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Gas phase alkylation of phenyltrimethylgermanes

Barbara Chiavarino, Maria Elisa Crestoni, Simonetta Fornarini *

Dipartimento di Studi di Chimica e Tecnologia delle Sostanze Biologicamente Attive, Università di Roma 'La Sapienza', P.le A. Moro 5, Roma I-00185, Italy

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Abstract

The reaction of $\text{Me}_3\text{GeC}_6\text{H}_5$ and $\text{Me}_3\text{GeC}_6\text{H}_4\text{Me}$ with Me_2CH^+ , Me_3C^+ , and Me_2Cl^+ has been studied in the gas phase at pressures spanning from 1 Torr (chemical ionization mass spectrometry) to 1 atm (radiolytic technique). The reactions conform to the general model of electrophilic aromatic substitution reactions, proceeding via σ -complex intermediates, which show a tendency to isomerize to arenium ions bearing a proton on the germylated carbon. Such 1,2-H shift processes occur in the time scale of 10^{-8} s. The fate of the germylated arenium ions is controlled by competing deprotonation and degermylation reactions showing a behavior similar to their silicon analogues. The Me_3X (X = Si, Ge) groups are seen to show a comparable electronic effect with regard to electrophilic attack at the unsubstituted ring positions of an attached phenyl group. © 1997 Elsevier Science B.V.

Keywords: Phenyltrimethylgermanes; Gas phase; Alkylation; σ -complexes; Radiolysis

1. Introduction

Whereas the gas phase ion chemistry of silicon containing ionic and neutral species has been extensively investigated [1–3], germanium containing species have received comparatively little attention [4–10]. The gas phase silylation of trimethylgermylbenzene (TGB) by Me_3Si^+ ions has been the topic of a recent study aimed to obtain aromatic silylation products via Me_3Ge^+ displacement [11]. The overall reactivity pattern was found consistent with a mechanistic scheme (Scheme 1) characterized by the following major features: (i) the reaction proceeds by Me_3Si^+ attack at either unsubstituted or germyl-substituted carbon to yield σ -complex intermediates **1a** and **1b**, respectively; (ii) **1a** may evolve to silylated products by deprotonation by a strong nitrogen base; in its absence, ubiquitous water or other nucleophiles will remove the Me_3Si^+ group, a well known behavior of silylated arenium ions [12,13]; (iii) *ipso*-type complex **1b** undergoes efficient nucleophilic degermylation giving high yields of $\text{Me}_3\text{SiC}_6\text{H}_5$; (iv) ions **1a** do not display any tendency to undergo 1,2-proton shift from the silylated to an adjacent carbon. The last feature

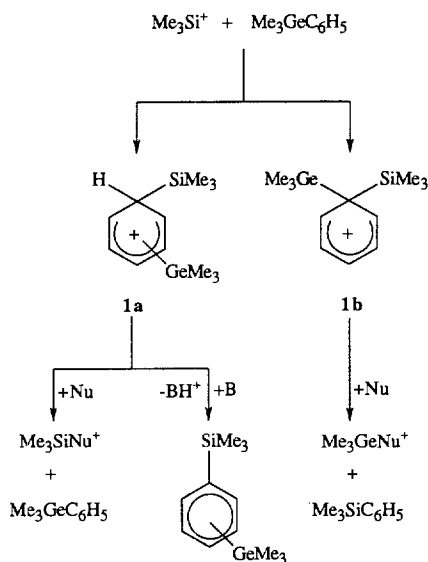
is ascribed to the enhanced basicity conferred by the Me_3Si group to the *ipso*-carbon (ca. 20 kcal mol⁻¹ greater than that of a benzene carbon) [14–16]. As the silylation reaction of TGB is directed to a great extent by the strong electronic effects of the Me_3Si group on the arenium ring [17], it appeared desirable to generalize the behavior of TGB towards typical carbon electrophiles. Our study reports on the reaction of naked carbenium ions, Me_2CH^+ and Me_3C^+ , and of the methylating agent Me_2Cl^+ , performed either at ca. 1 Torr in chemical ionization mass spectrometry (CI-MS) [18] or at ca. 1 atm, by using the radiolytic technique [19–21].

