Aromatic Reactivity. Part LVI.[1] Solvent Isotope Effects in Cleavage of Aryltrimethylstannanes by Acetic Acid and Aryltrimethylsilanes by Trifluoroacetic Acid

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Values of the product isotope effect, corresponding with the product ratio XC_6H_5:XC_6H_4D obtained on cleavage in a 1 :1 SH (ordinary acid)–SD (*O*-deuteriated acid) medium, have been determined for cleavage of (*a*) $XC_6H_4SnMe_3$ compounds by acetic acid at 50°, and (*b*) $XC_6H_4SiMe_3$ compounds by trifluoroacetic acid at 21°. For system (*a*) the values range from 5·9 for X = *p*-OMe to 4·9 for X = *m*-CF_3, and for (*b*) all the values lie between 6·0 and 6·5. In both systems, for compounds for which the overall solvent isotope effects, given by the ratios of the separate rates in SH and SD media, have also been measured, the overall solvent isotope effects are the same within experimental error as the product isotope effects, indicating that there is no significant secondary solvent isotope effect for the proton transfers from the acids. It is suggested that the proton transfer to form the Wheland intermediate is rather more than half-complete in both cases. In the cleavage of the *m*-$CF_3C_6H_4MMe_3$ (M = Si or Sn) compounds by trifluoroacetic acid, on average significantly more than one deuterium atom per molecule is incorporated into the benzotrifluoride product, and this anomaly is discussed.

In order to throw further light on the mechanism of acid cleavage of aryl–silicon and aryl–tin bonds, and at the same time provide information on the nature of solvent isotope effects in anhydrous acetic and trifluoroacetic acid, we have studied the cleavages of $XC_6H_4MMe_3$ compounds (M = Si or Sn) in ordinary (SH) and *O*-deuteriated (SD) acids. Reactions of this type are believed to involve rate-determining proton transfer to the aromatic ring to give the Wheland intermediate.[2-5]

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[1] Part LV, R. Alexander, W. A. Asomaning, C. Eaborn, I. D. Jenkins, and D. R. M. Walton, *J.C.S. Perkin II*, 1974, 304.

[2] R. W. Bott, C. Eaborn, and P. M. Greasley, *J. Chem. Soc.*, 1964, 4804.

[3] C. Eaborn, P. M. Jackson, and R. Taylor, *J. Chem. Soc.* (*B*), 1966, 613.

[4] R. Taylor in 'Comprehensive Chemical Kinetics,' eds. C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, 1972, pp. 324—348.

[5] J. Nasielski, O. Buchman, M. Grosjean, and M. Jauquet, *J. Organometallic Chem.*, 1969, **19**, 353.

For the tin compounds we determined the values of the product isotope effect (p.i.e.) which correspond to the $XC_6H_5 : XC_6H_4D$ product ratio obtained on cleavage in 1 : 1 CH_3CO_2H–CH_3CO_2D. (In practice, since the p.i.e. values were fairly large, a 1 : 2 SH–SD mixture was usually used, with appropriate adjustment of the results, because the resulting higher XC_6H_4D content makes for greater accuracy.) For several of the compounds we also measured the rates of cleavage, k_{SH} and k_{SD}, in CH_3CO_2H and CH_3CO_2D media, respectively, in order to derive the overall solvent isotope effect $(k_{SH} : k_{SD})_s$. For cleavage of the silicon compounds in CF_3CO_2H–CF_3CO_2D we measured only the p.i.e. values, but the $(k_{SH} : k_{SD})_s$ ratio has previously been measured for one representative compound, *viz.* *p*-$ClC_6H_4SiMe_3$.[3]

The results are shown in Table 1, and the main features are as follows.

