

SYNTHESIS AND SPECTROSCOPIC CHARACTERISTICS OF ARYLTRIMETHYL-SILICON, -GERMANIUM, AND -TIN COMPOUNDS

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Summary

The synthesis and spectroscopic characteristics of 28 *para*-substituted aryltrimethyl-silicon, -germanium, and -tin compounds are described. The infrared spectra show characteristic bands at 1245–1165 (methyl bend), 840–765 (methyl rock), and 1105–1020 (in-plane aromatic H bend) cm^{-1} ; the frequency of the last band was found to depend on the sum of the aromatic substituent masses, the presence or absence of metallic constituents in the substituent having little influence. The mass spectral fragmentation patterns are interpreted in terms of localization of positive charge on the metal atom, with subsequent bond cleavage behavior which obeys the rules for mass spectra of carbon compounds.

Introduction

During radiohalogenation studies using arenes bearing fourth group metals [1–4], a series of aryltrialkyl organometallics of silicon, germanium, and tin were synthesized. An opportunity thus presented itself for the identification of changes in the spectroscopic characteristics of these organometallics brought about by changes in the organic ligand or the central metal, and we describe here the synthesis and some spectroscopic characteristics of several *para*-substituted aryltrimethyl-silicon, -germanium, and -tin compounds.

Results and discussion

Synthesis of organometallics

The aryltrimethyl derivatives of Group IVb elements prepared in this work are listed along with pertinent physical data in Table 1. Although the emphasis was on

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TABLE 1

YIELDS AND PROPERTIES OF *p*-Me₃MC₆H₄X COMPOUNDS

M	X	B.p. (°C/mmHg) or m.p. (°C)	n_D^{25}	d^{25}	Yield (%)	Analysis (Found (calcd.)(%))	
						C	H
Si	NO ₂	36.5	—	—	81	55.5 (55.4)	6.7 (6.7)
	CF ₃	88-89/60	1.4412	1.0556	76	55.1 (55.0)	6.2 (6.0)
	Br	98.8/23	1.5272	1.2324	79	46.9 (47.2)	5.6 (5.7)
	H	168-169/760	1.4863	0.8627	90	71.8 (72.0)	9.3 (9.3)
	F	173-174/760	1.4688	0.9306	86	64.1 (64.3)	7.9 (7.7)
	Me	51.4/4.5	1.4893	0.8270	76	73.0 (73.2)	9.9 (9.7)
	OMe	223-224/760	1.4983	0.9288	84	66.2 (66.6)	8.8 (8.9)
	OH	74.5	—	—	63	65.2 (65.0)	8.7 (8.5)
	SiMe ₃	87.8	—	—	60	64.9 (64.8)	9.9 (10.0)
	OSiMe ₃	121/24	1.4785	0.9054	91	60.2 (60.4)	9.4 (9.3)
Ge	NO ₂	45.5	—	—	62	44.9 (45.1)	5.5 (5.5)
	CF ₃	59.5/6	1.4594	1.1855	70	45.8 (45.7)	5.2 (5.0)
	Br	102.5/12	1.5465	1.4840	68	39.2 (39.5)	4.5 (4.8)
	H	183/760	1.5043	1.1144	81	55.5 (55.5)	7.2 (7.2)
	F	50.8/6	1.4869	1.1870	91	50.8 (50.8)	6.3 (6.1)
	Me	71.9/9	1.5041	1.0904	75	57.5 (57.6)	7.7 (7.7)
	OMe	85.8/5.5	1.5155	1.1531	92	53.6 (53.4)	7.0 (7.1)
	OH	77.9	—	—	51	51.1 (51.3)	6.5 (6.7)
	GeMe ₃	95.6	—	—	52	46.1 (46.3)	7.2 (7.1)
	OSiMe ₃	127/28	1.4962	1.0430	82	51.1 (50.9)	7.9 (7.8)
Sn	CF ₃	52-3/1	1.4897	1.4373	66	38.8 (38.9)	4.3 (4.2)
	Br	121-122/6	1.5673	1.5968	64	33.8 (33.8)	4.2 (4.1)
	H	66.5/4.5	1.5309	1.3189	78	44.9 (44.9)	5.9 (5.9)
	F	49/1	1.5153	1.4015	87	41.8 (41.8)	5.2 (5.0)
	Me	72.4/4	1.5304	1.2927	79	46.8 (47.1)	6.3 (6.3)

