was subsequently refluxed for 30 min, and then allowed to cool. Insoluble products were removed by filtration and then extracted (by the Soxhlet procedure) with hot toluene (100 ml). The combined filtrates were fractionated to give anisole (4.3 g, 8 %), b.p. 152°, n_D^{20} 1.5163, benzyltrimethylsilane (5.5 g, 6.7 %), b.p. 191°, n_D^{20} 1.4906, unchanged *p*-chloroanisole (1.4 g, 2 %), b.p. 198°, n_D^{20} 1.5350, and (*p*-methoxyphenyl)-trimethylsilane (69.9 g, 77.5 %), b.p. 222.5–223°, n_D^{20} 1.5020.

Analysis of products by vapour-phase chromatography. The couplings were carried out, on a 0.3 molar scale, as described above, and the filtrates were analysed on a 60 × 0.4 cm column of dinonyl phthalate (5 wt-%) on kieselguhr (60–80 mesh) at 115°. An argon ionisation detector was used. In some cases ethyldimethylsilyl chloride was used in place of chlorotrimethylsilane (see Table 1) to facilitate the chromatographic separations.

Acknowledgements

This work was supported by a grant from the Office of Aerospace Research, United States Air Force, through its European Office. We thank Dr. L. SPIALTER, of the Chemistry Research Laboratory, Aerospace Research Laboratories, Wright Patterson Air Force Base, for his interest and encouragement.

The Chemical Laboratory, University of Sussex,
Brighton, Sussex (Great Britain)

C. EABORN
D. R. M. WALTON

1 C. EABORN, *Organosilicon Compounds*, Butterworth, London, 1960, pp. 26–31.
2 C. EABORN, *Organosilicon Compounds*, Butterworth, London, 1960, p. 27.
3 C. EABORN AND O. W. STEWARD, *J. Chem. Soc.*, in press.

Received October 14th, 1964

Aromatic reactivity

XXX*. Acid cleavage of (5-halo-2-methoxyphenyl)trimethylsilanes

Interest attaches to the reactivity of polysubstituted benzene derivatives in electrophilic aromatic substitutions, and Stock and Brown[1] have recently observed that "the scope and limitations of the application of the additivity principle deserve further attention". The principle seems to apply reasonably well to the reactivity of polymethylbenzenes[1–5] and gives at least a semi-quantitative interpretation of the isomer distributions in substitutions in many di-substituted benzenes[6]. However, deviations have been noted, and de la Mare and Ridd[6] have shown that the principle tends to underestimate the ease of substitution at a position which is activated, or slightly deactivated, by one substituent but strongly deactivated by another, as for example in nitration at the 2-position of 4-chlorotoluene[6] or 4-nitrotoluene[7]. More

---

* For Part XXIX, see ref. 16.

recently Stock and Baker have shown that the principle does not apply satisfactorily to chlorination of 4-halotoluenes[8].

Acid-cleavage of aryltrimethylsilanes provides a simple method of investigating substituent effects in electrophilic aromatic substitution, and much information has been gained from it about effects of isolated substituents, X, in $XC_6H_4SiMe_3$, compounds[9, 10]. Additivity of substituent effects has been observed[11] for the following di-substituted phenyltrimethylsilanes: 2,4-, 2,5-, 3,5-, and 3,4-dimethyl-, 2,4-diethyl-, 2,4-di-*tert*-butyl-, and 2,4-dimethoxy-. We now report a study of the acid-cleavage of (5-halo-2-methoxyphenyl)trimethylsilanes, in which, in the light of de la Mare and Ridd's observation noted above, departure from additivity might be expected.

TABLE I

CLEAVAGE OF $5\text{-X-2-MeOC}_6H_3SiMe_3$ COMPOUNDS BY A MIXTURE OF METHANOL (5 vol) AND 6.76 *M* PERCHLORIC ACID (2 vol) AT 50.0°

X	10^3k (*min*$^{-1}$)	*f*	*f'*	λ (*mμ*)
H	254	1.00	—	285
Cl	3.04	0.012	0.010	300
F	5.4	0.021	0.018	300
Br	2.85	0.011	0.010	300
I	4.3	0.017	—	300

In Table 1 are shown the first-order rate constants, *k*, for the cleavages of the compounds $5\text{-X-2-MeOC}_6H_3SiMe_3$, and also the rate factors, *f*, the rates relative to those of the compound $2\text{-MeOC}_6H_4SiMe_3$, which represent the effects of the halogens, *meta* to the trimethylsilyl group.

