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CLEAVAGES OF ARYL—SILICON AND RELATED BONDS BY ELECTROPHILES

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Introduction

My first independent research, begun in 1947 upon my appointment as an Assistant Lecturer at the (then) University College of Leicester, was concerned with the breaking of carbon—silicon bonds by an electrophilic reagent, namely iodine in the presence of aluminium iodide; not surprisingly, the Ph—Si bond was found to be much more readily cleaved than alkyl—Si bonds [1]. My first quantitative study of electrophilic cleavage of aryl—Si bonds was made possible by the receipt in 1952 of a grant from the Royal Society for purchase of a Unicam SP 500 spectrophotometer, which was the first, and for some years the only, piece of spectroscopic equipment in the Department of Chemistry at Leicester. The investigation concerned the cleavage of *p*-methoxyphenyltrimethylsilane by hydrochloric acid in aqueous dioxane, and the important features of the resulting publication are as follows [2]:

(a) Cleavage of aryl—silicon bonds was treated for the first time as an electrophilic aromatic substitution.

(b) It was demonstrated for the first time that in aromatic substitutions involving proton transfer to the ring, the effects on the rate of variations in the medium can be interpreted in terms of acidity functions.

(c) The ease of spectrophotometric determination of the rates of acid cleavage of aryl—silicon bonds (protodesilylation) was demonstrated, and the conditions were established for what has now become a standard method of investigating aromatic reactivity.

(d) The mechanism of the reaction was expressed for the first time in terms of the sequence shown in Scheme 1. However, in the light of the interpretations placed on acidity function dependencies at that time, step (ii) was wrongly favoured as the rate-determining process, a view which was soon abandoned [4,5]*.

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* For additional refs. see ref. 3. This 1953 paper provides an interesting example of the persistence in subsequent literature of a conclusion later shown, and frequently stated to be, incorrect. Almost every year some article cites the 1953 conclusions without reference to the many later papers on the matter.

SCHEME I

$$p\text{-}Me_3SiC_6H_4OMe + H^+ \rightleftharpoons [p\text{-}Me_3SiC_6H_5OMe]^+ \qquad \text{(i)}$$

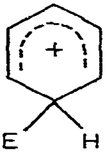
$$[p\text{-}Me_3SiC_6H_5OMe]^+ + H_2O \rightarrow Me_3Si\overset{+}{O}H_2 + C_6H_5OMe \qquad \text{(ii)}$$

$$Me_3Si\overset{+}{O}H_2 \rightarrow Me_3SiOH + H^+ \qquad \text{(iii)}$$

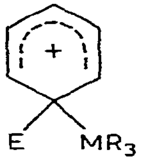
While the 1953 paper laid down foundations, it was a 1956 paper, concerned with substituent effects in cleavages of $XC_6H_4SiMe_3$ compounds by aqueous-methanolic perchloric acid, which established the pattern for much future work on cleavage of aryl—silicon, —germanium, —tin, and, to a lesser extent, —lead bonds, and which constitutes Part I of my series of papers on Aromatic Reactivity [4]. But further chronological presentation of the development of these researches would be inefficient and tedious, and instead the more important aspects will be summarized below in the light of current knowledge.

Mechanistic aspects

The cleavage of aryl—MR_3 bonds (demetallations) by electrophilic reagents are closely analogous to familiar aromatic substitutions; in the latter, the aryl—H bond is broken in the direction C^- H^+, and in the demetallations the aryl—MR_3 bond is broken in the direction C^- MR_3^+ [5]. Just as the common aromatic substitutions involve carbonium ion intermediates of type I (E = electrophile),

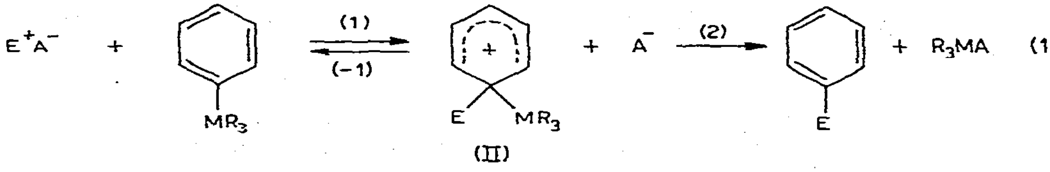


(I)



(II)

known as Wheland intermediates or σ-complexes, so the demetallations are thought to involve intermediates of type II. As in the familiar aromatic substitutions such as nitration, bromination, etc., the question then arises of whether the rate-determining step is the formation of II or the loss of the MR_3 group from it. Which of steps 1 and step 2 in eqn. 1 is rate-determining depends upon whether the R_3M or the E group is lost more readily from the intermediate, either as the ion R_3M^+ or E^+, or under nucleophilic attack, say by A^-, to give the species R_3SiA or EA. When E is H (as in cleavage by acids), Cl, Br, or I (as in cleavage by halogens), SO_3 (as in cleavage by sulphonating agents), or NO_2 (as in cleavage by nitrating agents) it seems highly likely that the R_3Si will separate more read-