2. Experimental section

2.1. Materials

Propane, *i*-butane, methyl chloride and oxygen were high-purity (> 99.9 mol%) gases from Matheson. The chemicals were purchased from Aldrich Chemical except $\text{Me}_3\text{GeC}_6\text{H}_5$ which was obtained from Alfa Products. Alkylation products of TGB to be used as reagents or GLC-MS standards were prepared from the reaction of Me_3GeBr with the Grignard reagent of the appropriate aryl bromide. They were purified by preparative

* Corresponding author.



GLC using a 4-m long, 4-mm i.d. stainless steel column, packed with 5% Carbowax 20 M-KOH (2%) on Supelcoport. Their identity was verified by NMR spectrometry and MS.

2.2. Mass spectrometric experiments

Mass spectra were recorded on a Hewlett-Packard 5989B quadrupole instrument operated in the CI mode, at a source temperature of 200°C. The reactant gas pressure of 1.3–1.7 Torr was measured by a thermal conductivity gauge.

2.3. Radiolytic experiments

The gaseous mixtures were prepared by conventional vacuum line techniques. Pyrex vessels (135 ml) were thoroughly outgassed and filled with the gaseous components in the selected ratio. Liquid components were already present in the vessel, each weighted within a fragile glass ampoule. The vessels were sealed and the homogeneous mixture of gases and vapours was submitted to γ -irradiation at 40°C in a 220 Gammacell from Nuclear Canada for 2 h at the dose rate of 10^4 Gy h⁻¹. The radiolytic products were extracted by freezing the vessel at 77 K and careful washing of its inner surface with ethyl acetate. The final solution, containing the unreacted substrate as major component (conversion into products is kept within ca. 1%) was analyzed by GC-MS using a Hewlett Packard 5890A gas chromatograph equipped with a Model 5970B mass selective detector.

The following columns were used: (i) a 100 m long, 0.32-mm i.d. Petrocol DH fused silica capillary column; (ii) a 50 m long, 0.32-mm i.d. PONA fused silica capillary column.

The radiolytic products were identified by comparisons of their retention times and EI mass spectra with those of authentic samples under the same operating conditions. Their yields were determined from the areas of the corresponding elution peaks using the internal standard calibration method. Blank experiments were performed to exclude any thermal contribution to the products of interest. To this end, gaseous mixtures, identical to the radiolytic specimens, were submitted to the same experimental procedure except for the γ -irradiation.

3. Results and discussion

3.1. Ionic reagents

Propane, *i*-butane and MeCl are well known CI reagents [18], used as source of Me₂CH⁺, Me₃C⁺ and Me₂Cl⁺ ions. Their formation follows from a sequence of EI ionization, fragmentation and ion–molecule reactions of the fragment ions with the bulk neutral. The same sequence of events accounts for the formation of the reactant ions in the radiolytic systems [19–21]. The major difference between the two routes to the selected reagent ions lies in the pressure of their gaseous environment. The nearly atmospheric pressure of the radiolytic experiments, ca. 10³ times higher than CI-MS, ensures fast thermalisation of excited ions, typically formed by high energy or highly exothermic processes, by unreactive collisions with the bulk gas. The same collisional quenching process may affect the ensuing ionic intermediates and product ions. Finally, the relatively high neutral concentration favours the association of the reactant ions to their neutral precursors [22] decreasing the exothermicity of their attack to the selected substrates by an amount equal to the corresponding binding energies.

3.2. Chemical ionization of TGB by Me₂CH⁺, Me₃C⁺ and Me₂Cl⁺ ions

CI mass spectra of TGB have been recorded using propane, *i*-butane and MeCl as the reactant gas. The spectra are shown in Figs. 1 and 2 and are summarized in Table 1. Germanium-containing ions are characterized by a cluster of peaks with relative intensities reflecting the isotopic abundancies of the germanium isotopes. In order to avoid direct ionization of TGB and to obtain clear information on the ionic products from the CI reagent ion, the concentration of TGB was kept below 1% with respect to the CI reagent gas, which accounts for the small relative intensities of the product ions.