TABLE 1

Isotope effects in acid cleavage of $XC_6H_4MMe_3$ compounds

M	X	Acid	P.i.e.	$(k_{SH} : k_{SD})_s$ [a]
Sn	*p*-OMe	Acetic	5·9 [b]	6·1
	p-Me		5·2	5·25
	H		5·2	4·9
	m-OMe		5·2	
	p-Cl		4·9	4·7
	m-CF_3		5·0	
Si	*p*-OMe	Trifluoroacetic	6·1 [c]	
	p-Me		6·5	
	H		6·5	
	p-Cl		6·0	6·2 [d]
	m-OMe		6·5	

[a] At 50° for M = Sn and 25° for M = Si. [b] P.i.e. values for cleavage in 1 : 2 CH_3CO_2H–CH_3CO_2D at 50°; estimated uncertainty ±0·2. [c] P.i.e. values for cleavage in 1 : 2 CF_3CO_2H–CF_3CO_2D at 21°; estimated uncertainty ±0·3. [d] From ref. 3.

(i) There is no significant difference between the values of the p.i.e. and those of $(k_{SH} : k_{SD})_s$ for the cases in which both ratios have been measured.* This means that there is no significant solvent isotope effect for proton transfer from these acids, and that both the p.i.e. and $(k_{SH} : k_{SD})_s$ ratios correspond with the primary isotope effect for proton transfer. This is the expected result, since the only hydrogen atom attached to the oxygen of the S–H bond is that which is being transferred.

(ii) The variation in the p.i.e. values as the substituent X is changed is fairly small in both cleavages. For the silicon compounds in trifluoroacetic acid there is no systematic variation of the p.i.e. with X, but we should note that in this acid the *p*-OMe group is markedly less electron releasing than it normally is,[6] so that the range of activation and deactivation is not as wide as might at first appear. (No p.i.e. values are listed for cleavage of the *m*-$CF_3C_6H_4SiMe_3$ compounds because more than one deuterium atom is incorporated into benzotrifluoride, as discussed later.) For the tin compounds in acetic acid there does seem to be a general trend in the p.i.e. values, from a maximum for the most reactive compound (X = *p*-OMe) down to the smallest values for the least reactive compounds (X = *p*-Cl and *m*-CF_3), and this trend can reasonably be regarded as real since it shows up in both p.i.e. and $(k_{SH} : k_{SD})_s$ values.

These cleavage reactions are thought to have mechanisms of the type generally associated with electrophilic aromatic substitutions, and to involve rate-determining formation of Wheland intermediates.[2-5] In terms of Schowen's approximations,[7] primary isotope effects of 5—6·5 for transfer of hydrogen from acetic or trifluoroacetic acid to carbon would correspond to an approximate O–H bond order of either 0·25—0·35 or 0·7—0·8, since insertion into Schowen's equations [6] of ν(O–H) values of **3280** and **3125** cm^{-1} for trifluoroacetic [8] and acetic acid,[9] respectively, leads to a maximum isotope effect of 11·2 at an O–H bond order of 0·56 for the former and of 10·0 at an O–H bond order of 0·54 for the latter acid. In our view the actual maxima probably lie at rather lower values, so that the O–H bond orders in the transitions states of the cleavages are more likely to be between, say, 0·3—0·4 or 0·65—0·7.

The similarity in the p.i.e. values for the silicon compounds in trifluoroacetic acid and the tin compounds in acetic acid could in principle arise from the fact that in one case the transition state is significantly before and in the other significantly beyond the point of half-proton transfer. It seems rather unlikely, however, that they will be so different, since the influence on the position of the transition state along the reaction co-ordinate of the markedly lower reactivity of the silicon than of the tin compounds will be counteracted by the influence of the markedly higher reactivity of the trifluoroacetic than of the acetic acid, and we favour the view that the degree of proton transfer at the transition state is similar in the two cases.

The question then arises of whether the proton transfer is less or more than half-complete in the transition state. Two features favour the conclusion that it is more than half-complete.

