The Gas-Phase Reactivity of *p*-Me_3Si-Substituted 1,3-Diphenylpropane Towards Charged Electrophiles: Intra- and Interannular Hydrogen Migrations

Maria Elisa Crestoni*

Abstract: The gas-phase reaction of *p*-$Me_3SiC_6H_4(CH_2)_3C_6H_5$ (*p*-TSDPP) with gaseous cations, including $C_2H_5^+$, Me_2Cl^+ and DCO^+, has been studied in the pressure range from 10^{-8} to 10^3 Torr by Fourier-transform ion cyclotron resonance (FT-ICR) and by the radiolytic technique. The protonated or alkylated intermediates undergo intramolecular migration and intermolecular transfer of protons and/or Me_3Si^+. The results underline the role of the spectator ring in providing internal solvation to an arenium moiety, as evidenced by the noticeable stability towards Me_3Si loss with respect to a single-ring model substrate, *p*-$Me_3SiC_6H_4Me$ (*p*-TST), upon reaction with the same gaseous ions. The extent of the alkylation route relative to the alkyldesilylation processes, measured as a function of the arenium ion lifetime, permits derivation of the rate constant for the conversion by proton transfer of the originally formed arenium ions to *ipso*-silylated isomers (k_i). The estimated values of $k_{i(p\text{-TST})} = 5 \times 10^9\ s^{-1}$ and $k_{i(p\text{-TSDPP})} = 2 \times 10^8\ s^{-1}$ at 120 °C suggest that intraannular H shifts are faster than ring-to-ring H transfer, in agreement with previous evidence from *tert*-butylated arenium ions. The reactivity of $[Me_3Si-arene]^+$ adducts, adequately described by the Wheland σ-complex model, does not exclude the intermediacy of an ion–neutral noncovalent complex.

Keywords: arenes · FT-ICR · gas-phase chemistry · hydrogen transfer · ion–molecule reactions

Introduction

Arenium ions have long been recognized as key intermediates in gas-phase aromatic substitution by charged electrophiles.[1] A salient mechanistic feature is the tendency to isomerise by 1,2-shifts of hydrogen or other groups. A related interannular hydrogen migration takes place following electrophilic substitution of α,ω-diphenylalkanes,[2] along pathways whose gas-phase kinetics have been the topic of several experimental[2,3] and theoretical investigations.[4] Mass-spectrometric investigations have revealed extensive hydrogen scrambling in protonated α,ω-diphenylalkanes that may lead to complete equilibration in the 10 μsec time frame, typical of metastable loss of benzene.[5] However, in order to confer a general validity to gas-phase kinetic studies and allow their comparison with condensed-phase results, the experimental technique adopted should ensure thermal equilibration of the reactant species and allow a meaningful definition of the reaction temperature. At the same time, it is desirable to work with a much higher time resolution than is possible in metastable decomposition studies. Fulfilling both conditions, the high-pressure radiolytic technique[1] has allowed a detailed kinetic study of the interannular proton transfer in protonated diarylalkanes,[6] disclosing the effect of the spectator ring on the stability of the charged intermediates.

The peculiar features of the trimethylsilyl substituent, namely its effect of increasing the basicity of the *ipso* carbon[7] and the ease of protolytic cleavage,[7b,8] have made the Me_3Si group a useful probe for elucidation of the proton motion within selected arenium ions.[9,3a] This probe is used in the present study to provide further evidence for the occurrence of both intraannular and interannular proton shifts, with the aim of assessing the relative rates of the two processes. At the same time the reactivity of simple silylated arenium ions is compared to that of the same species bound to a remote, neutral aryl group.

Results

FT-ICR reactions: The reaction of Me_3Si^+ ions with toluene (C_7H_8) introduced by a pulsed valve into the ICR cell yields $[Me_3Si-C_7H_8]^+$ ions (**1**), whose stability was checked following their decay in the presence of C_7D_8 at 3.0×10^{-8} Torr. Although the admission of C_7H_8 by the pulsed valve ensures a partial collisional stabilization of the excited adduct ions such as **1**, allowing their detection, the only reaction pathway

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observed was the dissociation of **1** into free Me_3Si^+ ions with a unimolecular decay rate constant of 8 s^{-1}. This result points to the facile desilylation of **1** under the low-pressure conditions prevailing in the FT-ICR experiments, which clearly do not allow silylation of C_7D_8, neither by Me_3Si^+ addition nor by Me_3Si^+ transfer from **1**. By contrast, efficient Me_3Si^+ transfer from **1** takes place when 1,3-diphenylpropane (DPP) at 4.2×10^{-8} Torr is added into the cell. Remarkably, the ionic product **2**, corresponding to $[Me_3Si-DPP]^+$ ($m/z = 269$), becomes the predominant species at long storage time, showing a noticeable reluctance both to dissociate unimolecularly and to transfer Me_3Si^+ to yield $[Me_3Si-C_7D_8]^+$. Protonation of *para*-trimethylsilyldiphenylpropane (*p*-TSDPP) provides an alternative route to **2**. $iC_3H_7CNH^+$ ions [proton affinity $PA(iC_3H_7CN) = 194.3$ kcal mol^{-1}][10] were chosen as a mild protonating agent for *p*-TSDPP, yielding **2**, which, when formed by this alternative route, does not undergo fragmentation and reacts only with adventitious water present in the cell, giving $Me_3SiOH_2^+$. This reaction of $[Me_3Si-DPP]^+$ has been verified by deliberately admitting H_2O into the ICR cell at 2×10^{-8} Torr. As shown in Figure 1, $Me_3SiOH_2^+$ and DPPH$^+$ ions are formed, which may arise by partition of a common ion–neutral intermediate complex [$DPP \cdot Me_3SiOH_2^+$; Eq. (1)]. Process (1c) involves an intracomplex