TABLE 1 (continued)

M	X	B.p. (°C/mmHg) or m.p. (°C)	n_D^{25}	d^{25}	Yield (%)	Analysis (Found (calcd.)(%))	
						C	H
Sn	OMe	86/0.9	1.5403	1.3424	94	44.4 (44.4)	6.1 (5.9)
	SnMe ₃	118.2	—	—	56	35.9 (35.7)	5.5 (5.4)
	OSiMe ₃	129–130/20	1.5199	1.1798	83	44.0 (43.8)	6.6 (6.7)

product purity rather than high yield, the yield exceeded 50% in all cases. Most of the $\text{XC}_6\text{H}_4\text{MMe}_3$ compounds ($\text{X} = \text{CF}_3, \text{Br}, \text{H}, \text{F}, \text{Me}, \text{OMe}$; $\text{M} = \text{Si}, \text{Ge}, \text{Sn}$) were made from the Grignard reagent formed from the relevant aryl bromide. *p*-Bis(trimethyl-silyl)-germyl- and -stannyl-benzenes were prepared from *p*-dibromobenzene, and were subsequently used in the synthesis of the *p*-nitrophenyl analogues via regiospecific introduction of a nitro group in place of one of the Me_3M groups [5,6]. *p*-Nitrophenyltrimethyl-silane and -germane were made by this technique, but it did not give the organotin analogue probably owing to the great sensitivity of carbon–tin bonds to protolysis [7]. Synthesis of the (*p*-hydroxyphenyl)trimethyl organometallics required protection of the hydroxyl group of *p*-bromophenol with trimethyl-silicon chloride prior to formation of the Grignard precursor and reaction with trimethylmetallic halide [8]. Subsequent removal of this protecting group with acid gave (*p*-hydroxyphenyl)trimethyl-silicon and -germanium, but attempts to generate the corresponding tin compound produced from the (*p*-trimethylsiloxyphenyl)trimethyltin precursor gave only phenol.

Refractive indices

There are excellent correlations between the indices of refraction of $\text{Me}_3\text{MC}_6\text{H}_4\text{X}$ compounds ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}$), regression analysis gave the following equations:

$$n_D^{25}(\text{Ge}) = 1.0048 n_D^{25}(\text{Si}) + 0.0106 \quad (r = 0.99)$$

$$n_D^{25}(\text{Sn}) = 0.8984 n_D^{25}(\text{Si}) + 0.1943 \quad (r = 0.99)$$

$$n_D^{25}(\text{Sn}) = 0.8936 n_D^{25}(\text{Ge}) + 0.1856 \quad (r = 0.99)$$

A similar relationship has previously been noted for compounds containing germanium and silicon [9]. Such good correlations between compounds bearing the same ligand mean that the purity of a sample of a derivative containing one of the metals may be judged by comparison of its refractive index with that of an analogous organometallic of known purity.

Infrared spectroscopy

Vibrational spectra of the title compounds were recorded in the rock salt region, from 4000–650 cm^{-1} . The spectra involve primarily vibrational modes within the organic moiety of each organometallic, since vibrations of bonds between fourth group metals and carbon fall in the far infrared for both alkyl [10] and aromatic [11] carbons.

The characteristic absorption bands for the organometallics are shown in Table 2. The other infrared absorption bands seen for these compounds were unremarkable

