SOME GROUP IVB DERIVATIVES OF 1,6-METHANO[10]ANNULENE. SYNTHESIS, SUBSTITUENT EFFECTS AND REACTIVITY

WILLIAM KITCHING*, HENRY A. OLSZOWY, INGE SCHOTT,

*Chemistry Department, University of Queensland, Brisbane 4067 (Australia)*

WILLIAM ADCOCK and D.P. COX

School of Physical Sciences, Flinders University, Bedford Park 5042, SA (Australia)

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Summary

Certain Group IVB derivatives of 1,6-methano[10]annulene have been synthesised, and their ^{13}C nuclear magnetic resonance spectra recorded and assigned, to provide a measure of the substituent effects exerted by metalloid-containing groups in this non-benzenoid aromatic system. Comparisons are made with the corresponding naphthalene and some anthracene derivatives. Protiodemetallations of a number of arylsilanes and -stannanes have been examined, and in protiodestannylation by CH_3CO_2H/dioxane at 27°C (an electrophilic aromatic substitution) the α- (or 2-) position of 1,6-methano[10]annulene is ca. 35 times as reactive as the α (or 1-) position of naphthalene, whereas in protiodesilylation by CF_3CO_2H/CH_3CO_2H at 27°C it is ca. 700 times the more reactive.

Introduction

Recently we discussed some aspects of the ^{13}C NMR chemical shifts of a range of α (2-) and β (3-)-substituted-1,6-methano[10]annulenes, and compared the substituent effects at non-proximate sites with the data for the isoelectronic naphthalene systems [1]. The blends of inductive (ρ_I) and resonance (ρ_R) effects were remarkably similar for corresponding substituent-probe dispositions in the two systems [1].
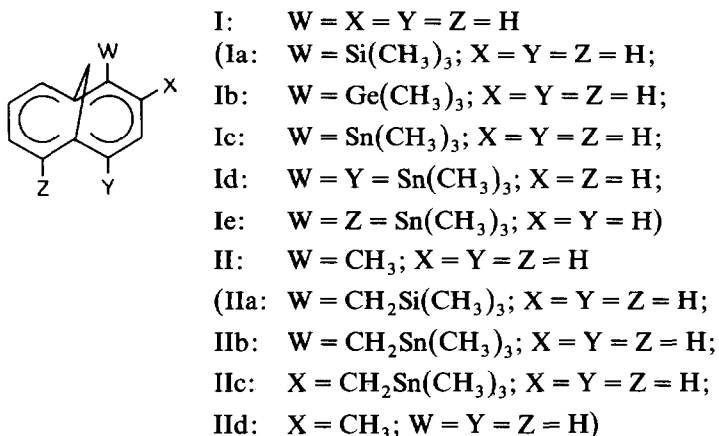

(I)
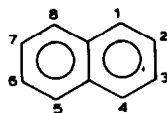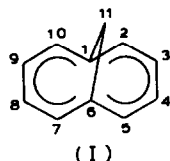
Some time ago we synthesised a number of silicon, germanium, and tin derivatives of I, and obtained and assigned their ^{13}C NMR spectra so that some comparisons of the interactions of these metalloidal groups with the non-benzenoid (I) could be made with the naphthalene data [2]. In addition, we have examined the

rates of protiodestannylation (and to a lesser extent the protiodesilylation) of a number of arylstannanes (including the 2-Sn(CH$_3$)$_3$ derivative of I) to provide a measure of the reactivity of the α-position of I in this simple electrophilic substitution [3]. As there is little likelihood of any further activity by us in this area, we have decided to report these results at this time.

Results and discussion

(a) Synthesis

Two series of derivatives were prepared, namely series I, in which the metalloid (M(CH$_3$)$_3$ is directly attached at position 2 (α-position; see numbering scheme in I), and series II, in which a methylene group is interposed, thus providing metalloidal-methyl substituents (CH$_2$M(CH$_3$)$_3$). To facilitate spectral assignments, some disubstituted derivatives were also synthesised.

I: W = X = Y = Z = H

(Ia: W = Si(CH$_3$)$_3$; X = Y = Z = H;

Ib: W = Ge(CH$_3$)$_3$; X = Y = Z = H;

Ic: W = Sn(CH$_3$)$_3$; X = Y = Z = H;

Id: W = Y = Sn(CH$_3$)$_3$; X = Z = H;

Ie: W = Z = Sn(CH$_3$)$_3$; X = Y = H)

II: W = CH$_3$; X = Y = Z = H

(IIa: W = CH$_2$Si(CH$_3$)$_3$; X = Y = Z = H;

IIb: W = CH$_2$Sn(CH$_3$)$_3$; X = Y = Z = H;

IIc: X = CH$_2$Sn(CH$_3$)$_3$; X = Y = Z = H;

IId: X = CH$_3$; W = Y = Z = H)

The precursor for series I is 2-bromo-1,6-methano[10]annulene, readily obtainable by direct bromination (N-bromosuccinimide) of I [4]. Bromine-lithium exchange (n-butyllithium), followed by treatment with trimethylchlorosilane or trimethylbromogermane, led to Ia and Ib, respectively.
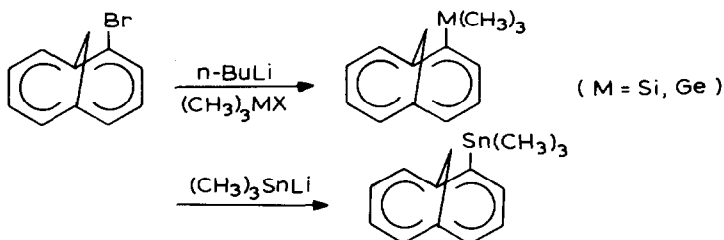
Direct reaction of the bromide with (CH$_3$)$_3$SnLi (in tetrahydrofuran) produced Ic. Dibromination of I yields predominantly ($\sim$ 70%) the 2,5-dibromo derivative (I, W = Y = Br; X = Z = H) together with the 2,7-dibromide. (I, W = Z = Br; X = Y = H) [5]. Trimethylstannylation of this mixture in the normal way [6] provided a stannane mixture (based on ^{119}Sn and ^{13}C NMR spectra) consisting of Ic (35%), Id (48%) and Ie ($\sim$ 17%). Allowing for the substantial reduction which normally accompanies stannylation of aryl bromides [7], this product distribution, with a preponderance of Id, is expected, in the absence of some bizarre substitution

mechanism. Nevertheless, the identities of the distannanes were established in the following ways: in the ^{119}Sn NMR spectrum, the major signal at -22.2 ppm (relative to internal $(CH_3)_4Sn$) exhibited [119]Sn–[117]Sn coupling of ca. 64 Hz, whereas in the other distannane (ca. 17%) (with $\delta(Sn)$ -21.9 ppm) such coupling was 17 Hz, consistent with the greater separation of the tin nuclei in the 2,7-isomer, Ie. In the ^{13}C NMR spectrum, the major distannane exhibited a signal at 130.5 ppm, boasting [119]Sn couplings of 55 and 34 Hz, and was therefore C(3,4) in the distannane Id. In the monostannane Ic, [119]Sn couplings to C(3) (30 Hz) and C(4) (56 Hz) were observed, and thus in the 2,7-distannane (Ie), no carbon signal could reasonably exhibit [119]Sn couplings of ca. 30 and 56 Hz.