In all cases, the major ion detected is Me₃Ge⁺, which cannot arise by direct ionization of TGB. The EI

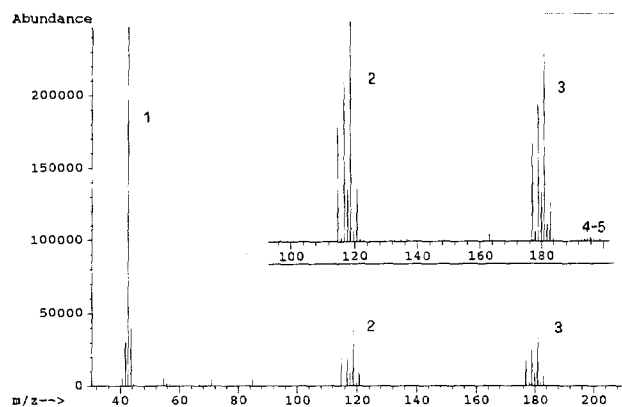
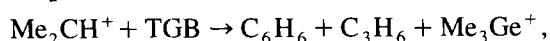
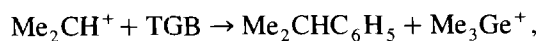


Fig. 1. C_3H_8 —Cl mass spectrum of TGB (M): (1) $C_3H_7^+$; (2) Me_3Ge^+ ; (3) $(M-CH_3)^+$; (4) M^+ ; (5) $(M+H)^+$.

mass spectrum of TGB is in fact dominated by the comparably abundant molecular ion (M^+) and a fragment ion deriving by methyl loss from the molecular ion ($[M-Me]^+$). The negligible intensity of M^+ in the CI mass spectra disproves any significant contribution of a direct ionization process, highly unlikely in the presence of the almost unperturbed reactant ion signal. Its formation in the propane and *i*-butane CI may instead be assigned to Me_3Ge^+ cleavage activated by protonation or alkylation of TGB, which is supported by the presence of minute but detectable signals corresponding to $[TGB+H]^+$. In addition to free Me_3Ge^+ and its MeCl adduct, the MeCl-CI mass spectrum of TGB shows a significant $[C_7H_7]^+$ ion which is indicative of methylation at the aromatic ring by the reactant Me_2Cl^+ ion probably followed by hydride transfer to form $[C_7H_7]^+$ and Me_3GeH as neutral fragment. The Me_3Ge^+ cleavage is thermodynamically allowed, as exemplified by the estimated thermochemistry of the Me_2CH^+ reactions shown in Eqs. (1) and (2) [23].¹

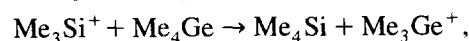


$$\Delta H^\circ = -7 \text{ kcal mol}^{-1} \quad (1)$$



$$\Delta H^\circ = -31 \text{ kcal mol}^{-1} \quad (2)$$

We may notice, from the enthalpy change of reaction Eq. (3) [24] that the formation of Me_3Ge^+ is somewhat favoured with respect to Me_3Si^+ and that the C_3H_8 /CI of TGB closely reproduces the behavior of $MeC_6H_4SiMe_3$ under similar CI conditions [25].



$$\Delta H^\circ = -10.2 \text{ kcal mol}^{-1} \quad (3)$$

¹ Thermochemical data for ions and neutrals were taken from Ref. [16]. $\Delta H_f^\circ(Me_3GeC_6H_5)$ was estimated as 8 kcal mol^{-1} by the group increment method.