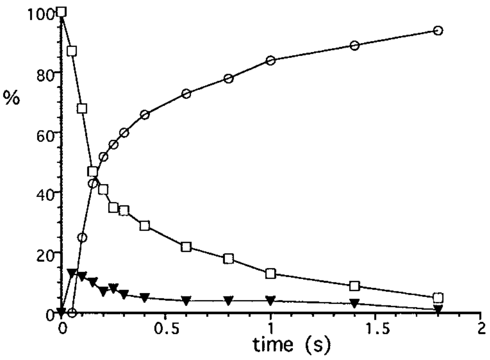


Figure 1. Normalized ion abundances of $[Me_3Si-DPP]^+$ (□), $Me_3SiOH_2^+$ (▼) and DPPH$^+$ (○) as a function of time. The pressure of H_2O was 2×10^{-8} Torr.

$$\mathbf{2} + H_2O \longrightarrow [\mathbf{2} \cdot H_2O] \longrightarrow [DPP \cdot Me_3SiOH_2^+] \tag{1a}$$

$$[DPP \cdot Me_3SiOH_2^+] \longrightarrow DPP + Me_3SiOH_2^+ \tag{1b}$$

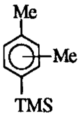
$$[DPP \cdot Me_3SiOH_2^+] \longrightarrow [DPPH^+ \cdot Me_3SiOH] \longrightarrow DPPH^+ + Me_3SiOH \tag{1c}$$

proton transfer, energetically favoured by the higher PA of DPP[11] with respect to Me_3SiOH [$PA(Me_3SiOH) = 194$ kcal mol^{-1}], whereas process (1a) is thermodynamically driven by the higher energy of the Si–O bond than of a typical Si–C bond. Accordingly, process (1a) reflects the larger Lewis basicity of oxygenated compounds towards Me_3Si^+ than towards aromatics.[12]

Structural insight was sought by forming silylated adducts from the Me_3Si^+ reaction with $C_6H_5(CH_2)_3C_6D_5$ ([D$_5$]DPP). The ensuing $[Me_3Si-[D_5]DPP]^+$ ions were isolated and allowed to react with triethylamine [$PA(Et_3N) = 232$ kcal mol^{-1}]. Efficient H^+/D^+ transfer to the base (100% of the ADO collision rate)[13] was observed, only minor amounts of $Et_3NSiMe_3^+$ ($m/z = 174$) being formed. This finding, in particular the observation of abundant ions at $m/z = 103$ corresponding to Et_3ND^+, provides strong evidence that the silyl group is covalently bound[14] within the $[Me_3Si-[D_5]DPP]^+$ intermediate.

Radiolytic experiments: The radiolytic reactions were carried out at 120 °C at a pressure of ca. 700 Torr of bulk gas (CH_4 or MeCl) in the presence of 10 Torr of O_2 as a radical scavenger. The absolute radiolytic yields of the products account for a major portion of the primary reactant ions formed by the ionization of the bulk gas and ensuing ion–molecule reactions. Furthermore, the depression of the yields upon addition of a base/nucleophile at increasing concentration, which competes with the substrate for the electrophile, confirms the ionic origin of the process under study. Conversion of the starting substrate was kept below 1% in order to minimize the extent of further secondary processes that would complicate the primary product pattern.[1]

Table 1 summarizes the distribution of the major products (species **3**–**6**, where R = Et, $(SiMe)_3$) from the radiolytic methylation of *p*-TST and *p*-TSDPP at nearly constant concentration, in the presence of MeCl as bulk gas and of varying amounts of basic additives. As expected from the use of a purely methylating agent, Me_2Cl^+ from the radiolysis of MeCl,[15] as reactant ion, only methylated and methyldesilylated products are detected for both substrates. The isomeric distribution of the desilylated products from *p*-TSDPP and *p*-TST shows that only a fraction (50% and 30%, respectively) of electrophilic attack is directed to the (silylated) *para* position. The significant yields of *o*- and *m*-methylated isomers formed together with the *p*-derivative indicate that, besides the direct nuclear substitution at the silylated position, alkyldesilylation can be traced to proton migration from the alkylated ring positions to the silylated site, followed by release of Me_3Si. The abundance of such a process, even if not completely suppressed, strongly declines in the presence of pyridine [$PA(cC_5H_5N) = 226$ kcal mol^{-1}] and at higher concentrations of $(MeO)_3PO$ [$PA(MeO)_3PO = 212$ kcal mol^{-1}], as inferred from the noticeable increase of the yield of alkylated products with respect to the alkyldesilylated ones. This trend is paralleled by an increasing fraction of the products bearing a methyl group *ortho* to the Me_3Si group of