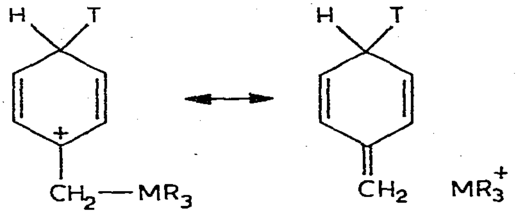


ily than the E group, and thus step 2 will be faster than step —1, which means that step 1 will be rate-determining [6]. For example, it is known that C—$SiMe_3$ bonds are usually broken much more readily by nucleophilic reagents than are corresponding C—H bonds, and when E = H it is unlikely that step —1 will be faster than step 2. (Indeed, this argument seems so obvious that it is difficult now to see why the loss of the Me_3Si group was favoured, even briefly, as the rate-determining step in protodetrimethylsilylation.) The position is not clear, however, for all electrophiles; e.g., when E = HgX one cannot confidently predict whether the HgX or R_3M group will be lost more easily.

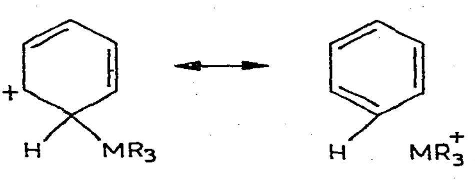
That the attachment of the proton is rate-determining in the protodemetallations of arylMR_3 compounds is demonstrated by two studies of solvent isotope effects. The first involved cleavage of various arylMR_3 compounds, with M = Si, Ge, Sn, and Pb, by hydrochloric acid in aqueous dioxane, and in all cases the reaction was significantly slower when deuterium oxide was used in place of protium oxide [7]. The second study involved cleavage of (i) $XC_6H_4SiMe_3$ compounds by trifluoroacetic acid, and (ii) $XC_6H_4SnMe_3$ compounds by acetic acid [8]. In case (i) cleavage by CF_3CO_2D was 4.7-6.1 times as slow as that by CF_3CO_2H, and in case (ii) cleavage by CH_3CO_2D was 6.0-6.5 times as slow as that by CH_3CO_2H, results consistent with rate-determining proton transfer; detailed analysis, and comparison with other systems, suggests that the proton transfer is rather more than half complete at the transition state in both cases.

It is of interest to examine, in the light of the favoured mechanism, the observation that the rate of cleavage of $ArMEt_3$ compounds by aqueous methanolic perchloric acid increases in the sequence (M =)Si $<$ Ge $\ll$ Sn $\ll$ Pb, the relative rates of cleavage being ca. (M =)Si, 1; Ge, 36; Sn, 3.5×10^5; Pb, 2×10^8 [10]. Since the sequence is also that of decreasing C—M bond strength, it is tempting to interpret it in terms of a mechanism involving breaking of the C—M bond in the rate-determining step, and, indeed, as recently as 1972 this feature led one author to doubt our conclusion that the C—M bond is broken in a fast step after the initial proton attachment [9].

The explanation of the sequence is to be found in the effectiveness of the stabilization of the Wheland intermediates of type II (and thus of transition states on the way to them) by electron release from the CH—MR_3 system. We drew attention in 1964 to the analogy between the influence of the Me_3SiCH_2 group on the rate of detritiation of p-$Me_3SiCH_2C_6H_4T$ (T = ^3H) and the influence of the Me_3Si group on the ease of attachment of a proton at the carbon atom of the Ph—$SiMe_3$ bond (and thus on the rate of cleavage); the analogy is



(III) (IIIa)



(IV) (IVa)

seen most clearly in terms of the β-carbonium ion canonical forms III and IV of the Wheland intermediates [7]. In view of the large activating effect of the p-Me_3SiCH_2 group in detritiation (amounting to a factor of almost 10^5 for exchange in trifluoroacetic acid at 70°C [11]), it is easy to see why the Ph—$SiMe_3$ bond should be cleaved by acids so much more readily than the Ph—H bond (a factor of ca. 4×10^4 applying in aqueous sulphuric acid at 25°C [10]) even though the Ph—$SiMe_3$ bond is not broken in the rate-determining step.