Introduction of the $CH_2Si(CH_3)_3$ group at the 2-position, to provide IIa, was achieved by a nickel(II) mediated reaction, as described for other systems by Kumada [8]. Addition of the Grignard reagent prepared from chloromethyltrimethylsilane $((CH_3)_3SiCH_2MgCl)$ to 2-bromo-1,6-methano[10]annulene in the presence of bis(triphenylphosphine)nickel(II)chloride gave IIa in excellent yield. (This Ni[II] mediated procedure was utilised for making other arylmethyltrimethylsilanes). The tin compounds (IIb and IIc) were made by trimethylstannylation $((CH_3)_3SnLi$ in tetrahydrofuran) of the 2- and 3-chloromethyl-1,6-methano[10]annulenes, which in turn were prepared by chlorination (thionyl chloride) of the hydroxymethyl derivatives. (The 3-hydroxymethyl-1,6-methano[10]annulene was a generous gift from Professor E. Vogel).
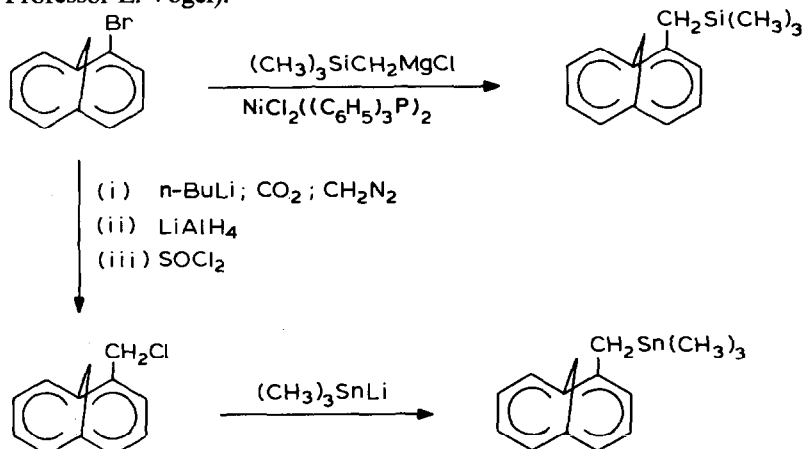
To complete some aspects of the study of the substituent effects of $M(CH_3)_3$ and $CH_2M(CH_3)_3$ as a function of the aryl group, some new 9-anthryl derivatives were required, and introduction of the $CH_2Si(CH_3)_3$ and $CH_2Sn(CH_3)_3$ groups proceeded readily, utilising the Ni[II] mediated reaction [8] with $(CH_3)_3SiCH_2MgCl$ (and $(CH_3)_3SnCH_2MgCl$) and either 9-bromo- or 9,10-dibromo-anthracene.

III   X = Y = H

(IIIa   X = $CH_2Si(CH_3)_3$; Y = H;

IIIb   X = Y = $CH_2Si(CH_3)_3$;

IIIc   X = $CH_2Sn(CH_3)_3$; Y = H;

IIId   X = $Si(CH_3)_3$; Y = H;

IIIe   X = $Sn(CH_3)_3$; Y = H)
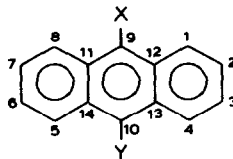
(IIId and IIIe are known [9,10], but an improved procedure for the latter is described in the Experimental section). Some comparisons are presented later with certain 1- (α) and 2-(β)-naphthyl compounds, some of which have been described previously. (IVc, IVd, IVg and IVh [11]). To complete the latter series, we also report the synthesis and ^{13}C NMR spectra of the Si and Ge derivatives (IVa, IVb, IVe and IVf).

IV   X = Y = Z = H

(IVa   X = CH$_2$Si(CH$_3$)$_3$; Y = H = Z;

IVb   X = CH$_2$Ge(CH$_3$)$_3$; Y = H = Z;

IVc   X = CH$_2$Sn(CH$_2$)$_3$; Y = H = Z;

IVd   X = CH$_2$Pb(CH$_3$)$_3$; Y = H = Z;

IVe   Z = CH$_2$Si(CH$_3$)$_3$; X = Y = H;

IVf   Z = CH$_2$Ge(CH$_3$)$_3$; X = Y = H;

IVg   Z = CH$_2$Sn(CH$_3$)$_3$; X = Y = H;

IVh   Z = CH$_2$Pb(CH$_3$)$_3$; X = Y = H)
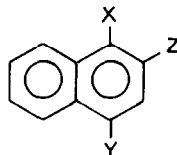
(b) ^{13}C NMR spectra

Previously we reported the ^{13}C NMR spectra of a wide range of 2(α)- and 3(β)-substituted 1,6-methano[10]annulenes, and analysed the substituent chemical shifts (SCS) in terms of the Dual Substituent Parameter (DSP) approach [1]. These spectra were assigned by consideration of some (or all) of the following: chemical shift trends, signal intensities, effects of specific incorporation of deuterium, ^{1}H-coupled spectra, coherent off-resonance decoupled spectra, and the spectra of certain disubstituted compounds. Some of these now largely routine approaches have been discussed fully elsewhere for these derivatives [12], and have been applied to the metalloidal derivatives described here. In the cases of the stannanes, an additional consideration is the regular pattern of readily observable ^{119}Sn–^{13}Sn couplings over one to four bonds. Extensive use of such couplings for assignment purposes has been reported, and needs no elaboration here. Because of interest in the magnitude of the anticipated shielding effects of the 2-CH$_2$Si(CH$_3$)$_3$ and 2-CH$_2$Sn(CH$_3$)$_3$ groups at formally conjugated positions, it was important to be certain of the assignments. For the silane, a tentative set of assignments was based on chemical shift considerations (bearing in mind the known π-donor capacity of this group), comparisons with the 2-CH$_3$ derivative, and a gated-decoupled spectrum. Some ambiguity remained, and in view of the relatively straightforward nature of the ^{1}H NMR spectra of these derivatives at 300 and 400 MHz, (see listing in Experimental part) a 2-D shift correlated spectrum was obtained, and this confirmed the assignments listed. The significant shielding effects of CH$_2$Si(CH$_3$)$_3$ at C(5), C(7) and C(9) would be greater for CH$_2$Sn(CH$_3$)$_3$, and this consideration, together with some observable ^{13}C–^{119}Sn couplings, lead to the assignments for the stannane. In these ways, the assignments for the 1,6-methano[10]annulenes shown in Table 1 were arrived at.