TABLE 2

CHARACTERISTIC VIBRATIONAL FREQUENCIES OF p -Me₃MC₆H₄X COMPOUNDS

M	X	Frequency (cm ⁻¹)		
		Symmetrical deformation $\delta_s(\text{CH}_3)$	Rock $\rho_r(\text{CH}_3)$	In-plane deformation $\beta(\text{C}_{\text{ar}}\text{H})$
Si	NO ₂	1245	830	1085
	CF ₃	1245	840	1080
	Br	1245	830	1065
	H	1240	830	1105
	F	1240	830	1090
	Me	1240	840	1100
	OMe	1240	840	1105
	OH	1245	835	1100
	SiMe ₃	1245	830	1080
Ge	OSiMe ₃	1245	830	1060
	NO ₂	1230	820	1075
	CF ₃	1235	820	1050
	Br	1230	815	1055
	H	1230	820	1090
	F	1230	820	1080
	Me	1225	815	1080
	OMe	1235	815	1085
	OH	1235	815	1080
Sn	GeMe ₃	1230	815	1045
	OSiMe ₃	1225	815	1065
	CF ₃	1190	775	1045
	Br	1185	775	1045
	H	1180	775	1070
	F	1185	775	1060
	Me	1180	785	1065
	OMe	1175	775	1065
	SnMe ₃	1180	775	1020
	OSiMe ₃	1165	765	1050

as there was little variation with change in the central metal atom. This included the stretching modes $\nu(\text{C}_{\text{ar}}\text{H})$ (3200–3000 cm⁻¹), $\nu(\text{C}_{\text{alk}}\text{H})$ (3200–2900 cm⁻¹), $\nu(\text{CC})$ (ca. 1590, 1490, 1380 cm⁻¹), and $\nu(\text{C}_{\text{ar}}\text{X})$ with various frequencies, as well as the out-of-plane deformation mode $\delta(\text{C}_{\text{ar}}\text{H})$ (740–725 cm⁻¹).

The characteristic bands shown in Table 2 can be attributed to absorption by either the alkyl or aryl portions of the organometallic. The first two modes listed refer to vibrations of the alkyl groups, and assignments have been made based upon those reported for tetramethyl-silicon, -germanium, and -tin [12–14]. The symmetrical deformation $\delta_s(\text{CH}_3)$ is a bending mode which appears at progressively lower frequencies as the mass and the electronegativity of the metal decrease; Si (1245–1240 cm⁻¹) > Ge (1235–1220 cm⁻¹) > Sn (1190–1165 cm⁻¹). The frequency of the rocking mode $\rho_r(\text{CH}_3)$ shows a similar relationship to the metal atom, with the frequencies of the bands decreasing in the sequence Si (840–830 cm⁻¹) > Ge (820–815 cm⁻¹) > Sn (785–765 cm⁻¹). As expected, the vibrational modes of these alkyl groups are effectively decoupled from the influence of the aromatic ring, and there is little change in the absorption frequencies on changing the substituent X.

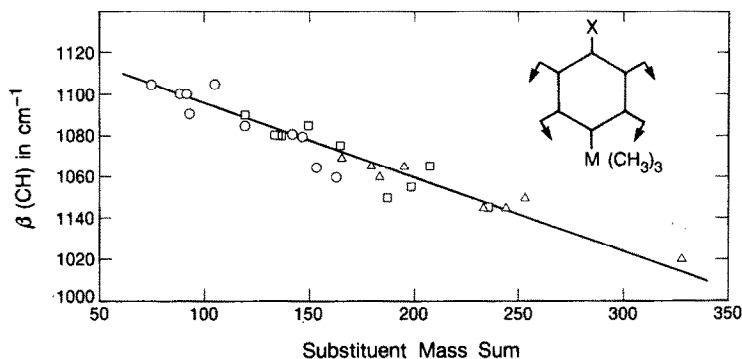


Fig. 1. Frequency of the in-plane deformation mode $\beta(\text{C}_{\text{ar}}\text{H})$ of *para*-substituted aryltrimethyl Group IVb organometallics as a function of substituent mass sum. $\circ$, $\text{M} = \text{Si}$; $\square$, $\text{M} = \text{Ge}$; $\triangle$, $\text{M} = \text{Sn}$.

The third characteristic absorption band for the organometallics shown in Table 2 involves the aromatic moiety. Assignments of vibrational bands of aromatic compounds are more complicated than those for the methyl groups. Substituted benzenes display thirty fundamental vibrations [15], and detailed assignments for *para*-substituted halobenzenes have been presented [16,17]. Among the vibrational modes of the latter compounds is the in-plane deformation $\beta(\text{C}_{\text{ar}}\text{H})$ ($1100\text{--}1040\text{ cm}^{-1}$) [16]. This mode involves mixing with other modes of the same symmetry class, making its frequency sensitive to the nature of the substituents on the aromatic ring. The $\beta(\text{C}_{\text{ar}}\text{H})$ mode of aryl derivations of fourth group has also been discussed by several groups [18–23].