3.3. Radiolytic reactions of TGB and trimethylgermyltoluenes

In the radiolytic systems the reagent ions were let to react with the selected substrates in the presence of O_2 , an alkyl radical scavenger, and of basic additives. Table 2 shows the system compositions and the relative and absolute yields of products. The % distributions are affected by a $\pm 3\%$ error whereas the absolute radiochemical yields (G_M values, $\pm 20\%$ error) reflect the uncertainty of the γ -cell dosimetry. Their trend, however is significant, decreasing with increasing concentration of basic additives. This fact suggests that the observed products are of ionic origin, reactive radicals being intercepted by O_2 , in excess concentration with respect to the substrate. The basic additives were chosen so as to have a proton affinity (PA) close to or higher than the reaction products. PA values ($[16]$, kcal mol^{-1}) are the following: Et_3N , 232.3; *c*- $C_5H_{10}NH$, 226.4; $(MeO)_3PO$, 212.0; TGB, ca. 212; the latter value, estimated by us, regards protonation at the germylated carbon, the thermodynamically favoured protonation site [26]. Table 2 includes some representative silylated substrates for comparison purposes.

The radiolysis products include isopropylation products and proto- and alkyldegermylation (henceforth referred to as proto- or alkyldegermylation) products (C_6H_6 and $Me_2CHC_6H_5$ from TGB, respectively). The combined information from the C_3H_8 -CI mass spectra and the radiolytic product pattern conform to the general mechanism for gas phase electrophilic aromatic substitution reactions by carbenium ions [19]. Me_2CH^+ ions are known to behave as both Brønsted and Lewis acids towards arenes [27] to give σ -complex intermediates excited by the considerable exothermicity of their formation process. Eq. (4) illustrates the

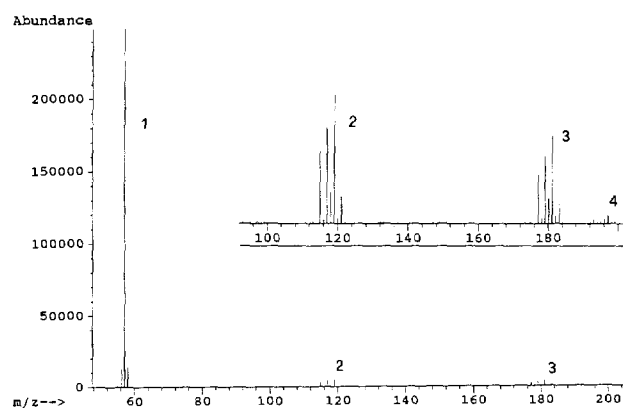


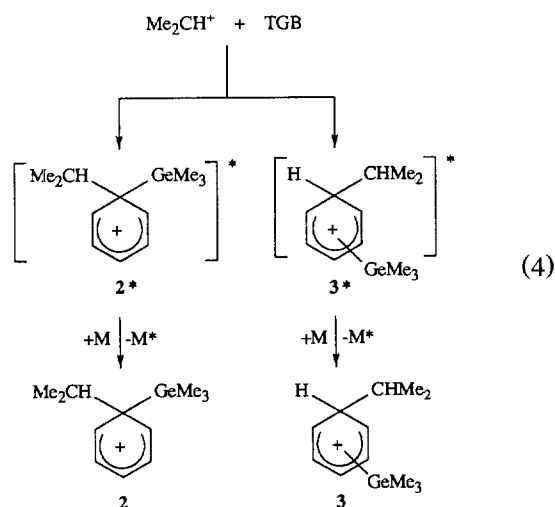
Fig. 2. *i*- C_4H_{10} —Cl mass spectrum of TGB (M): (1) Me_3C^+ ; (2) Me_3Ge^+ ; (3) $(M-CH_3)^+$; (4) $(M+H)^+$.