(*a*) In trifluoroacetic acid there appears to be a very close similarity between the cleavage of *p*-chlorophenyltrimethylsilane and the detritiation of 4-tritio-*m*-xylene, and these reactions proceed at similar rates suggesting that the transition states lie at similar positions between the reactants and the Wheland intermediates in the two cases.[3] The transition state in the detritiation would certainly be expected to lie beyond the point of half-proton transfer, since the reaction involves a relatively weak, neutral electrophile and only a moderately strong nucleophile, or, in other words, since the conversion of the reactants into the Wheland intermediate must be a strongly endothermic process. The large ρ value in

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* Our value (6·1) of $(k_{SH} : k_{SD})_s$ for cleavage of *p*-methoxyphenyltrimethylstannane in acetic acid at 50° is substantially smaller than that (10) obtained by Nasielski and his colleagues by extrapolation from results in CH_3CO_2H–CH_3CO_2D mixtures.[5]

[6] R. Baker, R. W. Bott, C. Eaborn, and P. M. Greasley, *J. Chem. Soc.*, 1964, 627; R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *J. Amer. Chem. Soc.*, 1963, **85**, 3146; P. E. Peterson, D. M. Chevli, and K. A. Sipp, *J. Org. Chem.*, 1968, **33**, 972.

[7] R. L. Schowen, *Progr. Phys. Org. Chem.*, 1972, **9**, 275.

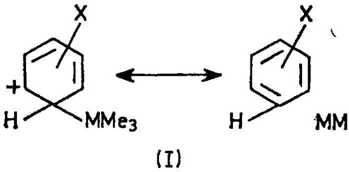
[8] J. R. Barcelo and C. Otero, *Spectrochim. Acta*, 1962, **18**, 1231.

[9] L. J. Bellamy, ' The Infrared Spectra of Complex Molecules,' Methuen, London, 1964, p. 165.

detritiation (−8·8 for substituted benzene,[10] though probably somewhat less for substituted 4-tritio-*m*-xylenes) is consistent with this view. Thus the proton transfer must apparently also be more than half-complete in the transition state for the cleavage of the silicon compounds.

(*b*) The small but definite fall in the p.i.e. values for the cleavage of the tin compounds in acetic acid as the reactivity of the compounds decreases is consistent with a transition state beyond the halfway point for the proton transfer. This is because the transition state will lie increasingly towards the Wheland intermediate as the reactivity falls, the degree of proton transfer will increase, and, since the point of maximum isotope effect has been passed, the p.i.e. value will fall.

There is one major difficulty associated with the above conclusion and that is to account for the fact that the ρ factor for the cleavage of the $XC_6H_4SnMe_3$ compounds in acetic acid is so small, −2·24 at 25°,[5] even though, as we suggest, rather more than half a unit of positive charge should have developed on the aromatic ring in the transition state. We faced a closely related problem previously when observing that the ρ factor for cleavage of substituted *p*-chlorophenyltrimethylsilanes in trifluoroacetic acid is probably markedly smaller than that for hydrogen exchange of substituted 4-tritio-*m*-xylenes in the same medium even though, as we have seen above, the two parent compounds react at about the same rate, so that the transition states presumably lie at about the same position along the reaction co-ordinate.[3] We suggested in that case that the explanation might lie in the operation of the effects of $(p\text{-}d)_\pi$-bonding in the initial state for the aryl–silicon compounds. Such an effect could have some influence also in the reactions of the aryl–tin compounds in acetic acid, but seem hardly sufficient to give rise to such a low ρ value. Possible factors may be (i) the large electron release from the $CH\text{-}MMe_3$ bonds in the Wheland intermediates; this release, which is especially large for the tin compounds, is predominantly of hyperconjugative (σ–π conjugative) origin, as illustrated in structures (I) (for leading references see ref. 11) and (ii) interaction between the forming acetate (or trifluoroacetate) anion and the metal centre. Further speculation is unjustified at present.