With respect to the anthracenes and naphthalenes, the assignments were determined by standard procedures [13,14] and presented in Tables 2, 3.

The primary purpose in examining the ^{13}C substituent induced shifts (SCS) in Ia, Ib and Ic was to compare the relative effects at the conjugated 4-position in the

TABLE 1

¹³C NMR SHIFTS OF SUBSTITUTED 1,6-METHANO[10]ANNULENES [a]

Compound [b]	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C(11)	Other
I	114.9	128.7	126.1	126.1	128.7	114.9	128.7	126.1	126.1	128.7	34.9	–
Ia	118.9	144.3	132.9	123.5	129.4	114.5	128.4	128.0	126.0	127.6	37.1	+0.8
Ib	117.9	145.9	131.3	123.5	128.6	114.3	128.5	125.9	125.9	127.5	36.7	+0.4
Ic	119.1	146.3 (406)	133.2	122.8 (56)	128.3 (~10)	114.2	128.9	125.8	125.8	127.8 (26)	36.8 (307?)	−7.7 (35)
Id	118.5 (40)	145.7	130.5 (52,32)	130.5 (52,32)	145.7	118.5 (40)	128.0	125.5	125.5	128.0	38.2	−7.7 (348)
Ie	118.5 (40)	146.6 (nl)	132.8 (30)	122.4 (52)	127.4	118.5 (40)	146.6 (nl)	132.8 (30)	122.4 (52)		36.6	−7.6 (nl)
II	114.4	138.3	126.7	126.3	126.7	116.3	127.5	126.4	126.2	127.7	35.3	19.0
IIa	113.5	142.1	126.5	126.3	125.1	117.1	127.1	126.5	126.0	127.7	35.2	24.3; −1.2
IIb	113.2	145.0	125.0	126.4	124.5	117.6	126.8	126.7	125.7	127.6	35.2	18.6; −9.2 (292)(322)
IIc	115.7 (~20)	123.5 (46)	142 (33)	126.6 (22)	128.9 (14)	112.4	128.5*	125.0	126.3	128.3*	36.1	25.5; −9.8 (300)(325)
IId	114.5	127.4	135.5	128.1	128.9	112.9	128.4	125.6	126.1	128.3	35.4	25.6

[a] For solutions in deuterochloroform and referenced to the central peak of the CDCl₃ triplet as 77.00 ppm. [b] The following ¹¹⁹Sn NMR shifts (relative to internal (CH₃)₄Sn) were measured for CDCl₃ solutions: Ic −20.9 ppm; Id −22.2 ppm; Ie −21.9 ppm; IIb −16.9 ppm; IIc +2.8 ppm. The chemical shifts for the 2-methyl (II) and 3-methyl derivatives (IId) are taken from ref. 7. Values in parentheses are ¹³C–¹¹⁹Sn coupling constants. nl = not located. Asterisked values may be interchanged.

TABLE 2

^{13}C NMR SHIFTS OF SOME ANTHRACENES

Compound	C(1,8)	C(2,7)	C(3,6)	C(4,5)	C(9)	C(10)	C(11,12)	C(13,14)	Others
III	128.2	125.3	125.3	128.2	126.2	126.2	131.7	131.7	
IIIa	125.4	124.5	124.7	129.0	134.2	123.6	131.6*	129.1*	19.0; −2.9
IIIb	126.1	123.9	123.9	126.1	130.4	130.4	128.9	128.9	18.6; −0.3
IIIc ^{a}	124.6	124.6	124.7	129.3	136.4	122.6	127.8	131.6	14.1; −8.6
					(47)	(23)	(21)	(~16)	
IIId	128.7	124.7*	124.4*	129.5	137.6	129.9	135.6	131.3	+4.5
IIIe ^{b}	130.1	124.7*	125.2*	129.4	143.2	128.5	138.3	131.6	−4.5
	(39)					(~15)	(27)	(39)	(343)

^{a} δ(Sn) +18.8 ppm. ^{b} δ(Sn) −72.8 ppm. Asterisked values may be interchanged.

1-naphthyl derivatives, with those at the (analogous) 5-position in the 2-(α)-sub-stituted-1,6-methano[10]annulenes. In the 1-naphthyl derivatives, we reported previously [10] that the SCS values for Si(CH$_3$)$_3$, Ge(CH$_3$)$_3$ and Sn(CH$_3$)$_3$ at C4 were +1.8, +1.2 and +0.9 ppm, respectively. In the corresponding annulene derivatives, the SCS values (at C(5)) are +0.7, −0.1 and −0.4 ppm, which indicate a lower net mesomeric electron withdrawal by Si(CH$_3$)$_3$, whereas the Ge(CH$_3$)$_3$ and Sn(CH$_3$)$_3$ groups are marginal donors. This is somewhat surprising, given that resonance transmission to C(5) in the α-substituted annulenes and to C(4) in the α-substituted naphthalenes are quite similar [1] (ρ_R = 19.19 and 19.98, respectively), based on a range of conventional substituents. However, for such feeble substituents, the imperfect electronic resemblance between these aromatic systems [15] may have comparatively larger effects on weak interactions. A large SCS at C(4) is manifested in these annulenes, being of the order of −2.5–3 ppm, whereas in the 1-substituted naphthalenes, the effect at the corresponding C(3) is negligible [13]. These are formally *meta*-type positions and such a large shielding effect is unanticipated, being larger than the upfield effect shift caused by "strong" substituents such as CN (+0.3) and COCH$_3$ (−1.8) etc. (It is of interest to note that H(3) in these compounds is also quite shielded). The effects of M(CH$_3$)$_3$ (M = Si, Ge, Sn) are minor at other positions, except for proximate carbons.

The CH$_2$Si(CH$_3$)$_3$ and CH$_2$Sn(CH$_3$)$_3$ have been demonstrated by various techniques to be strong resonance donors [11,16], and this is borne out by the SCS comparisons below for various dispositions in the α- and β-naphthyl and 1,6-methano[10]annulene derivatives. The corresponding methoxy derivatives, as conventional resonance donors, are included for comparison. (The σ_R° values of these groups are as follows: −0.20 (CH$_2$Si(CH$_3$)$_3$); −0.20 (CH$_2$Ge(CH$_3$)$_3$); −0.24 (CH$_2$Sn(CH$_3$)$_3$); −0.24 (CH$_2$Pb(CH$_3$)$_3$); −0.42 (OCH$_3$) [17].