Also shown, as *f'*, are calculated values of the rate factor for cleavage of $m\text{-XC}_6H_4SiMe_3$ compounds in the same medium. In the case of the *m*-chloro substituent, the value of *f'* is derived from the experimental figure of 0.0119 for cleavage of (*m*-chlorophenyl)trimethylsilane by sulphuric acid/acetic acid[12] at 50°, by use of the relationship $\log k'_{rel} = 0.96 \log k_{rel}$, where k'_{rel} and k_{rel} refer, respectively, to cleavage in that medium and in aqueous methanolic perchloric acid[10]. The value of *f'* for the *m*-bromo is assumed to be the same as that for the *m*-chloro compound, as it is for cleavage in acetic acid/sulphuric acid[12]. The value for the *m*-fluoro compound is derived from that for the *m*-chloro compound and those for cleavage[13] of the (*m*-fluoro- and (*m*-chloro-phenyl)triethylgermanes in acetic acid/sulphuric acid at 50° by assuming a linear free energy relationship, $[\log k_{rel}\ (m\text{-F})]/[\log k_{rel}\ (m\text{-Cl})] = [\log k^*_{rel}\ (m\text{-F})]/[\log k^*_{rel}\ (m\text{-Cl})]$. The free energy relationships used are fairly exact[12, 13], and the *f'* values are probably accurate to within ± 5 %.

The *m*-halogens deactivate only slightly, if at all, less in the $5\text{-X-2-MeOC}_6H_3SiMe_3$ compounds than in the $3\text{-XC}_6H_4SiMe_3$ compounds. We think the differences between *f* and *f'* are probably real, and the direction of the deviation is in accord with de la Mare and Ridd's observation[6] on departure from additivity of substituent effects noted above. In our opinion, such departure from additivity is to be regarded as normal, and, indeed, it is somewhat surprising that we find such a small departure, if any. The transition state for substitution in the more reactive (*o*-methoxyphenyl)-

trimethylsilane should lie closer to the initial state than that for the less reactive phenyltrimethylsilane, and the charge developed on the ring, and thus the influence of another substituent, should be smaller. Departure from additivity should be greatest for reactions showing a large spread of rates (*i.e.*, a large ρ factor), for it is in these cases that there are the greatest differences between the structures of the transition state for the various aromatic compounds concerned*, and the smallness of the departure from additivity in protodesilylation may be associated with the relatively small ρ factor for this reaction.

Experimental

*Preparation of 4-chloro-, 4-bromo-, and 4-iodo-2-(trimethylsilyl)anisole***. A mixture of *p*-chloroanisole (71 g, 0.5 mole) and phenyl-lithium (0.5 mole, prepared from bromobenzene and lithium in ether) in ether (600 ml) was set aside at room temperature for 50 h. Chlorotrimethylsilane (54.3 g, 0.5 mole) in ether (50 ml) was added with stirring and the reaction mixture was set aside for a further 24 h. Addition of saturated ammonium chloride, followed by separation, drying and fractionation of the ethereal layer gave hexamethyldisiloxane (8.0 g), trimethylphenylsilane (4.6 g), and material (73 g) of b.p. 84°/2 mm, which crystallised in the receiver. Three recrystallisations from ethanol gave 4-chloro-2-(trimethylsilyl)anisole (64 g, 60%), m.p. 51–51.5°. (Found: C, 55.7; H, 7.2. $C_{10}H_{15}ClOSi$ calcd.: C, 55.9; H, 7.0%.)

Similarly were prepared, 4-bromo-2-(trimethylsilyl)anisole (44%), b.p. 99–100°/2 mm, m.p. 58–58.5°, (Found: C, 46.6; H, 5.8. $C_{10}H_{15}BrOSi$ calcd.: C, 46.3; H, 5.8%) and 4-iodo-2-(trimethylsilyl)anisole (58%), b.p. 111–112°/2 mm, m.p. 50–50.5°. (Found: C, 39.7; H, 4.9. $C_{10}H_{15}IOSi$ calcd.: C, 39.2; H, 4.9%.)

*Preparation of 4-fluoro-2-(trimethylsilyl)anisole***. A mixture of phenyl-lithium (0.25 mole) and *p*-fluoroanisole (0.25 mole) was kept at room temperature for 30 min, during which lithium fluoride gradually precipitated. Chlorotrimethylsilane (0.25 mole) in ether (30 ml) was added, the mixture was stirred for 4 h; working up as above gave trimethylphenylsilane (24.0 g) and a fraction (11.2 g) of b.p. 60–65°/2 mm. Redistillation of the second fraction gave 4-fluoro-2-(trimethylsilyl)anisole (6.3 g, 13%), b.p. 62–64°/2 mm. (Found: C, 60.9; H, 7.7. $C_{10}H_{15}FOSi$ calcd.: C, 60.6; H, 7.6%.)