(I)

Another aspect worthy of brief notice is not specific to the aryl–metal cleavages under discussion but arises for a wide range of electrophilic aromatic substitutions. We have implicitly assumed in the above discussion that the reaction can, for practical purposes, be regarded as proceeding directly from the original reactants to the Wheland intermediate (σ-complex), the possible π-complexes, if formed at all, being so little removed in energy and position along the reaction co-ordinate from the initial state that they can be disregarded. In this case the conversion of the original reactants into the Wheland intermediate should, certainly when the electrophile is a highly stable neutral species such as acetic or trifluoroacetic acid, be a highly endothermic process, and thus in terms of the Hammond postulate the transition state should lie well over towards this intermediate,[12] whereas we have concluded that transition states for the cleavages do not lie greatly beyond the region of half-proton transfer. The difficulty is decreased if significant participation of π-complexes is postulated, since the endothermicity of the proton-transfer process will be smaller by the energy difference between the reactants and the π-complex. Furthermore, since in general a substituent which stabilizes a σ-complex also stabilizes a π-complex, to some extent the effects of variation of ring substituents on the degree of proton transfer will be dampened down, which would be in accord with the fairly small observed changes in the solvent isotope effects as X is varied. Indeed, since different types of substituent effects operate in π- and σ-complexes, there might well be no simple pattern of variation of isotope effects with X in cases in which the overall variation is small, as in the cleavage of the silicon compounds in trifluoroacetic acid. It is noteworthy that the pattern of substituent effects even on the overall reaction rate is best interpreted in terms of a transition state having substantial π-complex as well as σ-complex character in the case of cleavage of aryltriorganosilanes by iodine in carbon tetrachloride.[13]

Anomalous Behaviour of m-$CF_3C_6H_4MMe_3$ *Compounds.*—The benzotrifluoride produced from *m*-trifluoromethylphenyltrimethylsilane during 10 days in 1 : 2 CF_3CO_2H–CF_3CO_2D at room temperature (*ca.* 21°) was found to give mass spectral peaks with intensity ratios as follows: $M : M + 1 : M + 2 : M + 3 = 7{\cdot}56 : 5{\cdot}58 : 1{\cdot}10 : 0{\cdot}50$. After allowance for the ^{13}C content, these ratios indicate that $CF_3{\cdot}C_6H_{5-x}D_x$ species were present in the ratios ($x =$) $0 : 1 : 2 : 3 = 7{\cdot}56 : 5{\cdot}00 : 0{\cdot}70 : 0{\cdot}4$. The figures for the D_2- and D_3-species are subject to considerable uncertainty, so that significance cannot at present be attached to the apparently strikingly high ratio of D_3- relative to D_2-species, but there is no doubt that significant amounts of these species are produced. (As would be expected in the light of this observation, the $D_0 : D_1$ ratio corresponds with an apparent p.i.e. value, 3·0, quite inconsistent with the values obtained for the other $XC_6H_4SiMe_3$ compounds.) Cleavage of *m*-trifluoromethylphenyltrimethylstannane by 1 : 1 CF_3CO_2H–CF_3CO_2D during 4 days at 21° gave benzotrifluoride showing $M : M + 1 : M + 2$ peaks in the ratios $7{\cdot}28 : 2{\cdot}28 : 0{\cdot}14$, indicating that an effect of the same type, but much smaller, is present in this case also.

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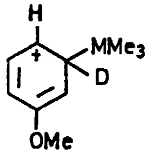
[10] R. Baker, C. Eaborn, and R. Taylor, *J.C.S. Perkin II*, 1972, 97.

[11] C. Eaborn, *J.C.S. Chem. Comm.*, 1973, 1255.

[12] G. S. Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 334.

[13] R. W. Bott, C. Eaborn, and J. A. Waters, *J. Chem. Soc.*, 1963, 681.

