoxy-group]; (ii) the relatively small difference between the effects of the group in the *meta*- and *para*-positions; (iii) the decrease in acid strength caused by the group in the *ortho*-position, surprisingly large in view of the existing generalization that all *ortho*-substituents increase the strength of benzoic acid (see Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 743). The facts are consistent with the operation of a large $+I$ effect from the silicon atom, particularly since the effect of replacing a methyl-hydrogen atom by the trimethylsilyl group falls off in the order $o > m > p$ (cf. Roberts, Clements, and Drysdale, *J. Amer. Chem. Soc.*, 1951, **73**, 2181). In o-(trimethylsilylmethyl)benzoic acid the $+I$ effect presumably operates so strongly that it outweighs the acid-strengthening steric effects which normally predominate for *ortho*-substitution. This strong electron supply to the *ortho*-position accounts also for the large proportion of *ortho*-substitution ($\sim$80% of products isolated) on nitration of benzyltrimethylsilane with copper nitrate in acetic acid (Benkeser and Brumfield, *ibid.*, p. 4770) or nitric acid in acetic anhydride (Eaborn and Parker, unpublished work).

Substitution of the trimethylsilyl group for a methyl-hydrogen atom in the toluic acids causes a bathochromic shift of the main ($\sim$235) maximum in all cases, but the shift is much greater for the *para*-acids, as the Table shows. Thus the silyl group in this position supplies electrons strongly, and by a delocalization rather than an inductive mechanism (Doub and Vandenbelt, *ibid.*, 1947, **69**, 2714; Crawford, *J.*, 1953, 2061), suggesting contributions from structures such as $Me_3Si^+ \; CH_2 = \langle\;\rangle = C\langle^{O^-}_{OH}$ in the excited state. This effect could not operate from the *meta*-position and would be sterically inhibited in the *ortho*-position.

Co-ordination of carbonyl oxygen to silicon would be geometrically easy in o-(trimethylsilylmethyl)benzoic acid. The absence of any unusual feature in the absorption

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spectrum indicates that such co-ordination (which would be analogous to the chelation suggested by Benkeser and Brumfield, *loc. cit.*, for trimethyl-*o*-nitrobenzylsilane) is not significant.　The low ionization constant of the acid supports this, since the co-ordination

Values of $\lambda_{max.}$ (in mμ) for acids R·C$_6$H$_4$·CO$_2$H, with corresponding values of log ε in parentheses.

R	o-Me	o-Me₃Si·CH₂	m-Me	m-Me₃Si·CH₂	p-Me	p-Me₃Si·CH₂
In hexane	205　(4·12)	210·5 (4·55)	206　(4·09)	210·5 (4·48)	<206	208·5 (4·17)
	234·7 (4·06)	238·5 (3·96)	235·5 (4·10)	239　(4·02)	240·5 (4·19)	256·5 (4·29)
	282　(3·22)	295·5 (3·45)	281　(3·15)	290·5 (3·23)	272　(3·02)	~270 *
	~290 *	—	291　(3·08)	—	283·2 (2·88)	—
In methanolic HCl	229　(3·92)	232·5 (3·91)	231·5 (4·03)	232　(3·95)	237·5 (4·15)	252·5 (4·26)
	279　(3·09)	290　(3·35)	286　(3·02)	289　(3·17)	281·5 (2·77)	—
	—	208　(4·6)	—	211　(4·5)	—	—

* Signifies a point of inflexion.

would be acid-strengthening; Sommer, Gold, Goldberg, and Marans (*J. Amer. Chem. Soc.*, 1949, **71**, 1509) took the lowered strength of trimethylsilyl-substituted aliphatic acids to signify the absence of co-ordination.

EXPERIMENTAL

M. p.s and b. p.s are corrected.

m-*Chlorobenzyl Bromide.*—*m*-Chlorotoluene was brominated by Barnes and Gordon's method for *o*-chlorotoluene (*ibid.*, p. 2644) to give *m*-chlorobenzyl bromide (61%), b. p. 122—124°/19 mm.