Acknowledgements

This work was supported by a grant from the Office of Aerospace Research, United States Air Force, through its European Office. We thank Dr. L. SPIALTER of the Chemistry Research Branch, Aerospace Research Laboratories, Wright Patterson Air Force Base, for his interest and encouragement, and the Royal Society for the loan of the apparatus.

The Chemical Laboratory, University of Sussex, C. EABORN
Brighton, Sussex (Great Britain) D. R. M. WALTON

---

* In detritiation in trifluoroacetic acid, which shows a large spread of rates, a *m*-Cl or *m*-Br substituent deactivates the 2-position more in 4-X-1,3-$Me_2C_6H_3$ compounds than in 4-X-1,3,5-$Me_3C_6H_2$ compounds[14], but the possibility of steric interaction between the halogen atoms and methyl groups cannot be ruled out.

** New compound.

1 L. M. STOCK AND H. C. BROWN, in V. GOLD, *Advances in Physical Organic Chemistry*, Academic Press, London and New York, Vol. 1, 1963, pp. 135–142.
2 F. E. CONDON, *J. Am. Chem. Soc.*, 70 (1948) 1963.
3 H. C. BROWN AND C. W. MCGARY, *J. Am. Chem. Soc.*, 77 (1955) 2310.
4 H. C. BROWN AND L. M. STOCK, *J. Am. Chem. Soc.*, 79 (1957) 1421.
5 W. M. LAUER AND G. STEDMAN, *J. Am. Chem. Soc.*, 80 (1958) 6439.
6 P. B. D. DE LA MARE AND J. H. RIDD, *Aromatic Substitution*, Butterworth, London, 1959, pp. 88–92.
7 J. G. TILLETT, *J. Chem. Soc.*, (1962) 5142.
8 L. M. STOCK AND F. W. BAKER, *J. Am. Chem. Soc.*, 84 (1962) 1661.
9 C. EABORN, *J. Chem. Soc.*, (1956) 4858; F. B. DEANS, C. EABORN AND D. E. WEBSTER, *J. Chem. Soc.*, (1959) 3031.
10 F. B. DEANS AND C. EABORN, *J. Chem. Soc.*, (1959) 2299.
11 R. A. BENKESER AND H. R. KRYSIAK, *J. Am. Chem. Soc.*, 76 (1954) 6353; R. A. BENKESER, R. A. HICKNER AND D. I. HOKE, *J. Am. Chem. Soc.*, 80 (1958) 2279; R. A. BENKESER, R. A. HICKNER, D. I. HOKE AND O. H. THOMAS, *J. Am. Chem. Soc.*, 80 (1958) 5289; C. EABORN AND R. C. MOORE, *J. Chem. Soc.*, (1959) 3640.
12 (Miss) P. M. GREASLEY, Ph.D. Thesis of the University of Leicester, 1961.
13 C. EABORN AND K. C. PANDE, *J. Chem. Soc.*, (1961) 5082.
14 C. EABORN AND R. E. SPILLETT, unpublished work.
15 G. WITTIG AND G. FUHRMANN, *Chem. Ber.*, 73 (1940) 1197.
16 K. C. C. BANCROFT, R. W. BOTT AND C. EABORN, *J. Chem. Soc.*, in press.

Received October 14th, 1964

J. Organometal. Chem., 3 (1965) 169–172

The crystal structure of trimethyltin hydroxide

Recently, there has been much interest in organotin compounds in which the tin atoms are penta- or hexa-coordinated. Though the spectroscopic studies on the structure of trialkyltin acetate[1], formate[2], perchlorate[3,4], nitrate[5], or trimethyltin hydroxide[6,7] suggested that the trialkyltin group in these compounds is weakly coordinated by two oxygen atoms to give a penta-coordinated tin atom, no X-ray diffraction study of these compounds has been reported. Therefore, it seemed worthwhile to determine the crystal structure of trimethyltin hydroxide, which is one of the simplest oxygen-containing organotin compounds.

Crystals of trimethyltin hydroxide, $(CH_3)_3SnOH$, are monoclinic. The dimensions of the unit cell are given in Table 1. The mean intensity of (*hkl*) reflections is

TABLE 1

THE UNIT CELL OF TRIMETHYLTIN HYDROXIDE

True cell	*Sub-cell 1*	*Sub-cell 2*
a = 13.34 Å	a' = 6.67 Å	a' = 6.67 Å
b = 33.20	b = 33.20	b' = 4.15
c = 22.42	c' = 11.21	c' = 11.21
β = 90°	β = 90°	
Z = 64	Z = 16	Z = 2
Pn ?	*Pn*	*P*2_1 *nm*