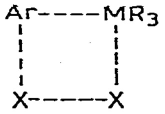
The electron-releasing ability of the CH_2MR_3 and $CHMR_3$ groups, which is known to increase in the order (M =)Si < Ge < Sn < Pb, is now associated largely with hyperconjugative (σ-π conjugative) electron release from the C—M bonds [12]. The ease with which the σ-electrons of the C—M bond take part in this hyperconjugation can be expected to increase with decreasing strength of the bond, as will be evident from considering the overall change in bond energies on going, for example, from structure III to IIIa or from structure IV to IVa. Thus the hyperconjugative stabilization of the intermediates IV will increase with the decreasing C—M bond energy in the sequence $Si < Ge \ll Sn < Pb$, and this accounts nicely for the fact that the relative ease of cleavage of Ph—MR_3 compounds reflects the strength of the Ph—MR_3 bonds even though these remain unbroken in the rate-determining step [11].

We were unable for some time to eliminate the possibility that the very high rates of reaction of the tin and lead compounds might be associated with enhancement of the electron release from the C—MR_3 bonds by coordination of hydroxylic solvent molecules to the metal centres [10]. This has recently been ruled out [11] by the observation that the logarithms of the relative rates of cleavage of the Ar—MMe_3 bonds correlate linearly with the absorption frequencies of the charge transfer complexes between Me_3MCH_2Ph compounds and tetracyanoethylene [13]; these frequencies, which also depend on the magnitude of the electron release from the M—C bonds, were determined in chlorohydrocarbon solvents [14,15] and would not correlate with the cleavage rates in hydroxylic media if coordination were involved in the latter [11].

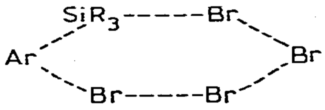
The cleavages of $XC_6H_4SiMe_3$ compounds by halogens in acetic acid containing 1.5% of water (e.g. eqn. 2) has also been the subject of detailed mechanistic studies [16,17]. The kinetics are wholly consistent with rate-determining

$$XC_6H_4SiMe_3 + Hal_2 \rightarrow XC_6H_4Hal + Me_3SiHal \qquad (2)$$

formation of a Wheland intermediate of type II ($\dot{E}$ = Br or Cl), and the fairly close analogy between the bromine cleavage and the bromination of comparably reactive aromatic compounds in similar media is in favour of this interpretation, as is the existence of an excellent linear free energy relationship between the effects of the substituents X in the bromine cleavage and those in the acid cleavage of $XC_6H_4SiMe_3$ compounds. However, there remains one item of evidence which



(V)



(VI)

would be consistent with a four-centre process [18] of type V and which is not easily explained in terms of the Wheland intermediate mechanism. This is the observation that iodine monochloride reacts with phenyltrimethylsilane in acetic acid some 8 times as rapidly as does chlorine, whereas in halogenation of ordinary aromatic compounds chlorine is much the more reactive [19]; this implies some marked difference between the two reactions, and would be consistent with a process of type V. There is, however, compelling evidence against such a mechanism for bromodesilylation in non-polar media such as benzene and tetrachloromethane, since the reaction proceeds with inversion of configuration at silicon, whereas process V would involve retention [20]*. It is in these weakly solvating media that such a process would be most expected, since it avoids the formation of and separation of ions, and so it seems unlikely that it operates in aqueous acetic acid. There remains the possibility, which is consistent with the observation that the cleavages in tetrachloromethane are of second order in bromine, that a six-centre process such as VI operates, since this would probably involve inversion at silicon [22].

The variation with the electrophile of the relative ease of cleavage of corresponding Ar—H and Ar—$SiMe_3$ bonds presents several other unsolved problems. On the simplest reasoning, one would expect the selectivity between Ar—MMe_3 and Ar—H bonds to fall with increasing reactivity of the electrophile. In agreement with this, the $PhH/PhSiMe_3$ reactivity ratio towards molecular bromine in acetic acid is ca. 10^8; towards the more reactive molecular chlorine the ratio is in the region of 10^6, while towards even more reactive acetylating species ($CH_3COCl + AlCl_3$ in CS_2) [23] or oxonium ion (in acid cleavage) it is ca. 10^3-10^4. There is, however, no apparent reason in terms of this simple picture, why the Ar—H bond should ever be broken by an electrophile more readily than the Ar—$SiMe_3$ bond, and thus it is anomalous that the nitrating species present in nitric acid—acetic anhydride mixtures cleaves Ar—H more readily than Ar—$SiMe_3$ bonds [24]. ($ArSiMe_3$ and $ArGeEt_3$ compounds are readily converted into $ArNO_2$ compounds by nitric acid in acetic anhydride [24-27], but this is the result of nitrosodemetallation followed by oxidation of the ArNO compounds formed [24].)