The SCS values for the annulene derivatives are generally in line with expectation, but there are some interesting differences with respect to the naphthalene data. For transmission to C(4) in naphthalene (4α) and C(5) in the annulene, the former is more efficient, but less efficient to C(5) (5α) compared with C(7) in the annulene, as expected from our previous correlative analysis [1]. (ρ_R(C(5)) = 0.59; ρ_R(C(7)) = 3.10). Although 5α is a formally conjugated disposition in naphthalene, the correlation of SCS for this position is unsatisfactory and generally does not reflect theoretical predictions [13]. In the β-substituted systems, we would have expected

TABLE 3

^{13}C NMR SHIFTS OF SOME NAPHTHALENES [a]

Compound	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	Others
IVa	137.1	124.6	125.4	124.7	128.5	125.3	125.2	124.9	131.7	134.0	23.48; -1.2
IVb	138.1	124.5	125.5	124.5	128.5	125.2	124.9	124.8	131.5	134.0	23.3; -1.7
IVe	125.1	138.3	127.9	127.5	127.6	124.3	125.7	127.0	133.9	131.0	27.4; -1.8
IVf	124.6	139.2	127.5	127.5	127.5	124.3	125.7	127.0	133.9	131.0	26.8; -2.3

[a] Naphthalene (CDCl$_3$ solvent; relative to (CH$_3$)$_4$Si): 127.9 (C(1)); 125.8 (C(2)); 133.5 (C(9)).

TABLE 4

SCS VALUES [a] FOR CH$_2$M(CH$_3$)$_3$ AT CONJUGATED POSITIONS IN ARYL SYSTEMS

System	M in CH$_2$M(CH$_3$)$_3$	Naphthalene position					Annulene position					Anthracene position		
		4	5	7	6	8	5	7	9	8	10	2	4	10
α-Aryl	Si	-3.20	+0.7	-0.6			-2.7	-1.6	+0.4			-0.8	+1.8	-2.6
α-Aryl	Ge	-3.40	+0.7	-0.9										
α-Aryl	Sn	-4.0	+0.7	-1.0			-3.1	-2.0	+0.2			-0.7	+1.2	-3.6
α-Aryl	(OCH$_3$)	-7.8	-0.4	-0.8			-4.9	-2.4	-0.2			-0.2	+0.3	-4.0
β-Aryl	Si				-1.6	-1.0				-1.1	-0.4			
β-Aryl	Sn				-2.0	-1.3				-1.2	-0.5			
β-Aryl	(OCH$_3$)				-2.2	-1.1								

[a] Defined as the difference (ppm) between the ^{13}C chemical shift of the designated carbon atom and that of the appropriate carbon in the parent hydrocarbon.

resonance transmission to C(8) (annulene) to be ca. 0.6 that to the analogous C(6) in the naphthalene ($\rho_R = 4.5$ and 7.74, respectively) and for the CH_2SnMe_3 group, the SCS values are -2.0 and -1.1 ppm, respectively. Overall it is seen that the comparison between $CH_2Sn(CH_3)_3$ and OCH_3 as electron donors in the ground state is not an unrealistic one in these systems and emphasises the similarities between naphthalene and its non-benzenoid counterpart [1].

In our previous discussions [11,16] of CH_2M substituent effects, we had no data for 9-substituted anthracenes, in which resonance transmission to C(10) would be expected to be substantial, and slightly greater than to C(4) in the 1-substituted naphthalenes (HMO coefficients are 0.284 and 0.20, respectively) [18]. We synthesised both 9-(trimethylsilylmethyl)- and 9-(trimethylstannylmethyl)-anthracenes by the Ni^{II} mediated reaction between 9-bromoanthracene and $(CH_3)_3SiCH_2MgCl$ and $(CH_3)_3SnCH_2MgCl$, respectively [8]. The SCS at C(10) are -2.6 ($CH_2Si(CH_3)_3$) and -3.6 ppm ($CH_2Sn(CH_3)_3$) compared with CH_3 (-0.9). These values are somewhat smaller than the corresponding ones (-3.20; -4.0 ppm, respectively) in the 4α naphthyl series [16], in agreement with a recent DSP analysis of ^{13}C SCS in a range of 9-substituted anthracenes [14] which provided $\rho_R = 13.85$ (at C(10)), compared with $\rho_R = 19.98$ for the 4α naphthyl series [13].

However, in making such comparisons, it should be borne in mind that, although the SCS parameter is an experimental measure of the π-charge density perturbation by the substituent at a remote site, it does not allow a differentiation between charge redistribution (π-polarisation due to mixing of the $\pi^\star$ into π orbitals within the π-system) [19] versus charge transfer. The relative magnitudes of the SCS (ppm) for CH_3 at the *para*-disposed carbons in benzene, naphthalene and anthracene (-3.05, -1.37 and -0.90, respectively) suggests that the charge redistribution mechanism decreases significantly with increasing size of the π-system, for this apparent donor substituent which effects very little charge transfer to an adjacent neutral π-substrate [19]. This phenomenon is probably largely responsible for the unexpected decrease in the donor behaviour (based on charge transfer) of the $CH_2Si(CH_3)_3$ and $CH_2Sn(CH_3)_3$ groups in anthracene (C(10)) versus naphthalene (C(4)).

Precise geometries and conformations are problems for substituents lacking linear or spherical symmetry, and this applies to the CH_2M groups, as peri-interactions may be significant. However, the (steric) γ-effect at C(1,8) (-2.8 ppm) is similar to that at C(8) (-3.0 ppm) in 1-trimethylsilylmethylnaphthalene. For resonance interaction to be maximised, the Si–C–C(9) plane must be orthogonal to the aromatic plane, and in simpler benzyl systems, estimates of this dihedral angle have been made [20]. Resonance effects of these groups are weakly transmitted to the formally conjugated C(2,7) positions (HMO coefficient of 0.071) with upfield shifts of 0.8 (Si) and 0.7 ppm (Sn). (DSP analysis indicated ρ_R (C(10))$/\rho_R$(C(2,7)) $\sim 14/3$). C(4,5) in all 9-substituted anthracenes seem to suffer downfield shifts, irrespective of the nature of the substituent [14], and this holds for $CH_2M(CH_3)_3$ as well as $M(CH_3)_3$ groups. This has analogy in the ^{19}F SCS values for 5-fluoro-1-substituted naphthalenes [21]. With respect to IIId and IIIe, with 9-$Si(CH_3)_3$ and 9-$Sn(CH_3)_3$ groups, the downfield effects at C(10) are $+3.7$ and $+2.3$ ppm, respectively, indicating substantial mesomeric electron withdrawal. These values are ca. twice those for the corresponding 4α naphthyl derivatives.