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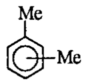

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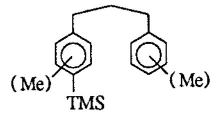

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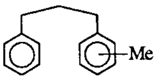

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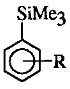

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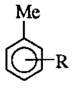

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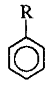

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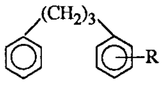

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Table 1. Gas-phase reaction of p-$Me_3Si-C_6H_4Me$ (p-TST) and p-$Me_3Si-C_6H_4(CH_2)_3C_6H_5$ (p-TSDPP) with radiolytically formed Me_2Cl^+ ions.

System composition (Torr)[a]				Relative yields [%]			
p-TST	p-TSDPP	Additives		**3** (1,2:1,3)	**4** (o:m:p)	**5** (X:Y)[b]	**6** (o:m:p)
0.36	0.15	$(MeO)_3PO$	(0.49)	10 (85:15)	90 (45:25:30)	17 (36:64)	83 (21:27:52)
0.41	0.1	$(MeO)_3PO$	(1.26)	15 (77:23)	85 (52:23:25)	68 (43:57)	32 (25:31:44)
0.42	0.16	$(MeO)_3PO$	(2.44)	23 (45:55)	77 (48:23:25)	83 (48:52)	17 (25:28:47)
0.30	0.12	$(MeO)_3PO$	(4.10)	33 (45:55)	67 (40:23:25)	90 (60:40)	10 (27:30:43)
0.53	–	pyridine	(0.51)	15 (48:52)	85 (41:32:27)	–	–
–	0.24	pyridine	(0.56)	–	–	71 (35:65)	29 (21:26:53)
–	0.17	pyridine	(0.61)	–	–	69 (38:62)	31 (20:28:52)
0.38	0.19	NEt_3	(0.47)	10 (60:40)	90 (46:27:28)	47 (43:57)	53 (20:23:57)
–	0.24	$N(iC_3H_7)_2Et$	(0.41)	–	–	30 (43:57)	70 (20:28:52)
0.52	0.30	$N(CH_3)_2(CH_2)_2OH$	(0.50)	11 (44:56)	89 (44:26:30)	33 (37:63)	67 (19:23:58)

[a] All gaseous systems contained MeCl (700 Torr) and O_2 (10 Torr). Reactions carried out at 120 °C. [b] X-type isomers have the methyl group on the substituted phenyl ring, while Y-type isomers result from alkylation at the unsubstituted ring.

p-TST. In particular, it may be noticed that the ratio of the yields of the isomeric products 1,2-dimethyl-4-trimethylsilylbenzene and 1,3-dimethyl-4-trimethylsilylbenzene changes by a factor of four with an almost tenfold increase of the $(MeO)_3PO$ concentration. In the case of p-TSDPP, two types of methylation products are identified, deriving from the attack of the cationic reagent either at the silylated ring (henceforth denoted as products of type X) or at the unsubstituted one (henceforth called products of type Y). Increasing amounts of $(MeO)_3PO$ favour the formation of X-type products over the Y type. A remarkable feature of the product pattern of Table 1 concerns the stronger positive dependence of alkylation/alkyldesilylation yield ratio on increasing $(MeO)_3PO$ concentration in the p-TSDPP reaction compared to p-TST.

Among the bases used at comparable concentrations, pyridine is most effective in promoting alkylation products, whereas alkyldesilylation is the dominant channel when $(MeO)_3PO$ is added. An intermediate behavior is shown by Et_3N and diisopropylethylamine, a sterically hindered base [PA ($i$$Pr_2NEt$) = 235 kcal mol^{-1}] and by 2-(dimethylamino)-ethanol, a strong nitrogen base containing an OH group [PA ($Me_2N(CH_2)_2OH$) = 236 kcal mol^{-1}]. It is noteworthy that the attempt to silylate DPP by Me_3Si^+ ions formed in a gaseous mixture of $CH_4/SiMe_4/O_2$ (70:2:1)[12,16] in the presence of 1.5 Torr of $(MeO)_3PO$ failed, in spite of the estimated comparable basicity of $(MeO)_3PO$ and p-TSDPP that could have ensured the neutralization of the intermediate $[Me_3Si-DPP]^+$ ion by proton transfer. In contrast, when Et_3N replaces $(MeO)_3PO$ in the Me_3Si^+ reaction with DPP, high yields of silylated products are obtained.