Table 1
CI mass spectra of TGB^a

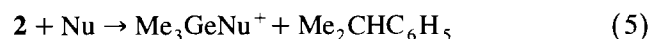
Reactant gas: C ₃ H ₈	C ₃ H ₇ ⁺ : 10.000; Me ₃ Ge ⁺ : 2300; (M-CH ₃) ⁺ : 2000; M ⁺ : 29; (M + H) ⁺ : 23
Reactant gas: <i>i</i> -C ₄ H ₁₀	Me ₃ C ⁺ : 10.000; Me ₃ Ge ⁺ : 530; (M-CH ₃) ⁺ : 390; M ⁺ : 12; (M + H) ⁺ : 34
Reactant gas: MeCl	Me ₂ Cl ⁺ : 10.000; C ₇ H ₇ ⁺ : 230; Me ₃ Ge ⁺ : 360; [MeCl + Me ₃ Ge ⁺]: 230; (M-CH ₃) ⁺ : 250

^a Ion intensities are normalized to the CI reagent ion taken as 10 000.

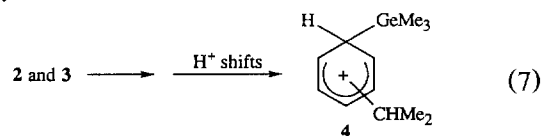
Me₂CH⁺ addition reaction, a similar scheme applying to the protonation route.



to the dominant Me₃Ge⁺ loss observed under CI conditions. At the high pressure of the radiolytic experiments the high frequency of unreactive collisions allows fast thermalisation with the bulk gas to give ground state **2** and **3**. Intermediates **2** and **3** are expected to undergo degermylation assisted by nucleophiles and deprotonation by strong bases, respectively (Eqs. (5) and (6)).



Furthermore, **2** and **3** may undergo thermal rearrangement into the conceivably most stable arenium isomers, namely those bearing a proton on the germylated carbon (Eq. (7)).



The excess energy content of **2**^{*} and **3**^{*} may promote isomerization and fragmentation processes leading

This is consistent with several pieces of information:
(i) previous studies pointed to the enhanced basicity of

Table 2
Gas-phase alkylation of arylgermanes and arylsilanes (XC₆H₄YMe₃; X = H, Me; Y = Si, Ge)

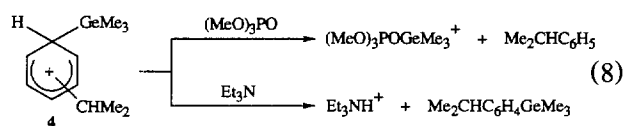
Ionic Reactant	System Composition (Torr) ^a		Product distribution (%)			G _M ^b	
	Substrate	Additives	C ₆ H ₅ X	RC ₆ H ₄ X(o/m/p, when X = Me)	RC ₆ H ₃ (YMe ₃)X(o/m/p, when X = H)		
Me ₂ CH ⁺ = R ⁺	X = H, Y = Ge (1.3)	—	17	55	28(2/68/30)	2.1	
	X = H, Y = Ge (1.3)	Et ₃ N(0.78)	17	38	45(2/69/29)	1.1	
	X = H, Y = Ge (1.3)	Et ₃ N(1.1)	10	36	54(2/68/30)	1.0	
	X = H, Y = Ge (1.5)	Et ₃ N(2.3)	6	30	65(3/65/32)	0.85	
	X = H, Y = Ge (1.2)	Et ₃ N(6.5)	5	26	69(4/62/31)	0.40	
	X = H, Y = Ge (1.5)	(MeO) ₃ PO(0.68)	7	67	26(3/79/18)	1.3	
	X = H, Y = Ge (1.3)	(MeO) ₃ PO(0.95)	7	58	35(3/77/20)	1.0	
	X = H, Y = Ge (1.6)	(MeO) ₃ PO(2.2)	5	47	48(2/74/24)	0.64	
	X = <i>p</i> -Me, Y = Ge (1.0)	Et ₃ N(0.42)	22	42(40/40/20)	36(2 isomers: 93/7)	1.4	
	X = H, Y = Si (0.70)	Et ₃ N(0.77)	16	42	42(2/53/45)	1.21	
	X = <i>p</i> -Me, Y = Si (1.0)	Et ₃ N(0.38)	43	45(51/33/16)	12(1 isomer)	1.75	
	Me ₃ C ⁺ = R ⁺	X = <i>o</i> -Me, Y = Ge (2.0)	<i>c</i> -C ₅ H ₁₀ NH(0.44)	≤ 10	41(0/10/100)	49(2 isomers: 60/40)	0.70
		X = <i>m</i> -Me, Y = Ge (1.9)	<i>c</i> -C ₅ H ₁₀ NH(0.40)	≤ 10	20(0/100/0)	70(1 isomer)	0.59
X = <i>p</i> -Me, Y = Ge (2.0)		<i>c</i> -C ₅ H ₁₀ NH(0.40)	40	54(0/0/100)	6(2 isomers: 80/20)	0.39	
X = <i>o</i> -Me, Y = Si (2.0)		<i>c</i> -C ₅ H ₁₀ NH(0.38)	≤ 7	46(0/5/95)	47(2 isomers: 60/40)	0.86	
Me ₂ Cl ⁺ , R = Me	X = H, Y = Ge (2.5)	—	—	80	20(25/47/28)	0.010	
	X = <i>p</i> -Me, Y = Ge (1.5)	Et ₃ N(0.48)	—	50(40/40/20)	50(2 isomers: 66/44)	0.015	
	X = <i>p</i> -Me, Y = Si (1.4)	Et ₃ N(0.45)	—	50(47/35/18)	50(2 isomers: 93/7)	0.011	