Electrophilic aromatic substitution: acid cleavage of some aryl silanes and stannanes

Protiodemetallion of arylsilanes (and to a lesser extent, arylstannanes) have been extensively studied, particularly by Eaborn and his group, and display the general characteristics of electrophilic aromatic substitutions [22]. Indeed, desilylation provides useful and convenient measures of aromatic reactivity, and since the 2-trimethylsilyl and -stannyl derivatives of 1,6-methano[10]annulene were available, pro-

$$ArM(CH_3)_3 + HX \rightarrow Ar-H + (CH_3)_3MX$$

tiodemetallation studies appeared worthwhile to provide a measure of reactivity and to provide data for comparison with those for other aryl derivatives. Previously, Taylor [23] had reported results for detritiation and protiodesilylation of the 1,6-methano[10]annulene systems under somewhat different conditions.

Because of the wider range of data for protiodesilylation, we first examined the trifluoroacetic acid cleavage (TFA) of Ia, but discovered that reaction (and possibly some decomposition) was rapid in 30% TFA in acetic acid, as monitored by direct ^1H NMR examination of the reaction. (The rate was based on the disappearance of the $(CH_3)_3Si$ singlet). The rate was established for 3% TFA (in acetic acid) so that a comparison could be made with 9-trimethylsilylanthracene (on which Eaborn had also reported) [24] which was cleaved too rapidly in 30% TFA.

In this way, we determined the following data.

RELATIVE RATES OF PROTIODESILYLATION (27°C)

System	Conditions [a]	$t_{\frac{1}{2}}$ (min)	k_{rel}	k_{rel} [b]
1-Naphthyl	30% TFA	147.6	1	1
2-1,6-Methano[10]annulene	30% TFA	2	740	1400
2-1,6-Methano[10]annulene	3% TFA	410		
9-Anthryl	3% TFA	6	51,100	13,600

[a] Refers to % TFA in acetic acid (volume). Reactions displayed satisfactory pseudo-first order behaviour in silane. [b] Relative rates for reactions in $HClO_4/MeOH/H_2O$ derived from data for reactions at 50°C reported by Eaborn and Taylor [23]. α-Naphthyltrimethylsilane undergoes protiodesilylation by $HClO_4/MeOH/H_2O$ ca. 8 times as rapidly as phenyltrimethylsilane [24].

It was possible to compare our relative rates with those based on data reported by Eaborn [24] and Taylor [23]. Compared with 1-naphthyl, our data indicate that the annulene based silane reacts considerably faster and the 9-anthrylsilane very much faster. Our values of k_{rel} are ca. $\frac{1}{2}$ and 4 times as great as those based on literature reports for reactions under different conditions. However, given the difference in conditions, the rapidity of the reaction of the annulene under our conditions ($t_{\frac{1}{2}} \sim 2$ min) and the uncertainty of the ^1H NMR technique (mixing, heating etc.) the agreement is satisfactory and confirms the abnormally high rate for the anthryl derivative, and the high reactivity of the α-position of 1,6-methano[10]annulene compared with the α-position in naphthalene. In fact, the α-position of the annulene is more reactive than the para-position of anisole in protiodesilylation [23]. The enhanced reactivity of the 9-anthryl derivative has been reasonably attributed to steric relief on formation of the Wheland-type intermediate, with the large $(CH_3)_3Si$ group moving out of the plane away from the peri-1,8-hydrogens [24].

TABLE 5

RELATIVE RATES OF PROTIODESTANNYLATION (27°C)

$ArSn(CH_3)_3 + HOAc \rightarrow Ar-H + (CH_3)_3SnOAc$
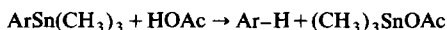
System	Conditions [a]	$t_{1/2}$ (min)	$k(\times 10^{-3})$ (min^{-1})	k_{rel}
Phenyl	AA	230	3.04	1
p-Tolyl	AA	43	17.4	5.3
m-Trifluoromethyl-phenyl	AA	4958	0.143	0.046
1-Naphthyl	AA	88	8.70	2.61
1-Naphthyl	50% D	1310	0.532	
4-Trimethyl-stannyl-1-naphthyl	AA	71	10.6	3.2
9-Phenanthryl	AA	83	9.07	2.8
2-Naphthyl	AA	158	4.56	1.5
2-Naphthyl	50% AA/D	2210	0.319	
2-(α)-1,6-Methano-[10]annulene	50% AA/D	37	20.4	
2-(α)-1,6-Methano-[10]annulene		191	3.6	90
	30% AA/D			
9-Anthryl	30% AA/D	19.4	38.8	882

[a] AA = acetic acid, D = dioxane.

Protiodestannylation of arylstannanes is known to be considerably faster than desilylation under comparable conditions [25], and it was possible to employ neat acetic acid or acetic acid/dioxane as the cleaving medium to provide reaction rates which could be conveniently monitored by ^1H NMR disappearance of the $(CH_3)_3Sn$ singlet, using an internal integration standard, such as cyclohexane. To accommodate the range of rates, some compounds were examined for acetic acid dioxane mixtures, and the "overlap" method then allowed overall rate comparisons. All reactions exhibited excellent pseudo-first order kinetics ($r \sim 0.995$).

The data are summarised in Table 5, and relative rates refer to phenyltrimethylstannane. Our technique is satisfactory as the value for the p-tolyl compound (5.3) is in good agreement with that based on the UV spectroscopic technique (5.2) [26]. With respect to the data for protiodesilylation, the striking feature is the greatly compressed range of rates, with the annulene (stannane) experiencing substitution ca. 35 times faster than 1-naphthyl, and 9-anthryl some 340 times faster. (In protiodesilylation, the comparable data are ca. 740 and 51,000 (or 1400 and 13,600)). This type of result has been observed with substituted phenylstannanes where the effect of substituents is feeble ($\rho = -2.24$ in acetolysis) [26], and for other electrophilic substitutions of polycyclic arylstannanes [24,27]. We measured the rate of protiodesilylation of the 9-anthrylsilane in acetic acid, and we can calculate that under similar conditions, the stannane is cleaved ca. 1500 times faster than the silane. Eaborn and Pande [25] observed that acid cleavage (aqueous ethanolic perchloric acid) of the aryl C–Sn bond was ca. 3.5×10^5 faster than C–Si cleavage in phenyltriethylmetal compounds, so that in the present case, the anthrylsilane is cleaved ca. 200 times faster than anticipated (or the stannane is cleaved more slowly). The first possibility agrees with Eaborn's conclusion that steric relief accounts for a rate enhancement of ca. 100 times for the silane [24]. The longer

C–Sn bond would reduce steric congestion in the ground state, and hence steric relief during cleavage would be less important.