As expected from the results of previous studies of aromatic hydrogen exchange in trifluoroacetic acid,[10] no detectable incorporation into benzotrifluoride was found to occur under the conditions used for the cleavages. It thus appears that deuterium incorporation occurs before or during the cleavage of the aryl–MMe_3 bonds, and viewed in isolation this could plausibly be associated with migration of either the D atom or the Me_3M group within a reversibly-formed Wheland intermediate, as illustrated in the Scheme for the migration of the Me_3Si group. [Such migrations of a trimethylsilyl group, which are analogous to the rearrangement of the ion $Me_3SiCH_2CD_2^+$ to $Me_3SiCD_2CH_2^+$,[14] are known to occur under rather special conditions, and notably when *o*-bis(trimethylsilyl)benzene is converted into the *m*-isomer by treatment with a small quantity of trifluoroacetic acid in benzene;[15] under such conditions, apparently, not only is the life of the Wheland intermediate prolonged because of the low concentration of the nucleophilic species needed to remove the Me_3Si group or the α-proton, but loss of the proton is strongly favoured over loss of the Me_3Si group.] When viewed against a wider background, however, the problems associated with this suggestion are considerable; in particular, there seems no good reason why the reversibility of the protonation and the Me_3Si group migration, should occur especially readily with *m*-trifluoromethyl compounds. More detailed study of this anomaly is clearly required.



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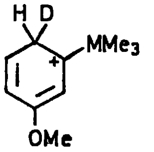

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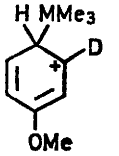

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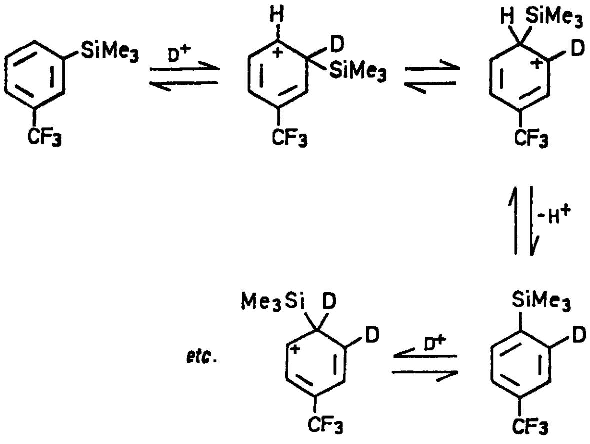

SCHEME

Because of the anomalous behaviour discussed above, we carefully examined the product from the cleavage of *m*-methoxyphenyltrimethylstannane by *O*-deuteriotrifluoroacetic acid containing *ca.* 2% of undeuteriated acid. The possibility of rearrangement would seem to be greater in this case because conversion of the ion (II) into (III) or (IV) should be especially favourable energetically, since the MeO group stabilizes the *meta*- much more than the *para*-carbonium ion. The anisole obtained after 5 min in CF_3CO_2D at 21° was found to contain 90 ± 2% of the $MeOC_6H_4D$ species. (This is the figure expected for a 2% CF_3CO_2H content if a product isotope effect of 5 operates.) The anisole was then converted into *p*-methoxyacetophenone, which was found to contain the same proportion of a D_1 species [89 ± 2% of the $(CH_3CO)(MeO)C_6H_3D$ species] within experimental error. Thus no significant amount of the deuterium had become incorporated into the *para*-position during the cleavage.

EXPERIMENTAL

Materials.—The preparations of the aryltrimethyl-silanes and -stannanes have been previously described.[16]

O-Deuterioacetic acid (>99·5%) was supplied by Ryvan. *O*-Deuteriotrifluoroacetic acid was made from trifluoroacetic anhydride by the addition of one equiv. of deuterium oxide (>99%) at 0°; it was estimated to contain up to 2% of CF_3CO_2H.