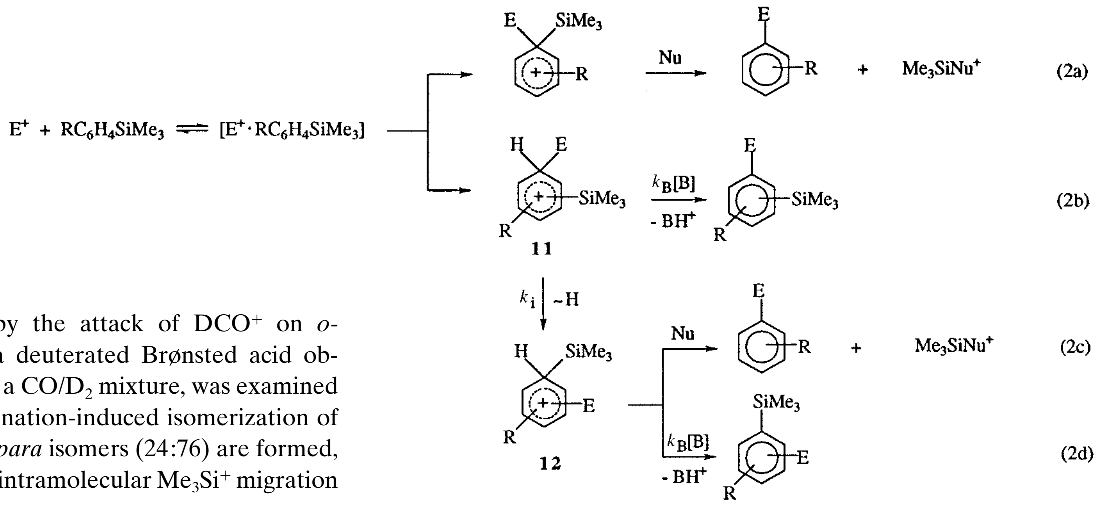
The composition of the gaseous systems containing CH_4 as the bulk component and the relative yields of the products (products **7**–**10**, R = Et, $(SiMe)_3$) are reported in Table 2. Attack of $C_nH_5^+$ (n = 1,2) ions from the radiation-induced reaction of methane on mixtures of trimethylsilylbenzene (TSB) and toluene or DPP yields three types of products: a) alkylation products retaining the Me_3Si group; b) proto- and ethyldesilylation products, where the Me_3Si group has been replaced by H or Et; c) silylation products. The last products are found only in the presence of a strong nitrogen base, such as pyridine or Et_3N, since no silylation products (i.e. trimethylsilyltoluenes or 1-(trimethylsilylphenyl)-3-phenylpropanes) could be detected with $(MeO)_3PO$. As in previous mass spectrometric and radiolytic results, alkyldesilylation represents the major reaction channel.[9b,12]

Table 2. Gas-phase reaction of p-$Me_3SiC_6H_5$ (TSB), o-$Me_3SiC_6H_4Me$ (p-TST), PhMe and 1,3-diphenylpropane (DPP) with $C_nH_5^+$ (n = 1,2) ions.

System composition (Torr)[a]				Relative yields of products [%][b]				Apparent
Substrates		Additives		**7**	**8**	**9**	**10**	k_{S1}/k_{S2}[c]
S_1	S_2			(o:m:p)	(o:m:p)		(o:m:p)	
TSB (0.48)	PhMe (0.64)	pyridine (0.36)	R = Et	2 (0:40:60)	53 (41:37:22)	37	–	
			R = $SiMe_3$	5 (0:51:49)	3 (0:24:76)	–	–	2.2
TSB (0.43)	DPP (0.20)	pyridine (0.39)	R = Et	4 (0:40:60)	–	48	48 (24:36:39)	
			R = $SiMe_3$	3 (0:45:55)	–		2 (0:26:74)	0.70
TSB (0.54)	DPP (0.29)	Et_3N (0.20)	R = Et	3	–	39	40 (24:33:43)	
			R = $SiMe_3$	10 (0:58:42)	–		8 (0:17:83)	0.74
o-TST (1.5)[d]	–	Et_3N (0.29)	R = $SiMe_3$	–	(0:24:76)		–	–

[a] All gaseous systems contained CH_4 (700 Torr) and O_2 (10 Torr) and were submitted to γ radiolysis at 120 °C. [b] Standard deviation ca. 3%. [c] $k_{S1}/k_{S2} = [P_1][S_2]/[P_2][S_1]$, where P_1 and P_2 are the products of the attack at the S_1 and S_2 substrates respectively. [d] The system contained CO/D_2 (20:600) and O_2 (10 Torr) at 37 °C.

The $k_{Substrate1}/k_{Substrate2}$ (k_{S1}/k_{S2}) values were obtained from the relative yields of the silylated products of TSB and toluene or DPP, corrected for the molar ratio of the respective substrates. The k_{TSB}/k_{C7H8} ratio is 2.2 and the k_{TSB}/k_{DPP} ratio is 0.7 in the presence of comparable amounts of base. A salient feature of the isomeric distribution of the silylated products is the lack of *ortho*-substitution and a noticeable 2*para*/*meta* selectivity, which ranges from approximately 2.0 for TSB to approximately 6.0 for both toluene and DPP. Finally, it may be noted that the alkylation products appear to be favoured over the alkyldesilylation products when Et_3N rather than pyridine is used.