Experimental

Compounds

2-Trimethylsilyl-1,6-methano[10]annulene

To a cooled solution of 2-bromo-1,6-methano[10]annulene [4] (2 g, 7 mmol) (b.p. 98–99°C/0.05 mmHg) in dry ether (10 ml; −50°C) was added n-butyllithium in hexane (9.2 ml, 11 mmol). The solution was allowed to warm, (−10°C) and trimethylsilyl chloride (2.0 g, 10 mmol) was added. A standard work-up and extraction with ether etc. provided a yellow oil which was distilled (93–94°C/0.4 mmHg) to yield the silyl compound (1.3 g) (66%) which was contaminated with 1,6-methano[10]annulene (4%) by GC-MS. (Found: C, 79.0; H, 8.3. $C_{14}H_{18}Si$ calcd.: C, 78.4; H, 8.4%). ^1H NMR (270 MHz): δ −0.38 and −0.48, (AB pattern, J 8 Hz, 2H, H(11)), +0.41 (s, $(CH_3)_3Si$), 6.98, (t, H(4)), 7.16 (m, H(8), H(9)), 7.20 (d, H(3)), 7.45 (m, H(5), H(7), H(10)).

2-Trimethylgermyl-1,6-methano[10]annulene

was obtained similarly except that the lithium derivative was quenched with trimethylbromogermane. B.p. 98–100°C/0.5 mmHg. (Found: C, 71.0; H, 7.1. $C_{14}H_{18}Ge$ calcd.: C, 72.5; H, 7.0%). ^1H NMR: δ −0.4 (brs, 2H, H(11)), +0.52 (s, $(CH_3)_3Ge$), 6.9 (t, H(4)), 7.1–7.6 (m, other ring protons).

2-Trimethylstannyl-1,6-methano[10]annulene

resulted from the reaction of 2-bromo-1,6-methano[10]annulene with trimethyltinlithium (($(CH_3)_3SnLi$) in tetrahydrofuran in the usual way [6]. B.p. 100–102°C/0.01 mmHg. (Found: C, 55.3; H, 6.0. $C_{14}H_{18}Sn$ cald.: C, 55.1; H, 5.90%). ^1H NMR: δ −0.38 (brs, 2H, H(11)), 0.4 (s, $(CH_3)_3Sn$), 6.86 (t, J 8.7 Hz, H(4)), 7.03 (m, 2H, H(8), H(9)), 7.15 (d, J 8.7 Hz (J(Sn–H) 56 Hz), H(3)), 7.19 (m, H(7)), 7.32 (d, J 8 Hz, H(5)), 7.39 (d, J 8Hz, H(10)). δ(Sn) −20.9 ppm relative to $(CH_3)_4Sn$ in $CDCl_3$.

2,5- and 2,7-bis(trimethylstannyl)-1,6-methano[10]annulenes

were obtained as a mixture (as discussed in the text) from the reaction of trimethyltinlithium (($(CH_3)_3SnLi$) with a mixture of the 2,5- and 2,7-dibromo-1,6-methano[10]annulenes (b.p. 144°C/.01 mmHg) which were obtained by dibromination (*N*-bromosuccinimide) of the parent annulene [4,5]. Distillation, after a standard work-up, provided the distannanes, b.p. 134–138°C/0.01 mmHg with the 2,5-isomer predominating. (See text). (Found: C, 47.3; H, 5.80. $C_{17}H_{26}Sn_2$ calcd.: C, 43.6; H, 5.6%).

Combined GC-MS analysis of the distilled reaction mixture showed the presence of the 2-trimethylstannyl derivative (*m/e* 306, *M* 1.7%) presumably arising from reduction, a 5- or 7-bromo-2-trimethylstannyl derivative (*m/e* 384, *M* 4.4%) as well as the distannanes (*m/e* 468, *M* 1% (2,5-isomer) and 3.4% (2,7-isomer)). Further careful distillation provided the predominantly distannane mixture that was analysed (The observed pattern for all *M* were in excellent agreement with those calculated from known isotopic distributions). ^1H NMR (of mixture) consisted of the $(CH_3)_3Sn$ singlet (δ 0.4; J(Sn–H) 54 Hz) and aromatic absorption from δ 7.0 ~ 7.30. A prominent singlet at δ 7.0 is attributed to H(3,4) in the 2,5-distannane. δ(Sn): −22.2 ppm (2,5-isomer) and −21.9 ppm (2,7-isomer).

2-(Trimethylsilylmethyl)-1,6-methano[10]annulene

A solution of trimethylsilyl methylchloride (1.1 g, 8.8 mmol) in dry ether (15 ml) was added to magnesium turnings (0.28 g, 20% excess) and the reaction initiated with methyl iodide. After ca. 2 h, this Grignard reagent was filtered into an ether solution (10 ml) of 2-bromo-1,6-methano[10]annulene (1.5 g, 6.8 mmol) and dichlorobis(triphenylphosphine)nickel(II) (55 mg) [8]. After an initial vigorous reaction, the vessel was flushed with nitrogen, sealed and stirred at room temperature for ca. 70 h. Standard work-up and Kugelrohr distillation (150°C/1 mmHg) provided the target compound as a yellow oil in good yield. (Found: C, 78.3; H, 8.5. $C_{15}H_{20}Si$ calcd.: C, 78.8; H, 8.8%). Mass spectrum: m/e 228 [M 7.3%], 73 [$(CH_3)_3Si$, 100%]. ^1H NMR: δ(ppm) -0.64(d) and -0.28 (d, J 9 Hz, 2H, H(11)), 0.0 (s, $(CH_3)_3Si$), 2.40 ("tight" AB pattern, 2H, CH_2Si), 6.81 (d, H(3)), 6.95 (t, H(4)), 7.12 (t) and 7.17 (t, H(8), H(9)), 7.23 (d, H(5)), 7.40 (d, H(7)) and 7.51 (d, H(10)).