Determination of Product Isotope Effects.—The method is described for a typical case as follows.

p-Tolyltrimethylstannane (160 μl, 0·8 mmol) was added to 1 : 2 v/v CH_3CO_2H–CH_3CO_2D (4 ml) in a small flask (*ca.* 5 ml) which was then tightly stoppered and kept in a thermostat at 50·0° for 4 days. After cooling, the contents of the flask were added to ice–water (10 ml) and n-pentane extraction (2 × 3 ml) was followed by washing of the extract with water (2 × 3 ml), drying (Na_2SO_4), and evaporation of the solvent. The small residual droplet was introduced into a Pye model 64 gas chromatograph linked to an Edwards E606 fast-scanning mass spectrometer operating at 9—12 eV, and the peak heights averaged over 20—30 scans. There was no significant peak at mass 94, and the 92 : 93 [*i.e.* $M : (M + 1)$] peak ratio was 2·17, which, after allowance for the ^{13}C content, corresponds with a $CH_3C_6H_5 : CH_3C_6H_4D$ ratio of 2·6. Taking into account the composition of the reaction medium, this gives a p.i.e. of 5·2. Several repetitions of this procedure gave values of 5·2 ± 0·2.

With the relatively unreactive compound *m*-$CF_3C_6H_4$-$SnMe_3$, reaction was carried on for 7 days at 50°.

For cleavage of the $XC_6H_4SiMe_3$ compounds in trifluoroacetic acid, because of the possibility of hydrogen exchange, the reaction time had to be varied considerably, depending on the nature of X. The time were as follows: (X=) *p*-OMe, 0·5 h; *p*-Me, 5 h; H, 3 days; *p*-Cl, 6 days. The compounds with X = *p*-NO_2 reacted too slowly for study.

Except for cleavages of the compounds with X = *m*-CF_3 in trifluoroacetic acid, in no case did the products show a significant $(M + 2)$ peak.

For the cleavages of some of the tin compounds some deuterium analyses were carried out as a check with the aid

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[14] M. A. Cook, C. Eaborn, and D. R. M. Walton, *J. Organometallic Chem.*, 1970, **24**, 301.

[15] D. Seyferth and D. L. White, *J. Organometallic Chem.*, 1971, **26**, C15; 1972, **34**, 119.

[16] C. Eaborn, *J. Chem. Soc.*, 1956, 4858; C. Eaborn and F. B. Deans, *ibid.*, 1959, 2299; C. Eaborn and J. A. Waters, *ibid.*, 1961, 542; C. Eaborn and P. M. Jackson, *J. Chem. Soc.* (*B*), 1969, 21; C. Eaborn, H. C. Hornfield, and D. R. M. Walton, *J. Organometallic Chem.*, 1967, **10**, 529.

of an Applied Research Laboratories Organic Analyser MPD850 linked to the gas chromatograph; the derived p.i.e. values agreed well with those obtained by use of the mass spectrometer.

TABLE 2

Rates of cleavage of $XC_6H_4SnMe_3$ compounds

	Temp. (°C)		λ/nm	$10^4k/s^{-1}$
p-OMe	30	CH_3CO_2H	283	57·1
		CH_3CO_2D		9·1
p-Me	50	CH_3CO_2H	273	26·7
		CH_3CO_2D		5·08
H	50	CH_3CO_2H	264	5·05
		CH_3CO_2D		1·04
p-Cl	50	CH_3CO_2H	275	1·84
		CH_3CO_2D		0·39

Overall Solvent Isotope Effects.—The spectrophotometric determination of rates of cleavage have been previously described.[2,3] A sample of the aryl–tin compound was dissolved in the appropriate acid contained in a 1 cm quartz absorption cell, which was then stoppered and placed in a thermostat in the cell compartment of the Unicam SP 500 spectrometer. Optical densities were measured at appropriate intervals, with the infinity value after 10 half-lives. The wavelengths λ used and the measured first-order rate constants *k* are shown in Table 2.

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