The reaction promoted by the attack of DCO^+ on *o*-$Me_3Si-C_6H_4CH_3$ (*o*-TST), a deuterated Brønsted acid obtained from the ionization of a CO/D_2 mixture, was examined for information on the protonation-induced isomerization of this substrate. The *meta* and *para* isomers (24:76) are formed, suggesting the occurrence of intramolecular Me_3Si^+ migration following protonation.

Discussion

The γ-radiolysis of CH_4 produces known yields of $C_nH_5^+$ ($n = 1,2$) ions, which are powerful acids [PA(CH_4) = 131.6 kcal mol^{-1}; PA(C_2H_4) = 162.6 kcal mol^{-1}]. Ionization of MeCl eventually yields Me_2Cl^+ ions, whose alkylation by methyl cation transfer may involve a sizeable activation barrier. Me_3Si^+ ions[17] are obtained from the reaction of $C_nH_5^+$ ions with $SiMe_4$, according to extensive mass-spectrometric[12] and radiolytic studies.[16] The pronounced positive charge located on the silicon atom of Me_3Si^+ combined with the pronounced basicity of its conjugate base [PA($(CH_3)_2Si=CH_2$) = 226 kcal mol^{-1}] confers upon this ion an exclusive Lewis acid character toward the selected substrates. The gaseous precursors used in this work generate the charged electrophiles according to a well-established sequence of ionization, fragmentation and ion–molecule reactions. In the radiolytic systems all ions undergo multiple unreactive collisions with the bulk gas, approaching thermal equilibration before interacting with the aromatic substrate.[1]

Alkylation vs alkyldesilylation: Several experimental[12,14,16] and theoretical investigations[7] have addressed the problem of the structure of Me_3Si-substituted arenium ions, pointing to the enhanced basicity of the ring carbon bearing the Me_3Si group of a silylated arene. This factor accounts for the easy cleavage of the Me_3Si group following protonation or alkylation of silylated arenes, such as TSB, *p*-TST, and *p*-TSDPP, directing the proton to the silylated position. The desilylation process is induced by a) direct electrophilic attack at the silylated carbon and b) electrophilic attack at any other aromatic carbon followed by an H shift to the silylated carbon, the most basic site even in the presence of other activating ring substituents[18]. The overall reaction sequence is depicted in Equation (2), where R = H, *p*-CH_3, $(CH_2)_3Ph$.

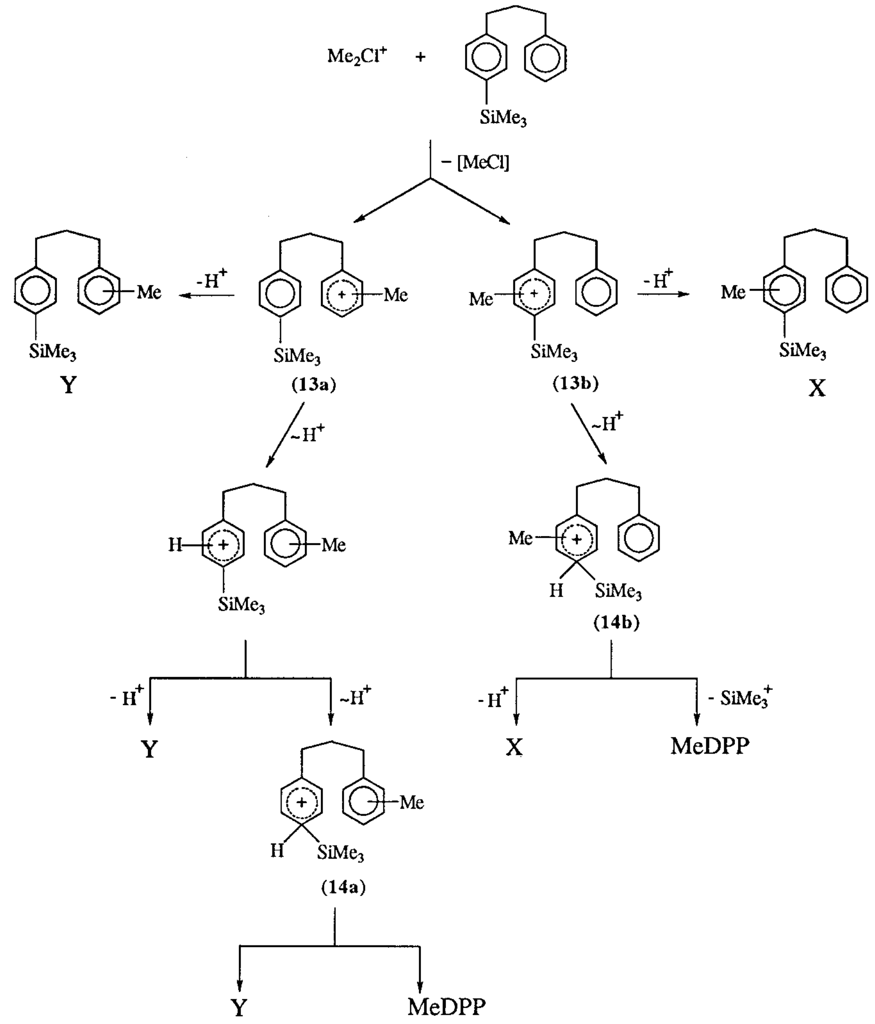
Previous mass spectrometric and radiolytic studies have demonstrated that also in the gas phase positively charged or positively polarised silicon also displays a noticeable oxophilicity,[19] which accounts for the pronounced tendency of oxygenated compounds to desilylate *ipso*-silylated arenium ions.