Webster and his colleagues (in a detailed study of the mechanism of the cleavage of $ArSiMe_3$ compounds by mercuric acetate in acetic acid, which revealed that $Hg(OAc)_2$ and $Hg(OAc)^+$ both act as electrophiles in this system) have pointed out the anomaly that the Ar—$SiMe_3$ bond shows markedly greater selectivity between $Hg(OAc)_2$ and $Hg(OAc)^+$ than does a comparably reactive Ar—H bond [28]**. It is possible that in both the mercuration and the mercuridesilylation a cyclic mechanism operates [28,29], but there is no firm evidence for it. Nasielski and his co-workers have observed yet another anomaly in the variation of selectivity of the demetallations towards different electrophiles, viz., that $ArSnMe_3$ compounds are cleaved more readily in methanol by iodine

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* Following this demonstration of the stereospecificity of bromine cleavage of aryl—silicon bonds, L.H. Sommer was able to derive new optically-active RMePhSiX systems from his $(1\text{-}C_{10}H_{11})$MePhSiX systems [21], and so demonstrate the wider applicability of his stereochemical findings.

** David Webster was one of the first two research students to work with me on aromatic desilylation (the other being F.B. Deans), and investigated mercuridesilylation as part of his work for his Ph.D. [30,31].

than by perchloric acid, whereas with $ArSiMe_3$ compounds the opposite is true [32]. The first kinetic studies of cleavages of $ArSnMe_3$ compounds revealed some features rather different from those in cleavages of $ArSiMe_3$ compounds [33,34], but the behaviour can be interpreted in the general context of understanding of electrophilic aromatic substitutions. Among the reagents used for kinetic studies of $ArSnMe_3$ cleavages are: (a) perchloric acid in aqueous ethanol [33]; (b) iodine in tetrachloromethane [34] or methanol [35]; (c) hydrogen chloride in methanol [36]; (d) bromine in methanol [37]; (e) mercuric acetate in tetrahydrofuran [38]; (f) sulphur dioxide in methanol [39]. Four-centre mechanisms have sometimes been favoured [38,39], mainly because of the low sensitivity to substituent effects (i.e., low ρ factors) in $XC_6H_4SnMe_3$ compounds, and better correlations with σ- than with σ^+-constants, but these features are equally compatible with Wheland-intermediate type mechanisms (see below). Multi-centre mechanisms [40] must nevertheless remain an attractive possibility for many of the demetallations.

Substituent effects

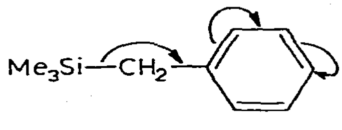
The effects on the reactivity of $ArMR_3$ compounds of varying the aryl group will not be considered in detail, since the results are consistent with treatment of the reactions as electrophilic aromatic substitutions, and have been extensively reviewed in this context [41-43]. In particular, the values, k_{rel}, of the rates of cleavage of $XC_6H_4MR_3$ compounds relative to that of the parent $C_6H_5MR_3$ can be interpreted very satisfactorily in terms of standard substituent constants for the X groups. Thus the k_{rel} values for acid and bromine cleavage of $XC_6H_4SiMe_3$ compounds correlate fairly well with the σ^+-constants of X, but in these cases, and more especially for proto-destannylation [33] and -deplumbylation [44], a better correlation is obtained by use of the Yukawa—Tsuno equation, $\log k_{rel} = \rho[\sigma + r(\sigma^+ - \sigma)]$. In general, both ρ and r would be expected to decrease with increasing proximity of the transition state to the initial state, and thus with increasing reactivity of either the $ArMR_3$ or the electrophile [45]. Such a trend is revealed in the following ρ and approximate r values for protodemetallations under fairly comparable conditions:

	$ArSiMe_3$	$ArGeEt_3$	$ArSn(C_6H_{11})_3$	$ArSnMe_3$	$ArPbMe_3$
$-\rho$	5.3	4.6	3.8	(2.2)	2.5
r	0.65	0.65	0.4		

It is not surprising that in reactions of $ArSnMe_3$ compounds with reactive electrophiles low ρ values are observed, frequently accompanied by better correlation with σ than with σ^+-constants.

One special feature of the substituent effects in protodetrimethylsilylation (it has not been sought for the other demetallations, but would certainly be expected to show up with germanium compounds) is that of steric acceleration which arises when the Me_3Si group is crowded by a neighbouring group, release of strain occurring as the Me_3Si moves from the plane of the aromatic ring in the formation of the Wheland intermediate [46]. For example, in cleavage in aqueous methanolic perchloric acid, 2,6-dimethyl- and 2,4,6-trimethyl-phenyltrimethylsilane react ca. 10 and 7 times, respectively, as rapidly as would be expected for simple additivity of the effects of the separate *o*- and *p*-Me groups [47]. An extreme example of such acceleration is thought to be provided by the case of 9-trimethylsilylanthracene, in which there is serious interference between the Me_3Si group and the 1- and 8-hydrogens, and which reacts about 100 times as rapidly as would be expected by comparison with other aromatic substitutions, and is ca. 10^5 times as reactive as phenyltrimethylsilane [48].