As indicated in Table 2, the frequency of the in-plane deformation mode for the organometallics studied in this work ranged from $1105\text{--}1045\text{ cm}^{-1}$. The frequency tends to decrease in the order $\text{Si} > \text{Ge} > \text{Sn}$, but there is much overlap in the bands for the various organometallics. Previous reports have attributed such variation in $\beta(\text{C}_{\text{ar}}\text{H})$ frequencies to differences in the electronegativity of the aromatic substituents [18,23], but the frequencies shown in Table 2 are best correlated with the sum of the masses of the *para* substituents. As illustrated in Fig. 1, there is a regular decrease in the frequency of the $\beta(\text{C}_{\text{ar}}\text{H})$ mode as the substituent mass sum decreases, suggesting that there is an admixture of the C–X and C–M stretching modes with $\beta(\text{C}_{\text{ar}}\text{H})$. Although a closer correlation was found between substituent mass and the $\beta(\text{C}_{\text{ar}}\text{H})$ frequency of arenes containing monoatomic substituents, the linearity ($r=0.96$) of the data shown in Fig. 1 is noteworthy in view of the complexity of the substituent groups involved.

Mass spectroscopy

Electron-impact mass spectra have been reported for tetramethyl-silicon, -germanium, and -tin [26–28]. In addition, the fragmentation patterns of mixed phenylethyl-germanium and -tin compounds have been discussed [29,30], but such fragmentation pathways may be expected to differ from those for the compounds studied here owing to the ease of ethylene elimination and the consequent presence of decomposition products. The 70 eV mass spectra of the $\text{XC}_6\text{H}_4\text{MMe}_3$ compounds investigated in the present work are listed in Table 3, and to the author's