Whereas all the bases employed in this study can deprotonate **11** and **12** exothermically, the branching between routes (2c) and (2d) depends on the specific features of the base. Nitrogen bases, especially when sterically crowded, behave as efficient deprotonating agents, leading to silylated products, whereas oxygen bases react as nucleophiles, selectively removing the Me_3Si group whenever it is bound to a tetracoordinate carbon.[16]

Equation (2) provides the framework to discuss the results of the present study. Methylation (E = Me) occurs when Me_2Cl^+ reacts with the aromatic substrate by an irreversible MeCl displacement. Probably as a result of steric constraints, Me_2Cl^+ ions attack the *para*-silylated carbon to only a minor extent, leading to a mixture of isomeric ions **11**, where the methyl group remains at the original site of attack, owing to the poor migrating ability of a methyl group within an arenium ring. Other factors being equal, the presence of $(MeO)_3PO$ in the place of a nitrogen base enhances the methyldesilylation route [Eq. (2c)] at the expense of the methylation route [Eq. (2d)], in that an oxygenated base promotes exclusive desilylation of ion **12**. Accordingly, DPP did not give silylation products in the presence of $(MeO)_3PO$, in spite of its high PA. Increasing $(MeO)_3PO$ concentrations enhance the rate of process (2b), allowing a faster sampling of **11** before its conversion to **12**. It follows that the isomeric composition of the methylation products is not representative of the positional selectivity of the electrophile, but rather reflects the average lifetime of the intermediate ions **11**. This view is confirmed by the increasing fraction of *ortho*-alkylated isomer in the presence of increasing amounts of $(MeO)_3PO$.

The dependence of the alkylation/alkyldesilylation ratio on the structural features of highly basic nitrogen compounds can be taken as an indication for the role of steric factors,[20] decreasing the rate of deprotonation of ions **11** and **12** and indirectly favouring desilylation of **12**. In fact, the ratio decreases along the series pyridine, Et_3N, iPr_2NEt. Although it is highly basic, $Me_2N(CH_2)_2OH$ can react either by proton transfer to the nitrogen atom or by nucleophilic attack of the OH group at silicon. Accordingly, the alkylation/alkyldesilylation ratio is intermediate between those obtained with $(MeO)_3PO$ and with the nitrogen bases.

An additional process comes into play when a second phenyl ring is covalently linked to the silylated arene by a methylene chain. The spectator ring is known to engage in proton[6] or Me_3C^+ transfer[21] with the arenium moiety, with efficiencies that depend, inter alia, on the features of the substituents[22] in the arenium ion and the spectator ring and on the length of the polymethylene chain[23,24] joining the two rings. Accordingly, the reactivity of *p*-TSDPP is expected to differ significantly from that of *p*-TST, a simple aromatic model. In the former case, the electrophilic attack, occurring either at the unsubstituted or at the silylated ring, may be followed by both interannular and intraannular proton migration, depicted in Scheme 1.



Scheme 1. Electrophilic attack on *p*-TSDPP occurs either at the unsubstituted or at the silylated ring, and may be followed by both interannular and intraannular H migration.

The silyl group is expected to direct the electrophilic attack by Me_2Cl^+ preferentially towards the silylated ring of *p*-TSDPP, leading to arenium ions that are prone to efficient intraannular H shift to the silylated position. Interannular H migration is instead predicted to follow methylation at the unsubstituted ring of *p*-TSDPP, finally ending in desilylation products through a sequence of inter- and intraannular H shifts.

Me_3Si loss from *p*-TSDPP is much less pronounced than from *p*-TST. This conspicuous difference is verified both by the alkylation/alkyldesilylation ratio of the radiolytic methylation and by the tendency towards Me_3Si^+ loss from ions **1** and **2** in the ICR cell. A major role may be ascribed to the favourable influence exerted by the spectator ring on the stability of the silylated arenium ion, which underlines the demand of charge delocalization and ion solvation in the gas phase.