2-(Trimethylstannylmethyl)-1,6-methano[10]annulene

Reduction ($LiAlH_4$/ether) of 2-carbomethoxy-1,6-methano[10]annulene [5] in the normal way provided 2-hydroxymethyl-1,6-methano[10]annulene which was distilled. (Kugelrohr 160–163°C/0.4 mmHg). (Found: C, 81.0; H, 6.9. $C_{12}H_{12}O$ calcd.: C, 83.7; H, 7.0%). Mass spectrum: m/e 172 [M 16.8%]; 154 [$M-18$, 52%]; 141 [$C_{11}H_9$, 100%]. ^1H NMR: δ(ppm): -0.5 (brs, 2H, bridging CH_2), 2.44 (s, 1H, OH), 4.8 (AB system, J 13 Hz, CH_2O), 6.9–7.8 (7H, ring protons). This alcohol was chlorinated (thionyl chloride in ether) to provide the chloromethyl derivative which was characterised by its ^1H and ^{13}C NMR spectra. ^1H NMR: δ(ppm): -0.34 and -0.54 ((AB) J 10 Hz, H(11)), 4.64 and 4.81 ((AB) J 12 Hz, CH_2Cl), 6.66–7.76 (m, 7H, ring protons). ^{13}C NMR: 35.3, 44.7, 113.1, 116.6, 126.3, 126.8 (2C), 127.2, 128.1, 128.3, 130.2, 136.7.

Trimethyltinlithium (5.7 mmol) was prepared from trimethyltin chloride and lithium in tetrahydrofuran as described elsewhere [6], and to this filtered solution was added the chloromethyl derivative (0.95 g, 5 mmol) dissolved in tetrahydrofuran (2 ml). After ca. 10 h the mixture was worked up to provide a yellow oil (1.6 g) which was distilled (Kugelrohr, 140–160°C/0.4 mmHg) to provide ca. 0.6 g of a yellow (almost solid) viscous oil. (A small amount of 2-methyl-1,6-methano[10]annulene was present). (Found: C, 57.4; H, 6.2. $C_{15}H_{20}Sn$ calcd.: C, 56.5; H, 6.3%). Mass spectrum: (m/e 320, M, 3.5%, 165, $(CH_3)_3Sn$, 100%). ^1H NMR: δ(ppm): -0.69 and -0.34 (AB system, J 8 Hz, H(11)), -0.12 (s, $(CH_3)_3Sn$), 2.5 and 2.7 (AB, J 12 Hz, CH_2Sn), 6.80 (d, H(3)), 6.93 (t, H(4)), 7.09 (t) and 7.15 (t, H(8), H(9)), 7.16 (d, H(5)), 7.38 (brd, H(7)), 7.49 (d, H(10)). δ(Sn) -16.9 ppm.

3-(Trimethylstannylmethyl)-1,6-methano[10]annulene

3-Hydroxymethyl-1,6-methano[10]annulene as provided by Professor E. Vogel (Cologne) was characterised as follows: Mass spectrum: m/e 172, M 15.9%; 141, $M-CH_2OH$, 100%. ^1H NMR spectrum: δ -0.4 (brs, 2H, H(11)), 2.6 (brs, OH), 4.87 (brs, 2H, CH_2O), 7.2–7.9 (m, 7H, ring protons). ^{13}C NMR spectrum: 35.1, 68.5, 114.0, 114.2, 125.6, 126.0, 126.1, 127.3, 128.3, 128.7, 129.4, 138.6. Chlorination (thionylchloride in ether) provided the chloromethyl derivative which was characterised by its 100 MHz ^1H NMR spectrum: δ(ppm): -0.32 ("tight" AB system, J 8 Hz, H(11)), 6.64 (brs, 2H, CH_2Cl), 6.9–7.6 (m, 7H, ring protons). Stannylation of this chloride with trimethyltinlithium in the standard way [6] provided, after

work-up and Kugelrohr distillation (160°C/0.02 mmHg), 1.2 g of yellow liquid (56% based on the starting alcohol). (Found: C, 56.2; H, 6.5. $C_{15}H_{20}Sn$ calcd.: C, 56.5; H, 6.3%). Mass spectrum: m/e 320, M, 5%, -165, $Sn(CH_3)_3$, 100%; 155, $C_{12}H_{11}$, $(M - Sn(CH_3)_3$, 60% (100 MHz) ^{1}H NMR spectrum: δ(ppm): -0.36 ("tight" AB system, J 8 Hz, bridging CH_2), $+0.8$ (s, $(CH_3)_3Sn$), 2.57 and 2.64 (AB system, J 11 Hz, CH_2Sn), 6.85 (d, J 9 Hz, H(4)), 7.10 (brs, H(2)), 7.10 (m, 2H, H(8), H(9)), 7.26–7.60 (m, 3H, H(5), H(7), H(10)). (In some respects, this spectrum resembles that of the 3-methoxy compound). δ(Sn) 2.8 ppm.

9-Trimethylstannylanthracene

To a solution of 9-bromoanthracene (2 g, 7.8 mmol) in dry tetrahydrofuran was added trimethyltinlithium (9.3 mmol) and the reaction allowed to proceed for ca. 5 h at room temperature. The heat sensitive product was recrystallised carefully from warm absolute ethanol (to remove any anthracene) to provide pale yellow needles (0.5 g). M.p. 65–66°C (Lit. 65–66°C). This procedure is simpler than that previously reported [10]. δ(Sn) 72.8 ppm.

9-Trimethylsilylanthracene [9] and 9-(Trimethylsilylmethyl)anthracene [8] were prepared as previously described.

9,10-Bis(trimethylsilylmethyl)anthracene

The trimethylsilylmethyl Grignard reagent (18 mmol) was added to an ethereal solution of 9,10-dibromoanthracene (2 g, 6 mmol) and bis(triphenylphosphine)-nickel(II) chloride (200 mg). The thick yellow solution slowly turned brown, and after ca. 40 h, the yellow solid had dissolved. Following further reaction (additional 30 h), the reaction was worked up, to provide a yellow solid, with a slight purple fluorescence (1.9 g). Recrystallisation from ethanol provided ca. 1.5 g of yellow needles, m.p. 144–145°C. (Found: C, 75.4; H, 8.6. $C_{22}H_{30}Si_2$ calcd.: C, 75.4; H, 8.6%). Mass spectrum: m/e 350 [M, 28.7%]; 277 [$M - 77$, 18.9%]; 73 [$(CH_3)_3Si$, 100%]. ^{1}H NMR spectrum: δ (ppm): 0.0 (s, $(CH_3)_3Si$), 3.23 (s, 4H, CH_2Si), 7.6 (m, 4H) and 8.4 (m, 4H, ring protons).