One feature revealed in the first systematic studies of substituent effects in these systems is worthy of special mention, viz., the large electron-releasing ability of the Me_3SiCH_2 group, which was revealed by the fact that the compound *p*-$Me_3SiCH_2C_6H_4SiMe_3$ undergoes acid cleavage of the aryl—Si bond some 300 times as rapidly as does the parent $PhSiMe_3$ [4]. The importance of this observation was that it was attributed clearly to hyperconjugation, as represented in VII, and this represents the first explanation of a reactivity effect in terms of hyperconjugation by R_3MCH_2 groups*.



(VII)

No mention has been made so far of the effects on the ease of cleavage of the Ar—MR_3 bond of varying the R groups. Such effects have been systematically studied only for acid cleavage with M = Si [56]. The results with Ar—$SiMe_2C_6H_4X$ compounds show that increasing the electron release towards Si from the R groups increases the rate of reaction, as would be expected for rate-determining formation of an intermediate of type II, but steric effects (possibly involving in part steric hindrance to solvation) can outweigh such influences, as shown by the fact that ArSi-i-Pr_3 are cleaved less readily than $ArSiMe_3$ compounds. The low reactivity of Ar—$SiPh_3$ compounds compared with Ar-$SiMe_3$ bonds in several cleavages can be attributed to a combination of electronic and steric effects. Similar behaviour is observed for cleavage by bromine in aqueous acetic acid [57]. As expected, aryl—$SiHal_3$ bonds are cleaved much less readily,

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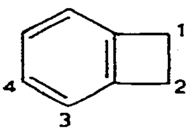
* I had, however, previously suggested that such hyperconjugation had a marked influence on the UV spectrum of the ion *p*-$Me_3SiCH_2C_6H_4CO_2^-$ [49], and for many years believed this to represent the first suggestion of hyperconjugation involving carbon—metal bonds, until I learned from T.G. Traylor [50] that Nesmeyanov and Lutsenko had explained the spectrum of some mercury-substituted ketones in terms of this effect in 1948 [51]. Later, for a few years, during a period when the importance of C—H hyperconjugation was being questioned, I did not use explanations based on C—MR_3 hyperconjugation, but returned [52,53] to this concept when it was revived by the work of Traylor. (For a brief historical review see refs. 11 and 3.) It is of interest that the most important single item of evidence for C—Si hyperconjugation was obtained by C.G. Pitt [54], who at the time of my first proposal of this phenomenon was working with me on the preparation of optically-active silicon compounds. He achieved the first fully-authenticated optical resolution of a tetravalent silicon compound, viz., $MeEtPhSiC_6H_4COOH$-*p*, and demonstrated the optical stability of such a system [54a]. We had planned to go on to cleave the Si—Ph bond by halogen in order to introduce greater functionality at the silicon atom (and the subsequently observed stereospecific cleavage of aryl—Si bonds, mentioned above, showed that this would have been practicable), but this was abandoned in the light of L.H. Sommer's successful resolution of a different organosilicon system [55].

e.g., by halogens, than aryl—$SiMe_3$ bonds [58]. Limited data indicate that analogous effects operate in $ArMR_3$ cleavages [33].

Quantitative applications of cleavage studies

Measurement of rates of protodetrimethylsilylation, i.e., of acid cleavage of Ar—$SiMe_3$ bonds, usually by $HClO_4/MeOH/H_2O$ or $H_2SO_4/CH_3CO_2H/H_2O$, have become a standard means of studying reactivity and substituent effects in aromatic systems, and substituent effects are known for a wider range of activating and deactivating effects in this than in any other aromatic substitution [59]*. Cleavage of Ar—$SnMe_3$ bonds [78] is less used, but is of special value when the aryl system will stand up only to very mild conditions. Some substituent effects are known only for protodegermylation [80], but this reaction has no advantages over protodesilylation. The results have been collated and examined thoroughly in the general context of reactivity in electrophilic aromatic substitution [41-43], and it is not proposed even to summarize them here. It should be pointed out, however, that the special utility of the demetallations comes from the high reactivity of Ar—MR_3 compared with the corresponding Ar—H bonds. Thus they can be used for (i) strongly deactivated aromatic systems not amenable to study in nitration, hydrogen-exchange, etc., (cleavage of $XC_6H_4SiMe_3$ compounds gave the first quantitative information on the effects of powerfully deactivating substituents such as NO_2, NMe_3^+, CF_3, CO_2R, PMe_3^+, and $P(O)(OR)_2$ [60,68,70,72-74]), and (ii) sensitive aryl systems which would not survive the more vigorous conditions necessary for the familiar aromatic substitutions. Two examples of (ii) must suffice.