TABLE 3. MASS SPECTRA OF $p\text{-Me}_3\text{MC}_6\text{H}_4\text{X}$ COMPOUNDS

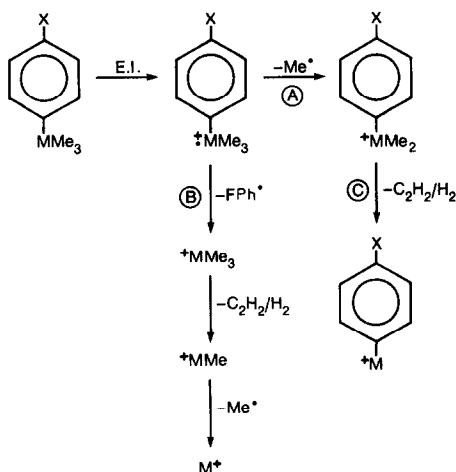
M	X	Major fragments (Relative intensities)
Si	NO_2	M^+ [195(8)]; $M-15$ [180/79(15/100)]
	CF_3	M^+ [218(3)]; $M-15$ [204/3(14/100)]
	Br	M^+ [230/28(12/12)]; $M-15$ [216/5/4/3(13/100/15/100)]
	H	M^+ [150(8)]; $M-15$ [136/5(13/100)]
	F	M^+ [168(8)]; $M-15$ [154/3(14/100)]
	Me	M^+ [164(10)]; $M-15$ [150/49(15/100)]
	OMe	M^+ [180(5)]; $M-15$ [166/5(15/100)]
	OH	M^+ [166(14)]; $M-15$ [152/1(14/100)]
	SiMe_3	M^+ [222(13)]; $M-15$ [209/8/7(20/43/100)]; SiMe_3 [73(47)]
	OSiMe_3	M^+ [239(19)]; $M-15$ [225/4/3(16/38/100)]; SiMe_3 [73(53)]
Ge	NO_2	M^+ [241(2)]; $M-15$ [220/218/6/4/210/6(27/15/100/36/83/68)]; $M-45$ [180/75/70(28/22/16)]
	CF_3	no M^+ ; $M-15$ [251/249/7/6/5(20/100/30/75/55)]; $M-45$ [219/7(15/10)]
	Br	M^+ [274(4)]; $M-15$ [261/0/259/8/7/5(70/18/100/17/73/30)]; $M-45$ [239(10)]
	H	M^+ [196(3)]; $M-15$ [183/1/0/179/7(20/100/25/75/55)]; $M-45$ [151/0/149(20/15/10)]
	F	M^+ [214(2)]; $M-15$ [201/199/8/7/5(15/70/20/55/40)]; $M-45$ [169/7/5(20/15/12)]; GeMe [95/3/2/1/89/7/5(22/83/17/74/100/13/32/23)]; Ge [75/3(18/13)]
	Me	M^+ [210(3)]; $M-15$ [197/5/4/3/1(20/100/25/75/55)]; $M-45$ [165/3(12/10)]
	OMe	M^+ [226(7)]; $M-15$ [213/1/0/209/7(20/100/27/75/55)]; $M-45$ [181(10)]
	OH	M^+ [212(14)]; $M-15$ [199/8/7/6/5/4/3(53/28/100/65/94/20/80)]; $M-45$ [167/6/5(47/33/34)]
	GeMe_3	M^+ [312/0(3/3)]; $M-15$ [301/0/299/8/7/6/5/4/3(26/18/78/40/100/36/96/25/52)]; $M-45$ [269/7/5(10/12/10)]; $M-75$ [240/237/4(17/12/10)]; GeMe_3 [119/7/5(18/12/10)]; GeMe_2 [105(12)]; GeMe [91/89/7/5(11/17/13/10)]
	OSiMe_3	M^+ [284/2/0(4/3/2)]; $M-15$ [271/0/269/8/7/6/4(26/22/100/36/78/15/60)]; $M-45$ [239/8(10/10)]; GeMe_3 [119/7(19/12)]; GeMe [89(14)]; SiMe_3 [73(56)]
Sn	CF_3	no M^+ ; $M-15$ [299/7/6/5/4/3/2/1(17/15/10/100/35/78/27/45)]; $M-45$ [265/3/1(33/23/14)]
	Br	no M^+ ; $M-15$ [309/7/6/5/4/3/2/1(13/62/20/100/28/62/13/27)]; $M-45$ [278/5/3(13/23/15)]
	H	no M^+ ; $M-15$ [231/229/7/6/5/4/3(17/15/100/33/75/27/45)]; $M-45$ [197/6/5/3(45/15/33/20)]
	F	no M^+ ; $M-15$ [245/3(27/21)]; $M-45$ [215/3(18/13)]; SnMe [139/8/7/6/5/4/3/2/1(100/22/78/22/88/14/35/10/22)]; Sn [120/119/8/7/6/5(7/18/43/14/24)]
	Me	M^+ [256(1)]; $M-15$ [245/3/1/0/239/8/7(15/12/100/30/73/25/40)]; $M-45$ [215/3/1/209/7(14/13/25/20/12)]
	OMe	M^+ [272/0(3/2)]; $M-15$ [262/0/258/7/6/5/4(17/13/100/35/75/25/43)]; $M-45$ [228/6/4/3(5/27/14)]
	SnMe_3	M^+ [403/2(1/1)]; $M-15$ [395/4/3/2/1/0/389/8/7/6/5/4/3(28/15/45/31/92/67/100/83/97/60/64/28/28)]; $M-45$ [361/0/359/8/7/6/5(19/12/23/16/22/12/12)]; $M-75$ [333/2/1/329/7/6/5(13/10/25/44/20/24/25)]; SnMe_3 [165/3(13/10)]; SnMe [135/4/3/0(33/11/25/16)]; Sn [120/119/7/5(22/10/17/10)]
	OSiMe_3	M^+ [330(3)]; $M-15$ [319/7/6/5/4/3/2/0(22/26/23/100/42/78/34/57)]; $M-45$ [285/3/2/0(22/11/18/11)]; SnMe_3 [165/3/1(22/16/10)]; SnMe_2 [150/148/6(10/28/10)]; SnMe [135/4/3(43/14/27)]; Sn [119/7(18/12)]; SiMe_3 [73(33)]

knowledge these have not previously been reported. For brevity, only peaks with intensities at least 10% that of the major fragment are listed.