^aAll systems contain 600–700 Torr of a bulk gas (C₃H₈ to form Me₂CH⁺, *i*-C₄H₁₀ to form Me₃C⁺, and MeCl to form Me₂Cl⁺) to which 10 Torr O₂ were added as alkyl radical scavenger.

^bAbsolute radiochemical yields (G_M) are in units of 10⁻¹ μmol J⁻¹.

the ring carbon bearing a Me_3Si group [28,29] ascribed to hyperconjugative stabilization of the formal β positive charge by the $\text{C}_{\text{aryl}}-\text{Si}$ bond; (ii) the comparable or even greater β -effect of the $\text{C}-\text{Ge}$ bond [30–32]; (iii) the well known tendency of alkylated arenium ions to undergo 1,2- H^+ shifts [33,34]. Arenium ions **4** are expected to undergo an easy degermylation process promoted by oxygen nucleophiles, either purposely introduced in the radiolytic mixture ($(\text{MeO})_3\text{PO}$) or formed by its radiolysis (e.g. H_2O), in competition with deprotonation by strong nitrogen bases [11].

The foregoing arguments provide a neat explanation for the trends of alkylation and alkyldegermylation relative yields as a function of the amount of added Et_3N or $(\text{MeO})_3\text{PO}$. At increasing concentration of both additives the relative yield of alkylation products increases, which is consistent with the faster deprotonation of a larger fraction of **3** not yet isomerized to **4**. However, other factors being equal, the presence of $(\text{MeO})_3\text{PO}$, in the place of Et_3N , enhances the alkyldegermylation at the expense of the alkylation process. This is again consistent with the proposed scheme, since any **4** formed will react with Et_3N by preferential H^+ transfer and with $(\text{MeO})_3\text{PO}$ by Me_3Ge^+ transfer (Eq. (8)).



This is clearly illustrated in Fig. 3 where the relative distribution of alkylation and alkyldegermylation products is plotted versus the average lifetime of the arenium ions determined by the first reactive collision with the additive. The rate constants for collision of the arenium ions with Et_3N and $(\text{MeO})_3\text{PO}$, assumed to be reactive in 100% of the events, were calculated by the ADO theory [35]. If the role of the *ipso* complex **2** to

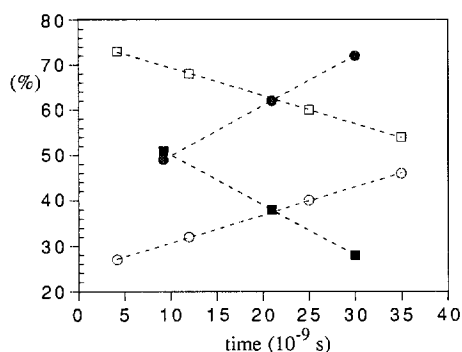


Fig. 3. Relative yields (normalized to 100%) of $\text{Me}_2\text{CHC}_6\text{H}_5$ (O, ●) and $\text{Me}_2\text{CHC}_6\text{H}_4\text{GeMe}_3$ (□, ■) plotted as a function of the average lifetime of the arenium intermediates, determined by the collision interval with the additive (blank symbols: Et_3N ; full symbols: $(\text{MeO})_3\text{PO}$). Data are taken from the experiments illustrated in Table 2.