By application of the steady-state treatment to Equation (2), the relative decrease of the alkyldesilylation products in Table 1 with increasing $(MeO)_3PO$ concentration can be utilized to evaluate the k_i rate constants that refer to the **11**$\rightarrow$**12** isomerization in the case of *p*-TST and the overall isomerization rate of a mixed **13a**/**13b** population to a mixed **14a**/**14b** population (Scheme 1) in the case of *p*-TSDPP. The latter process involves a combination of inter- and intraannular proton transfer steps. A linear relationship is predicted between the ratio (r) of the yields of alkylated and alkyldesilylated products and the $(MeO)_3PO$ concentration, shown by the plots of Figure 2. The slopes, which correspond to k_B/k_i, allow evaluation of the k_i values, relying on the assumption that the highly exothermic deproto-

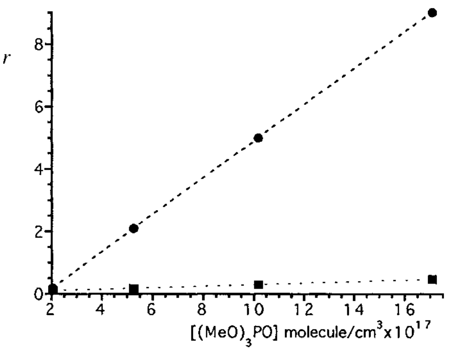


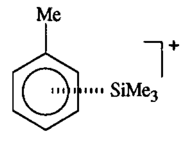
Figure 2. Plots of ratios r = [Me-*p*-TSDPP]/[Me-DPP] (●) and r = [Me-*p*-TST]/[xylenes] (■) vs. $[(MeO)_3PO]$ concentration from the radiolytic reaction of Me_2Cl^+ with *p*-TST/*p*-TSDPP mixtures.

nation by the base B proceeds at the collision frequency ($k_B = k_{collision}$), which can be calculated by the ADO theory.

At 393 K, in MeCl at ca. 1 atm, the rate constant for the process **11**$\rightarrow$**12** ($k_{i(p\text{-TST})} = 5 \times 10^9\,s^{-1}$) is considerably higher than that for the **13a/13b**$\rightarrow$**14a/14b** process ($k_{i(p\text{-TSDPP})} = 2 \times 10^8\,s^{-1}$). From these data a valuable insight can be gained on the overall proton shift sequences. In fact, the lower rate for the **13a/13b**$\rightarrow$**14a/14b** process can be ascribed to the lower rate of a (possibly) rate-determining interannular proton shift and/or to a decreased rate of intraannular proton shift when compared to the same process occurring within the single-ring arenium ion. The data in Table 1 show that, whereas higher amounts of the base enhance the relative yield of both X and Y products with respect to methyldesilylation products, the effect is more pronounced for X products. This finding supports the hypothesis that 1,2-H shifts within the trimethylsilylated arenium ion are faster than ring-to-ring migrations, in agreement with previous findings on *tert*-butylated arenium ions, for which the different rates have been traced to the lower preexponential factor of interannular compared with 1,2-H transfer.[6]

Intermolecular Me_3Si group transfer: The exceptional mobility of Me_3Si^+, especially when it is originally bound to carbon and directed to an oxygen or halogen atom as the migration terminus, prompted the study of Me_3Si^+ transfer processes in parallel with the observed proton migration processes. Evidence for Me_3Si^+ transfer from $[Me_3Si-arene]^+$ to aromatic compounds is provided by mass spectrometry and radiolysis. The dependence of the efficiences of Me_3Si^+ transfer on energetic factors emerges clearly from the relative reactivity scale (DPP > TSB > toluene), which follows the relative PA scale. Me_3Si^+ transfer is observed only when thermodynamically favourable. No thermoneutral or endothermic silyl migration occurs, for example, from $[Me_3Si-arene]^+$ (arene = $[D_8]$toluene, DPP) to toluene. The reluctance of $[Me_3Si-DPP]^+$ to undergo arene exchange is consistent with the stability of adduct **2** with respect to unimolecular dissociation, in marked contrast to $[Me_3Si-C_7H_8]^+$. These results point to the role played by the spectator phenyl ring of DPP in stabilizing adduct **2**, probably through a chelate-type interaction. In fact, when the conformation of the linking chain allows, as in this case, the parallel arrangement of the two ring planes, a substantial intramolecular solvation effect has been found to provide a most effective electrostatic stabilization. Examples where this effect was found include the DPP adduct ions $DPPCr^+$,[25] $DPPH^+$,[24] and $DPPCMe_3^+$.[21]

Structure of $[Me_3Si-DPP]^+$ complexes: The study of the reactivity of $[Me_3Si-DPP]^+$ complexes provides further valuable structural insight. Both a π-complex (**15**) or a σ-complex (**16**) structure can account for the observed Me_3Si^+ transfer to H_2O. In fact, while **15** can react only by ligand exchange, **16** can in principle undergo both proton transfer and Me_3Si^+ transfer, which is especially favoured when an oxygenated partner is involved. However, the isolation of silylated neutral products when Me_3Si^+ is allowed to react with DPP in the presence of Et_3N under radiolytic conditions, as well as the pronounced D^+ transfer from $[Me_3Si-[D_5]DPP]^+$ to Et_3N in the FT-ICR cell, speak in favour of a σ complex with a covalent C–Si bond. The existence of both π and σ complexes cannot be excluded, however. The intervention of a π complex with some degree of orientation along the reaction coordinate to silylated products from the Me_3Si^+ reaction with arenes appears reasonable and may also be involved in the protonation-induced isomerization of *o*-Me_3Si–toluene. The isomerization to the *meta* and especially to the *para* isomers in a ratio close to that obtained from the direct silylation of toluene by Me_3Si^+ ions suggests that **16** dissociates to an intermediate ion–neutral complex, corresponding to the species obtained from reaction of free Me_3Si^+ with toluene, probably resembling **15**, before undergoing Me_3Si^+ attack at an aromatic carbon.