In the first, protodetrimethylsilylation was used to establish the reactivities of the 3- and 4-positions of benzocyclobutene (VIII), which are of special importance for understanding the influence of fused aliphatic rings on the neighbouring aromatic systems. With this compound, the predominant reaction under ordinary substitution conditions is opening of the four-membered ring, but no such complication occurs in acid-cleavage of the 3- and 4-trimethylsilyl derivatives [71]. The results show that the 4-position is normally reactive and the 3-position markedly less reactive when compared with analogous open-chain sys-



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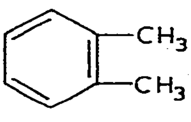

(IX)

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* However, the best reference reaction for investigation of aromatic reactivity is undoubtedly detritiation in anhydrous trifluoroacetic acid, and it is thus noteworthy that I initiated studies of this reaction because of its analogy to protodesilylation, in order to provide comparative data [81]. My first research student concerned with this reaction was Roger Taylor, who, initially in association with me, but later mostly independently, has contributed substantially to knowledge of reactivity effects in this and other electrophilic aromatic substitutions, not only through his experimental work but also through his comprehensive and critical reviews [41-43].

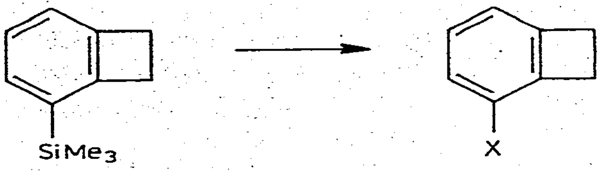
tem, IX, and this observation enables some decisions to be made between contending interpretations of the strain effect.

The second example concerned the study of the influence of C≡CH and C≡C—C≡CH groups on the reactivity of the benzene ring. Common substitutions cannot be used with PhC≡CH and PhC≡C—C≡CH because the electrophiles attack the triple bond more readily than the ring; indeed, even the Ar—$SiMe_3$ bond is not sufficiently reactive to direct reaction away from the side-chain, and so acid cleavage of the *m*- and *p*-$XC_6H_4SnMe_3$ compounds (X = C≡CH or C≡C—C≡CH) was used [79]. The results show that both substituents have substantial electron-withdrawing inductive effects (that for the C≡C—C≡CH group probably being comparable with that of a bromo substituent) coupled with significant electron-releasing resonance effects.

Applications of the cleavages in synthesis

Cleavages of Ar-MR_3 bonds have been extensively used in synthesis, but there is still a vast potential to be exploited. The demetallations have distinct advantages over direct electrophilic substitution in the corresponding ArH compounds; in particular, they (a) give a single isomer not a mixture, and can be used to give isomers formed only to a very small extent in conventional substitutions; (b) can be carried out with aromatic systems too unreactive in ArH compounds to be attacked by some of the common electrophiles; (c) can be used to direct reaction to a ring position and away from a side-chain readily attacked by electrophiles; and (d) can be carried out under much milder conditions, and so can often be used with aromatic compounds which would not stand up to the conventional substitution conditions. The $ArMR_3$ cleavages also have advantages over the reactions of the corresponding ArMgX and ArLi compounds, since (e) the latter often react further with the functional groups introduced (e.g., the $ArMR_3$ cleavages can be used to make ketones ArCOR and nitro compounds $ArNO_2$), and (f) the ArLi compounds are often best produced by metallation, which may give a mixture of isomers, so that direct reaction with an electrophile will give a mixture of products, whereas conversion of the ArLi into $ArMMe_3$ compounds, and separation of isomers (usually a simple process), can be followed by treatment with electrophiles to give specific isomeric products. A good example which illustrates all the advantages (a)-(f) above, is provided by the preparation of a range of 3-derivatives of benzocyclobutene. With this compound, the 3-halogeno derivatives cannot be obtained directly by halogenation of the hydrocarbon, though the 3-chloro compound has been made rather tediously, by forming the ring system with the halogen already in place [71], so the corresponding Grignard and lithium reagents are not easily available. Moreover, direct treatment of benzocyclobutene with common electrophilic species gives the 4-derivative as the greatly dominant substitution product and usually with much opening of the 4-membered ring. However, metallation of the hydrocarbon gives a mixture of lithio derivatives, of which the 3-derivative forms a substantial part, and treatment with Me_3MCl (M = Si or Sn) followed by fractionation of the products gives the 3-trimethyl-silyl- or -stannyl-benzocyclobutene [82]. Demetallations can then be carried out as in the following examples [82,83]:

(a)

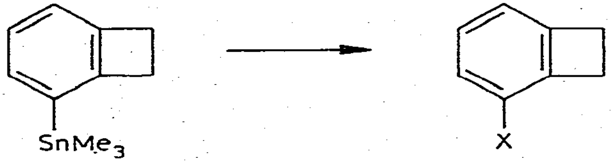


(VIII)

ICl $\longrightarrow$ VIII (X = I)

$Hg(OAc)_2$ $\longrightarrow$ VIII (X = HgOAc)

(b)



(IX)

Br_2 $\longrightarrow$ IX (X = Br)

NOCl $\longrightarrow$ IX (X = NO) $\xrightarrow{O}$ IX (X = NO_2)

The equations below illustrate the present scope of the use of $Ar{-}MR_3$ cleavages in introducing groups at specific points in aromatic rings. Along with some generalized equations are given those involving compounds of some special interest.