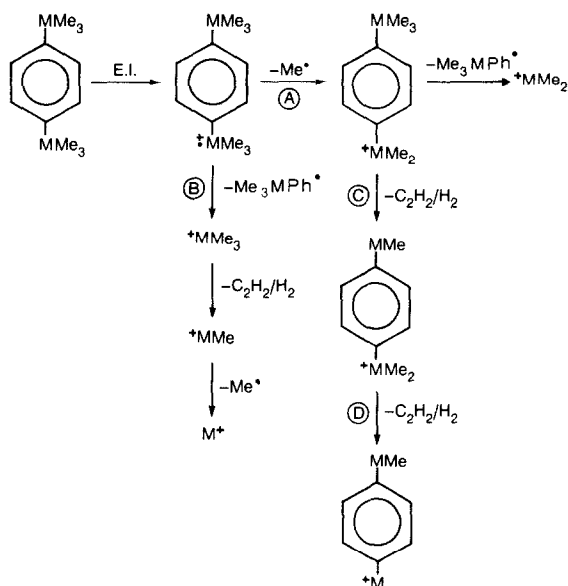
As can be seen from Table 3, the mass spectra of these organometallics are complicated by the isotopic distribution of the fourth group elements, with the number of isotopes increasing in the order $^{28,29,30}\text{Si} < ^{70,72,73,74,76}\text{Ge} < ^{112,116,117,118,119,120,122,124}\text{Sn}$. However, owing to the structural simplicity of these organometallics, trends in the decomposition patterns can be discerned.

The most general features of the results in Table 3 are the absence or near-absence of molecular ions and the lack of hydrocarbon fragment ions. Both of these facts can be attributed to the low ionization energies of the metals, which tend to localize the electron deficiency caused by electron impact on to the silicon, germanium, or tin atoms, and to the low carbon-metal bond energies, which favor loss of organic ligands from the central metal. As illustrated in Schemes 1-3, electron impact initially generates odd-electron molecular ions in which the positive charge is concentrated on the metal atom. Subsequent cleavages involve loss of neutral organic fragments, with the positive charge remaining on the metal-containing ion.

The decomposition behavior of the organometallics in which $\text{X} = \text{NO}_2$, CF_3 , Br , H , F , CH_3 , OCH_3 , and OH are summarized in Scheme 1. In keeping with the odd-even rules developed for organic mass spectra [31], the odd-electron molecular ion decomposes by elimination of a neutral odd-electron fragment to yield an even-electron ion. The electronic delocalization properties of the aromatic ring and the higher phenyl-metal bond energies ($\text{Si/Ge/Sn} = 84/74/62 \text{ kcal mol}^{-1}$ [32]) relative to those for the methyl carbon-metal bond ($\text{Si/Ge/Sn} = 77/62/54 \text{ kcal mol}^{-1}$ [32]) generally favor loss of an odd-electron fragment (step A) over the loss of an aryl radical from the molecular ion. Exceptions to this generalization are found when $\text{X} = \text{F}$ and $\text{M} = \text{Ge}$ or Sn , for which loss of the fluorophenyl radical (step B) is apparently preferred due to hyperconjugative stabilization of the neutral fragment by the aromatic fluoro substituent. For the majority of the arenes,



SCHEME 1

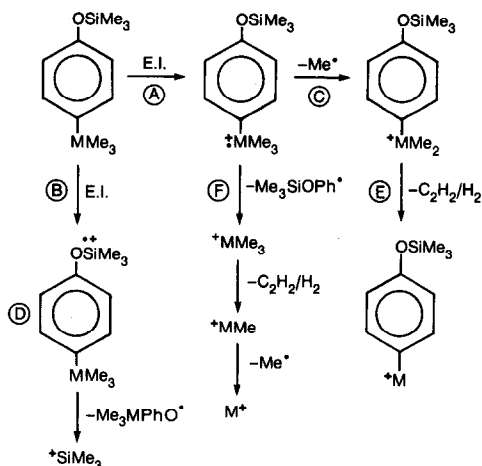


SCHEME 2

however, decomposition is via step A, to generate an even-electron aryldimethylmetallic ion, which can further decompose by heterolytic bond cleavage and elimination of neutral even-electron fragments [31]. Elimination of the even-electron ethylene and molecular hydrogen (step C) is not favored by organosilicon compounds owing to the relatively high carbon–silicon bond energy, and $M - 45$ ions are seen only for germanium and tin organometallics. The prevalence of $M - 15$ and $M - 45$, but not $M - 30$, ions for these compounds indicates that the odd-even rules for the decomposition of organic ions is also applicable to compounds containing metallic members of the carbon group.