9-(Trimethylstannylmethyl)anthracene

The Grignard reagent prepared from trimethylstannylmethyl chloride (2 g, 9.4 mmol) was added to 9-bromoanthracene (0.91 g, 3.6 mmol) in dry ether (10 ml) containing bis(triphenylphosphine)nickel(II) chloride (29 mg) [8]. The bromoan-thracene dissolved and the mixture turned brown and then dark yellow green (after several hours). After stirring for 2 d at room temperature, the mixture was worked up and a yellow oil was isolated. The product was heat sensitive, and the anthracene was removed on a Florisil column (pentane eluant). 1.1 g of a yellow oil was obtained (ca. 80%). Mass spectrum: m/e 356, M, v; 191, $C_{14}H_9CH_2$, 100%. 60 MHz ^{1}H NMR: δ -0.08 (s, J(Sn–H) 52 Hz, $(CH_3)_3Sn$), 3.3 (s, 2H, J(Sn–H) 65 Hz, CH_2Sn), 7.1–8.7 (m, 9H, ring protons). The ^{13}C NMR spectrum confirms the identity of this stannane. δ(Sn) 18.8 ppm.

1,4-Bis(trimethylstannyl)naphthalene

To 1,4-dibromonaphthalene (1.0 g, 3.5 mmol) was added trimethyltinlithium (7 mmol) in tetrahydrofuran in the normal way [6]. Standard work-up, and chromatography (Florisil/pentane) followed by distillation (180–190°C/0.3 mmHg) provided

a slightly yellow oil which did not crystallise. A second distillation (135–140°C/0.1 mmHg) provided (on cooling) 0.86 g of white crystals, m.p. 76–77°C. (Found: C, 42.2; H, 5.4. $C_{16}H_{24}Sn_2$ calcd.: C, 42.4; H, 5.3%). Mass spectrum: m/e 454, M, 15.0%; 439, $M - CH_3$, 100%. 100 MHz ^{1}H NMR: δ(ppm): 0.34 (s, 18H, J(Sn–H) 53 Hz, $(CH_3)_3$Sn), 7.44–7.96 (m, 6H, ring protons). A sharp singlet (δ 7.65) is assigned to H(2), H(3). δ(Sn) −30.3 ppm. ^{13}C NMR spectrum: −8.36 (350,334); 125.5, C(6,7); 131.1(34), C(5, 8) 134.1 (30,50), C(2, 3); 138.7(31), C (9,10); 143.54, C(1,4).

9-Phenanthryltrimethylstannane was prepared as described previously [28], from 9-bromophenanthrene and n-butyllithium, followed by quenching with $(CH_3)_3$SnCl (72%). B.p. 140–160°C/0.01 mmHg (Kugelrohr). Mass spectrum: m/e 342, M, 15%; 327, $M - CH_3$, 100%. ^{1}H NMR: δ (ppm): +0.51 (s, $(CH_3)_3$Sn), 7.6–7.7 (m, 4H, H(2,3,6,7)), 7.85–7.9 (m, 2H, H(1,8) 7.92, (s, 1H, H(10) (J(Sn–H) 58 Hz), 8.65–8.8 (2H, m, H(4,5)).

Naphthylmethyltrimethylsilanes and -germanes (IVa, IVb, IVc and IVf) were prepared by treating 1- or 2-naphthylmethylpotassium with the appropriate metal-loidal halide. The ^{13}C NMR shifts are listed in Table 3.

1-Naphthylmethyltrimethylsilane had b.p. 100°C/0.1 mmHg. (Lit. 29 90°C/0.003 mmHg) n_D^{22} 1.5665. ^{1}H NMR: δ0.0 (s, $(CH_3)_3$Si), 2.57 (s, 2H, CH_2), 7.10–7.93 (m, 7H, aromatic).

1-Naphthylmethyltrimethylgermane; n_D^{22} 1.5821. ^{1}H NMR: δ (ppm): 0.0 (s, $(CH_3)_3$Ge), 2.58, (s, 2H, CH_2), 7.10–7.93, (m, 7H, aromatic).

2-Naphthylmethyltrimethylsilane was obtained as prisms from methanol, m.p. 60°C. (Lit. 29 m.p. 61°C). ^{1}H NMR δ (ppm): 0.0 (s, $(CH_3)_3$Si), 2.13 (s, 2H, CH_2), 6.77–7.58 (m, 7H, aromatic).

2-Naphthylmethyltrimethylgermane was acquired as prisms from methanol, m.p. 57–58°C. ^{1}H NMR: δ (ppm): 0.13 (s, 9H, $(CH_3)_3$Ge), 2.28 (s, 2H, CH_2), 6.79–7.61 (m, 7H, aromatic).

Other compounds referred to in the text were previously known, and the samples had physical and spectral properties in agreement with those reported. The ^{13}C NMR data are summarised and discussed in the text.

Kinetics

All kinetic runs were conducted with an appreciable excess of cleaving acid, either trifluoroacetic acid, or in some cases acetic acid, in dioxane. Neat acetic acid was employed for some "slow" reactants. Generally, substrate concentrations were ca. 0.0025 M i.e. ca. 2–15 mg of silane or stannane was dissolved in ca. 1 ml of the acid (and solvent) where appropriate. The progress of the reaction was followed by the disappearance of the $(CH_3)_3$Si or $(CH_3)_3$Sn singlet in the ^{1}H NMR spectrum (100 MHz). Spectral calibration against internal cyclohexane was performed so that signal heights represented concentrations of unreacted material. For some reactions, the 5 mm NMR tube remained in the probe for the duration of the reaction, whereas for slower reactions, it was placed in a constant temperature both (27°C) and removed periodically for examination. To facilitate comparisons between different reactants of differing reactivity, the "overlap" method (whereby rates for several acid concentrations for the one reagent were obtained) was employed. This is clear from the kinetic comparisons presented in the text, which provide meaningful

relative reactivities. For the cleavage reactions, NMR analysis confirmed only hydrocarbon and $(CH_3)_3MX$ were formed. The kinetic data were treated with a standard program to provide the "best fit" (to the first order expression) and the resultant rate constants listed. Excellent linearity was observed.

Spectra

NMR spectra

300 MHz ^1H NMR spectra were obtained on the Bruker CXP-300 spectrometer of the Brisbane NMR Centre, and some 270 MHz ^1H spectra were obtained at the National NMR Centre in Canberra. 100 MHz spectra were obtained with either a JEOL JNM-MH-100 or JEOL JNM-FX-100 spectrometers. 25 MHz ^{13}C spectra were obtained with the latter machine, whereas 75.46 MHz ^{13}C spectra were measured on the Bruker CXP-300 spectrometer, all for $CDCl_3$ solutions, and chemical shifts are referenced to the central peak of the $CDCl_3$ triplet at 77.00 ppm. ^{119}Sn spectra were recorded at 37.08 MHz (JEOL FX-100) for $CDCl_3$ solutions and are referenced to internal $(CH_3)_4Sn$. Positive shifts are to lower field.

Combined Gas Chromatography-Mass Spectrometry

This was performed on a Hewlett-Packard 5992 B instrument, fitted with an OV101 capillary column (Operator: Mr. V. Alberts).

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