(i) Hydrogen isotopes

$XC_6H_4SnMe_3 + CH_3CO_2D \rightarrow XC_6H_4D$ [84]

$p\text{-}Me_3Si(CH_2)_nC_6H_4SiMe_3$ ($n = 2,3$) + ^3HOH + acid $\rightarrow$ $p\text{-}Me_3Si(CH_2)_nC_6H_4{}^3H$ [11]

(ii) Halogens and pseudohalogens

$ArSiMe_3 + Br_2 \rightarrow ArBr$ [16]

$ArSnMe_3 + ICl \rightarrow ArI$ [82]

$p\text{-}BrCH_2C_6H_4SiMe_3 + ICl \rightarrow p\text{-}BrCH_2C_6H_4I$ [85]

$XC_6H_4SnMe_3 + CNCl\ (+AlCl_3) \rightarrow XC_6H_4CN$ [86]

$C_6H_5SnMe_3 + (SCN)_2 \rightarrow C_6H_5NCS$ [87]

(iii) Nitro and nitroso groups

$XC_6H_4SiMe_3 + HNO_3/(CH_3CO)_2O \rightarrow XC_6H_4NO_2$ [24-26]

$p\text{-}Et_3GeC_6H_4GeEt_3 + HNO_3/(CH_3CO)_2O \rightarrow p\text{-}Et_3GeC_6H_4NO_2$ [27]

$XC_6H_4SnMe_3 + NOCl \rightarrow XC_6H_4NO$ [86]

$p\text{-}Me_3SnC_6H_4SnMe_3 + NOCl \rightarrow [p\text{-}Me_3SnC_6H_4NO] \xrightarrow{[O]} p\text{-}Me_3SnC_6H_4NO_2$ [83]

(iv) Sulpho, sulphino, sulphonyl, sulphinyl, and thioalkyl groups

$XC_6H_4SiMe_3 + SO_3 \rightarrow XC_6H_4SO_3SiMe_3 \xrightarrow{H_2O} XC_6H_4SO_3H$ [88]

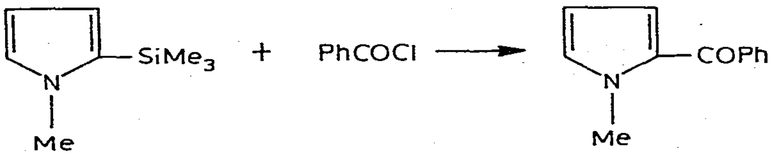
$p\text{-}Et_3GeC_6H_4GeEt_3 + SO_3 \rightarrow p\text{-}Et_3GeC_6H_4SO_3GeEt_3 \rightarrow$
$p\text{-}Et_3GeC_6H_4SO_3H$ [89]

$XC_6H_4SiMe_3 + RSO_2Cl\ (+AlCl_3) \rightarrow XC_6H_4SO_2R$ [90]

$XC_6H_4SnR_3 + RSY \rightarrow XC_6H_4SR\ (X = Hal, SCN)$ [91]

(v) Acyl and alkyl groups

$XC_6H_4MMe_3\ (M = Si\text{ or }Sn) + RCOCl\ (+AlCl_3) \rightarrow XC_6H_4COR$ [92]

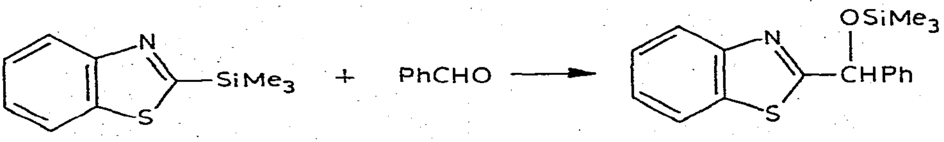


[93]

$PhSiMe_3 + PhCH_2Br\ (+AlCl_3) \rightarrow Ph_2CH_2$ [92]

$p\text{-}MeOC_6H_4SiMe_3 + (CH_3CO)_2O\ (+AlCl_3) \rightarrow p\text{-}MeOC_6H_4COCH_3$ [94]

Note. Aldehydes are sufficiently electrophilic to react with highly activated $ArSiMe_3$ and $ArMMe_3$ compounds: e.g.