(*Chlorobenzyl)trimethylsilanes.*—Chlorotrimethylsilane (1·1 moles) and the Grignard reagent from 1 mole of *o*- or *p*-chlorobenzyl chloride or *m*-chlorobenzyl bromide in ether (600 ml.) were boiled under reflux for 8 hr.　Aqueous sulphuric acid was added until two clear layers separated and the ethereal layer was washed, dried (Na₂SO₄), and fractionated, to give ~60% yields of o-, b. p. 222—223°, n_D^{20} 1·5128 (Found : C, 60·5; H, 7·8. C₁₀H₁₅ClSi requires C, 60·4; H, 7·6%), p-, b. p. 231—232°, n_D^{20} 1·5154 (Found : C, 60·7; H, 7·8%), and m-*chlorobenzyltrimethylsilane*, b. p. 228—229°, n_D^{20} 1·5108 (Found : C, 60·4; H, 7·6%).

(*Trimethylsilylmethyl)benzoic Acids.*—The lithium aryl from the chlorobenzyltrimethylsilane in ether was poured on solid carbon dioxide.　When the mixture had warmed to room temperature dilute sulphuric acid was added until two clear layers separated.　The ethereal layer was repeatedly extracted with 0·2N-aqueous sodium hydroxide, the extracts being immediately added to excess of aqueous hydrochloric acid.　The organic acid was extracted with ether, and recovered by evaporation of the solvent.　There were obtained in 75—85% yield : o-(*trimethylsilylmethyl)benzoic acid*, m. p. 77·5° (from aqueous ethanol) (Found : C, 63·4; H, 7·7. C₁₁H₁₆O₂Si requires C, 63·4; H, 7·7%) [*anilide*, m. p. 113° (Found : C, 72·3; H, 7·7; N, 4·8. C₁₇H₂₁ONSi requires C, 72·1; H, 7·5; N, 4·95%)]; the m-*acid*, m. p. 96·5° (from light petroleum) (Found : C, 63·3; H, 7·6%) [*anilide*, m. p. 111·4° (Found : C, 72·3; H, 7·5; N, 4·8%)]; and the p-*acid*, m. p. 179° (from acetone–light petroleum) (Found : C, 63·5; H, 7·8%) [*anilide*, m. p. 137·4° (Found : C, 71·7; H, 7·6; N, 5·2%)].　Anilides were recrystallized from light petroleum.

The structures of the acids were confirmed by boiling them with N-aqueous sodium hydroxide, the expected toluic acids being obtained.

Determination of Apparent Ionization Constants.—Roberts and Regan's method (*loc. cit.*) was used, except that a Marconi-Ekco T.F.511C pH meter was employed, and the temperature was 18° ± 0·5°.　The same assumptions are made in calculating the apparent ionization constants.

Absorption Spectra.—A Unicam S.P.500 spectrophotometer was employed.　In hexane, the value of ε$_{max.}$ of the toluic acids and their trimethylsilyl derivatives at the ~235 maxima departed markedly from Beer's law below 10⁻⁴M.

" Methanolic hydrochloric acid " was prepared by adding 10 vol. % of 11N-aqueous hydrochloric acid to methanol.

The following spectral data are not listed above.

Acids in aqueous alkali.　The molar ratio of alkali to acid was *ca.* 3 : 1, and the spectra are probably those of the carboxylate ions; Doub and Vandenbilt (*loc. cit.*) give $\lambda_{max.}$ = 235 mμ for the *p*-toluate ion in water.　The *ortho*-compounds have ill-defined inflexions at ~230 mμ (log ε ~4·2) probably corresponding to the maxima of the other isomers in this region.

R (in R·C$_6$H$_4$·CO$_2$H)	o-Me		o-Me$_3$Si·CH$_2$		m-Me			m-Me$_3$Si·CH$_2$			p-Me	p-Me$_3$Si·CH$_2$
10^4 × [NaOH], N	160	160	2·4	160	2·4	120	120	1·2	1	120	2·4	2·4
λ$_{max.}$, mμ	262·5	270	205	277·7	229·5	275·5	~283*	206	230*	284	235	250
log ε$_{max.}$	2·64	2·61	4·42	2·97	3·83	2·90	—	4·54	(3·9)	3·03	4·03	4·21

* Denotes inflexion.

Anilides in aqueous methanol. The *ortho*-compounds were examined in 3 vol. % water in methanol, the others in 32 vol. % water in methanol. The spectra of the *meta*-compounds coincide at 250—278 mμ.

R (in R·C$_6$H$_4$·CO·NHPh)	o-Me	o-Me$_3$Si·CH$_2$	m-Me	m-Me$_3$Si·CH$_2$	p-Me	p-Me$_3$Si·CH$_2$
λ$_{max.}$, mμ	250·5	253	263·5	263·5	265	270
ε$_{max.}$	4·19	4·16	4·11	4·11	4·21	4·32

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