the formation of products is neglected, the difference in relative yield between $\text{Me}_2\text{CHC}_6\text{H}_5$ and $\text{Me}_2\text{CHC}_6\text{H}_4\text{GeMe}_3$ formed in $(\text{MeO})_3\text{PO}$ and Et_3N for the same lifetime of the intermediate arenium ions can be related to the fraction of **4** present in the isomeric arenium ions mixture. For example, the ions intercepted at 1×10^{-8} s contain a ca. 20% contribution of isomer **4** which becomes ca. 30% at 2×10^{-8} s.

In order to obtain information on the relative extent of Me_2CH^+ attack at a germylated aromatic carbon, the reaction of *p*-trimethylgermyltoluene (*p*-TGT) was examined. As shown by the data in Table 1, only 20% of the alkyldegermylation products is given by *p*- $\text{Me}_2\text{CHC}_6\text{H}_4\text{Me}$, in spite of the para directing effect of the methyl group. The situation is different in the Me_3C^+ reaction where the entering Me_3C group retains almost completely the original position of the leaving Me_3Ge group in the alkyldegermylation products of *p*-TGT. This result may reflect either an intrinsic selectivity of Me_3C^+ (a much milder electrophile than Me_2CH^+) towards the germylated carbon or the restraint of the Me_3C group from attaining an ortho relationship with the Me or Me_3Ge group. The second factor seems to be the major one. This is suggested both by the negligible yield of alkylation products from *p*-TGT and by the product pattern from *o*-TGT showing instead a large extent of alkylation products and predominant formation of *p*- $\text{MeC}_6\text{H}_4\text{CMe}_3$ as alkyldegermylation product.

Me_2Cl^+ ions behave exclusively as methylating agents by a methyl transfer process involving irreversible MeCl displacement by the arene molecule [36]. Accordingly, no protodegermylation products are formed. However, the methylation process is followed by extensive degermylation which may be due either to significant *ipso* attack or to fast isomerization by H^+ -shift following attack at an unsubstituted carbon, both ending in degermylation. The statistical distribution of methyldegermylation products from *p*-TGT lends support to the second hypothesis.

The irreversible character of the methylation process, known to involve a remarkable activation barrier [37,38], which can not be accompanied by possibly undetectable reaction channels such as proton transfer processes, suggests its use to establish a relative reactivity order. *p*-Xylene was chosen as reference substrate, in view of the fact that both benzene and toluene are unreactive towards Me_2Cl^+ under radiolytic conditions [36]. Competition experiments yielded the relative reactivity values listed in Table 3. The reactivity of TGB is found to be intermediate between *p*-xylene and toluene (unreactive) and twice as high as that of its silicon analogue, $\text{Me}_3\text{SiC}_6\text{H}_5$. This result may appear in contrast with the higher proton affinity of $\text{Me}_3\text{GeC}_6\text{H}_5$ (ca. 212 kcal mol^{-1} [26]) with respect to that of *p*-xylene, equal to 192 kcal mol^{-1} [16]. However, it should be noted that

Table 3
Relative reactivities of gaseous Me_2Cl^+ ions with arylgermanes and arylsilanes

Substrate (S)	k_S/k_{xyl}^a
$\text{C}_6\text{H}_5\text{GeMe}_3$	0.37
$p\text{-MeC}_6\text{H}_4\text{GeMe}_3$	0.63
$\text{C}_6\text{H}_5\text{SiMe}_3$	0.16 ^b
$\text{C}_6\text{H}_5\text{CH}_2\text{SiMe}_3$	3.6 ^b

^a Values derived from competing reactions of S and xyl (*p*-xylene- d_{10}) for the gaseous electrophile. The standard equation $k_S/k_{\text{xyl}} = ([\text{P}_S]/[\text{P}_{\text{xyl}}]) \times ([\text{xyl}]/[\text{S}])$ where P_S and P_{xyl} are the overall methylated products of S and xylene, respectively.