The presence of two metal atoms on the aromatic ring complicates the decomposition pattern, as illustrated in Scheme 2 for the *p*-bis(trimethylmetallo)benzenes. Loss of a methyl radical (step A) predominates, but elimination of the trimethylmetallophenyl radical to generate alkylmetallic ions (step B) is also significant for all three organometallics. The relatively weak methyl–germanium and –tin bonds permit further fragmentation of the trimethylmetallic ions initially generated. For the organo-germanium and -tin compounds which decompose via step A, the presence of a second aromatic trimethylmetal substituent conjugated with the charged metal also leads to the loss of methyl groups from both metal atoms, which accounts for the appearance of $M - 75$ (step D) as well as $M - 45$ (step C) ions.

In the case of the compounds $p\text{-Me}_3\text{MC}_6\text{H}_4\text{OSiMe}_3$, as shown in Scheme 3 resonance between the metal atoms is not a predominant factor, and separate decomposition products result from initial ionization at the aromatic metal atom (step A) or the ether silicon atom (step B). Step A, with subsequent loss of methyl radical (step C) predominates, but step B, which is followed by homolytic cleavage of the silyl ether bond to generate the trimethylsilicon ion is also a major fragmentation pathway for all three organometallics. As in the other schemes, the relatively



SCHEME 3

labile carbon–germanium and –tin bonds make possible the formation of $M - 45$ fragment ions (step E) and the trimethylmetal–ions (step F), the latter preceding the formation of smaller molecular weight species.

The results are consistent with those for the fragmentation of tetraalkyl and mixed arylalkyl derivatives of silicon, germanium, or tin, which have been comprehensively discussed elsewhere [27–30]. For both types of organometallic compounds the relative intensities of the parent ions are very low, and the fragmentation patterns indicate dominance of the ion current by the metal-containing species, which are generally even-electron ions.

Experimental

General

All the compounds used were of reagent grade and the solvents employed were of analytical quality purchased from Merck. Elemental analyses were performed by the Mikroanalytisches Labor Pascher (Bonn). Melting points were determined in open capillary tubes on a Mettler FP-61 melting point apparatus and were corrected. Refractive indices were measured on a Zeiss Model 44007 refractometer linked to a thermostatically-controlled water bath.

Instrumental analyses

Infrared spectra were recorded with a carefully-calibrated Perkin–Elmer Model 257 spectrophotometer. The spectra were obtained in the sodium chloride region by use of KBr disks for solid compounds and neat liquid films for liquid organometallics.

Mass spectra were obtained with an AEI MS-30/74 mass spectrometer operated at 70 eV. The source temperature was 220°C. Liquid samples were introduced directly without heating, whereas solid samples were heated to a temperature of not more than 100°C. Data acquisition and manipulation were performed with a Kratos DS-55 data system.

Proton NMR spectra were recorded with a Bruker WP-80 high resolution NMR spectrometer. Samples were dissolved in acetone- d_6 , and proton chemical shifts are relative to internal tetramethylsilane.