[95]

(vi) Metallo and metalloido groups

$XC_6H_4SiMe_3 + Hg(OAc)_2 \rightarrow XC_6H_4HgOAc$ [30,31,96]

$XC_6H_4SnEt_3 + Hg(OAc)_2 \rightarrow XC_6H_4HgOAc$ [38]

$C_6Hal_5SnMe_3\ (Hal = Cl\text{ or }F) + BCl_3 \rightarrow C_6Hal_5BCl_2$ [97]

$p\text{-}Me_3SiC_6H_4SiMe_3 + PCl_3\ (+AlCl_3) \rightarrow p\text{-}Me_3SiC_6H_4PCl_2$ [98]

$XC_6H_4SiMe_3 + Pb(OAc)_4 \rightarrow XC_6H_4Pb(OAc)_3$ [99]

$XC_6H_4SiMe_3 + Pb(O_2CCF_3)_4 \rightarrow XC_6H_4Pb(O_2CCF_3)_3$ [100]

$XC_6H_4SnMe_3 + Th(O_2CCF_3)_3 \rightarrow XC_6H_4Th(O_2CCF_3)_2$ [101]

$C_6H_5SnR_3 + AgNO_3 \rightarrow C_6H_5Ag \cdot nAgNO_3$ [102]

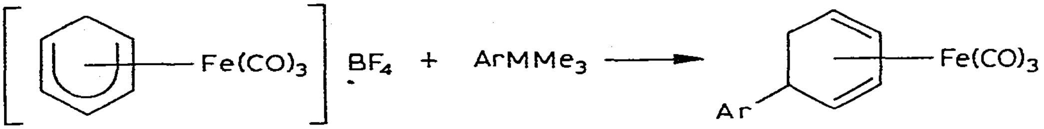
An interesting very recent example of reactions of type (vi) above is provided by the interaction of chloroplatinum complexes with $ArSnMe_3$ compounds [103], e.g.,

$ArSnMe_3 + [PtCl_2(COD)] \rightarrow [PtClAr(COD)]$

$ArSnMe_3 + [PtClAr(COD)] \rightarrow [PtAr_2(COD)]$

In this reaction the $ArSnR_3$ compounds have considerable advantages over the corresponding ArMgX and ArLi compounds in the cleanness of the reaction, yields, and ease of handling, and furthermore, they can be used in cases in which the Grignard and lithium reagents are not accessible. The ease of the reaction of the $ArSnMe_3$ compounds varies with the nature of the Ar group in the order expected for an electrophilic aromatic substitution.

In yet another novel reaction involving transition metal complexes, $ArMMe_3$ compounds (M = Sn or Si) have been shown to arylate an electrophilic olefin centre in the cationic species $[Fe(C_6H_7)(CO)_3]^+$, as in eqn. 3 [103a].



(3)

Again the reactivity of the $ArMR_3$ compounds varied as expected for an electrophilic aromatic substitution. The tin compounds are more reactive than the silicon compounds, but the latter are effective when the aromatic ring is strongly activated (e.g. Ar = p-$MeOC_6H_4$, 2-thienyl, etc.)

The potential utility of Ar—SiR_3 cleavages has recently been greatly extended by the observation that $XC_6H_4SiMe_3$ (and no doubt other $ArSiMe_3$) compounds may be prepared directly from the bromides XC_6H_4Br by reaction with hexamethyldisilane catalysed by $[Pd(PPh_3)_4]$ [104]. This makes readily accessible $ArSiMe_3$ compounds for which the corresponding ArMgX or ArLi reagents cannot be made, e.g., p-$NO_2C_6H_4SiMe_3$. It seems likely that analogous catalytic routes to $ArSnMe_3$ compounds will be found, which will further extend the applicability of the demetallations.

It should finally be noted that other types of C—MR_3 bonds are readily broken by electrophilic reagents [5,6], and cleavages analogous to those described above but involving alkynyl— [105-107] or allyl—MR_3 [108] bonds have already been used with considerable success in synthesis.

The future

The greatest impact of the work described above can be expected to come in the organic and organometallic syntheses, so that aryl$SiMe_3$, and even more probably arylSnR_3 compounds, and their alkynyl and allyl analogues, become fairly common laboratory reagents; this development will be greatly assisted by the discovery of new routes to the $R'MR_3$ compounds which avoid intermediates of the Grignard or organolithium type. Only a small number of the potential range of electrophiles which could be used have yet been examined, and use of electrophilic centres in transition metal complexes seems especially promising.

There seems little doubt that the use of demetallations in quantitative studies of aromatic substitutions will be extended as standard practice, and that detailed mechanistic studies of the reactions will assist general understanding of electrophilic aromatic substitution processes and of the nature and transmission of substituent effects in organic systems.

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