^b Ref. [39].

the favoured protonation site, the *ipso*-carbon, allows the greatest hyperconjugative stabilization by the Me_3X (X = Si, Ge) group [30–32]. On the other hand, the methylation reaction is directed only to a minor extent to the Me_3X substituted (*ipso*) carbon, as evidenced not only by the *p*-TGT reaction but also by the *p*- $\text{MeC}_6\text{H}_4\text{SiMe}_3$ reaction also reported in Table 1. In conclusion, the Me_2Cl^+ electrophile does not react appreciably at the *ipso*-carbon of TGB, *p*-TGB and their silicon analogues, probably due to steric hindrance in a tight transition state, and its reactivity at unsubstituted ring positions shows that the electronic effect of the Me_3Ge and Me_3Si group is similar and comparable to that of a methyl group. The last compound included in Table 3, $\text{C}_6\text{H}_5\text{CH}_2\text{SiMe}_3$, shows a remarkably higher reactivity towards Me_2Cl^+ , due to the fact that methylation at the ortho/para unsubstituted ring positions may benefit from the $\text{CH}_2\text{-Si}$ bond hyperconjugation [11,17,30].

The similar reactivity of TGB and its silicon analogue towards Me_2Cl^+ is paralleled by the closely similar product pattern from the Me_2CH^+ , Me_3C^+ and Me_2Cl^+ reactions with TGB and *p*-TGT and their silicon counterparts. These results legitimate the use of the known reactivity behaviour of silicon compounds to model that of the germanium analogues and points to the similar effect of the two Me_3X (X = Ge, Si) groups in directing the reactivity of the aromatic ring to which they are bound.

4. Conclusions

The gas phase reactions of TGB and TGTs with positively charged alkylating species proceed efficiently at atmospheric pressure, to give alkylation and alkyldegermylation products, accompanied by protodegermylation products when the reactant ion may behave as Brønsted acid as well as Lewis acid. The overall reactivity pattern is characterized by the following major features: (i) excited σ -complexes are formed in the primary protonation/alkylation event which may

undergo fragmentation (CI conditions) or collisional quenching (radiolytic conditions); (ii) at atmospheric pressure alkylation is directed mostly at unsubstituted ring positions; (iii) the ensuing thermalised arenium ions undergo isomerization by 1,2- H^+ shifts till the proton sits on the germyl-substituted carbon; (iv) the latter *ipso* protonated species undergo competitive degermylation by oxygen nucleophiles ($(\text{MeO})_3\text{PO}$, $\text{H}_2\text{O} \dots$) and deprotonation by nitrogen bases (Et_3N , $c\text{-C}_5\text{H}_{10}\text{NH}$).

The gas phase reactions of TGB and TGTs examined in this study show a remarkably similar behaviour to the corresponding reactions of their silicon analogues. They share also a similar intermolecular reactivity towards Me_2Cl^+ , conforming to the poor selectivity typically displayed by gaseous electrophiles [19]. This finding may be contrasted with the marked reactivity difference reported for protonation induced cleavage of Et_3X (X = Ge, Si) from $\text{Et}_3\text{XC}_6\text{H}_5$ (X = Ge, Si) compounds in aqueous ethanolic perchloric acid, where $\text{Et}_3\text{GeC}_6\text{H}_5$ reacts 36 times faster than $\text{Et}_3\text{SiC}_6\text{H}_5$ [40–42]. Whereas the different medium and electrophiles amply justify the observed differences, a significant contributing factor may be represented by the different sites of the rate determining electrophilic attack (*ipso*-carbon vs. unsubstituted ring positions) involved in the two classes of reactions.

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