Preparation of compounds

Three methods were used for the preparation of the organometallics listed in Table 1. For the majority of the compounds tabulated ($X = CF_3$, Br, H, F, Me, OMe), the *para*-substituted aryltrimethylmetal compound was synthesized from the Grignard reagent of the corresponding *para*-brominated arene. The conditions used were identical for the three metal types. In a typical procedure, the Grignard compound was prepared by dropwise addition of a solution of *p*-bromotoluene (17.1 g, 0.1 mol) in 50 ml dry tetrahydrofuran to magnesium metal (2.7 g, 0.11 mol), with initiation by 0.5 ml methyl iodide. After 2 h stirring at 25°C under dry argon, a solution of trimethylgermanium chloride (15.3 g, 0.1 mol) in 50 ml dry tetrahydrofuran was added dropwise, and the mixture was refluxed for 2 h. The mixture was then cooled and treated with 5% aqueous ammonium chloride, and the organic products extracted into dichloromethane. The extract was washed with water, then dried (Na_2SO_4). Fractionation gave pure *p*-tolyltrimethylgermanium (16.1 g, 75%). B.p. 71.9°C/9 mmHg, n_D^{25} 1.0541, d^{25} 1.0904. Analysis. Found: C, 57.5; H, 7.7. $C_{10}H_{16}Ge$ calcd.: C, 57.6; H, 7.7%. IR (neat): 3090–2990, 2960, 2890, 1225, 1080, 815, 790, 760 cm^{-1} . 1H NMR (acetone- d_6): δ 0.30 (s, 9H); 2.31 (s, 3H); 7.33 ppm (dd, J 11 and 8 Hz, 4H). MS: $m/e = 210$ (M^+).

The preparation of the (*p*-nitrophenyl)trimethylmetal compounds are listed in Table 1 required the two-step synthesis described earlier [5,6]. Whereas nitration of the silyl and germyl derivatives resulted in the *p*-nitrophenyl analogues, treatment of the bis(trimethylstannyl)benzene compound with nitric acid gave only benzene. For the representative case with $M = Ge$, *p*-bis(trimethylgermyl)benzene was prepared in 52% yield from *p*-dibromobenzene via the Grignard compound as described above. M.p. 95.6°C. Elemental analysis. Found: C, 46.1; H, 7.2. $C_{12}H_{22}Ge_2$ calcd.: C, 46.3; H, 7.1%. IR (KBr): 3000–2880, 1380, 1230, 1045, 815, 800 cm^{-1} . 1H NMR (acetone- d_6): δ 0.30 (s, 18H); 7.56 ppm (s, 4H). MS: $m/e = 312/310$ (M^+). Treatment of the *p*-bis(trimethylgermyl)benzene with nitric acid [5,6] gave a 62% yield of (*p*-nitrophenyl)trimethylgermanium, m.p. 45.5°C. Analysis. Found: C, 44.9; H, 5.5. $C_9H_{14}GeNO_2$ calcd.: C, 45.1; H, 5.5%. IR (KBr): 3080–3020, 1590, 1510, 1345, 1230, 1075, 820, 740, 715 cm^{-1} . 1H NMR (acetone- d_6): δ 0.42 (s, 9H); 8.19 ppm (dd, J 35 and 9 Hz, 4H). MS: $m/e = 241$ (M^+).

Synthesis of the (*p*-hydroxyphenyl)trimethylmetal compounds was by the multi-step procedure previously used for $M = Si$ [8]. The synthesis of (*p*-hydroxyphenyl)trimethylsilicon and -germanium was successful, but treatment of (*p*-trimethylsiloxyphenyl)trimethyltin with hydrochloric acid gave only phenol. For $M = Ge$, use of the Grignard reagent made from *p*-bromophenoxytrimethylsilicon [8] gave an 82% yield of (*p*-trimethylsiloxyphenyl)trimethylgermanium. B.p. 127°C, n_D^{25} 1.4962, d^{25} 1.0430. Elemental analysis. Found: C, 51.1; H, 7.9. $C_{12}H_{22}GeOSi$ calcd.: C, 50.9; H, 7.8%. IR (neat): 3000–2880, 1585, 1490, 1255, 1225, 1065, 900, 835, 815 cm^{-1} . 1H NMR (acetone- d_6): δ 0.24 (s, 9H); 0.34 (s, 9H); 7.40 ppm (dd, J 33 and 8 Hz, 4H). MS: $m/e = 284/282/280$ (M^+). The hydroxyl group was liberated as previously described [8] to give (*p*-hydroxyphenyl)trimethylgermanium in 51% yield. M.p. 77.9°C. IR (KBr): 3100, 2980, 2900, 1585, 1500, 1420, 1250,

1235, 1080, 815, 760 cm^{-1} . ^1H NMR (acetone- d_6): δ 0.25 (s, 9H); 7.04 ppm (dd, J 30 and 9 Hz, 4 H). MS: $m/e = 212$ (M^{+}).

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