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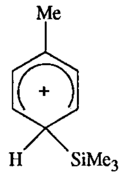

16

Conclusions

The gas-phase reactions of charged electrophiles, including Me_2Cl^+ and $C_2H_5^+$, with *p*-TSDPP and with *p*-TST as model substrates demonstrate the occurrence of proton and Me_3Si^+ migration processes. Furthermore, the efficiency of the processes is affected by the presence of an additional aryl ring providing internal solvation to the arenium ring. Whereas the $[Me_3Si-DPP]^+$ ion is adequately described by a σ-complex structure, by analogy to the $[Me_3Si-toluene]^+$ ion, it displays an enhanced stability with regard to unimolecular loss of Me_3Si^+. The Me_3Si group has been successfully used to probe the intra- and interannular proton migrations within alkylated *p*-TSDPP, pointing to a higher rate for the intraannular proton shift. This result confirms previous views regarding the relative rates of the two processes based on the comparison with single-ring arenium ions.

Experimental Section

Materials: The gases were research-grade products from Matheson, with a stated purity exceeding 99.98 mol%. Most other chemicals used were purchased from commercial sources. *p*-$Me_3SiC_6H_4Me$ (*p*-TST) and *o*-$Me_3SiC_6H_4Me$ (*o*-TST) were prepared from the reaction of trimethylsilyl methanesulfonate with the Grignard reagent of the aromatic precursors, *p*-BrC_6H_4Me and *o*-BrC_6H_4Me, respectively. *o*- and *p*-TST were purified by preparative GLC in a 1.5-m stainless steel column packed with SE 30 (20% w/w). *p*-$Me_3SiC_6H_4(CH_2)_3C_6H_5$ (*p*-TSDPP) was a kind gift from Prof. D. Kuck.[26] The identity of the products was confirmed by NMR and mass spectrometric analysis.

Radiolytic experiments: The gaseous systems were prepared by standard vacuum procedures in sealed 135-mL Pyrex vessels. The competition experiments between *p*-TST and *p*-TSDPP required a long equilibration time (at least 2 h at 120 °C) owing to the low vapour pressure of the less volatile substrate. The resultant gaseous mixtures were submitted to γ irradiation at 120 °C in a 220 Gammacell (Nuclear Canada) to a total dose of 10^4 Gy, at a dose rate of 10^4 Gy h^{-1}. A solution of the radiolytic products in cyclohexane was recovered after repeated freeze–thaw cycles and analyzed by GLC-MS using a Hewlett Packard 5890 A gas chromatograph equipped with a Model 5970B mass-selective detector or by a GC-AED System (HP 5890 gas chromatograph, in line with an AED HP 5921 A detector under the control of a HP 5895 A chemstation). The following columns were used: a) a 100-m, 0.32-mm i.d. Petrocol DH fused silica capillary column; b) a 50-m, 0.25-mm i.d. poly(ethyleneglycol) (Supecolwax 10) bonded-phase column (0.25 µm film thickness). The identity of the products was verified by comparison of their retention volumes and mass spectra with those of authentic standard samples.

FT-ICR experiments: The experiments were performed on a Bruker Spectrospin Apex TM 47 e FT-ICR spectrometer with an external ion source and a cylindrical Infinity® cell situated between the poles of a 4.7 T superconducting magnet. The reactant Me_3Si^+ ion, generated in the external ion source operated at 160 °C by 70 eV electron impact on Me_4Si (nominal pressure 5×10^{-6} Torr), was transferred into the cell and reacted with C_6X_5R (X = H, D; R = H, D, CX_3), introduced by a pulse valve up to peak values of about 10^{-5} Torr for 10^{-2} s. In this way a partial cooling of the $[Me_3SiC_6H_5R]^+$ adduct was achieved by collisional stabilization. A C_3H_8/$i$$C_3H_7CN$ (90:10 mol%) mixture at a total pressure of 5×10^{-5} Torr was used to prepare $i$$C_3H_7CNH^+$ ions, which were allowed to protonate p-TSDPP present in the cell at the stationary pressure of 3.0×10^{-8} Torr at 300 K. After isolation of the parent ion of interest by soft ejection techniques, the progress of the reaction with the neutrals was followed. The pressure readings of the ion gauge were calibrated by means of a standard reaction $CH_4^{\cdot+} + CH_4 \rightarrow CH_5^+ + CH_3^{\cdot}$ ($k = 1.5 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1})[27] and corrected for the response factor of each neutral.[28] All parent and product ions were characterized by exact mass measurements. The gases, the inlets and the pulsed valves were at room temperature, except in the case of DPP and p-TSDPP, loaded in reservoir chambers kept at a constant 120 °C because of their low volatility. The pseudo-first-order rate constants were determined from the exponential decay rate of the reactant ion intensity and converted into second-order rate constants from the known value of the neutral pressure.

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