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Gas-Phase Alkylation of Phenyltrimethylsilanes. Using the Trimethylsilyl Group To Probe Proton Shifts in Gaseous Arenium Ions

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Abstract: The reactivity of (trimethylsilyl)benzene (TSB) and (trimethylsilyl)toluenes (TST) toward i-$C_3H_7^+$ and $(CH_3)_2F^+$ has been studied in the gas phase in the interval from 0.6 to 3040 Torr and from 37.5 to 100 °C by mass spectrometric and radiolytic techniques. The systematic investigation of the dependence of the relative rate of the alkylation and alkyldesilylation processes promoted by i-$C_3H_7^+$ on the nature and the concentration of gaseous bases has allowed an evaluation of the rate constant of the isomerization via proton 1,2-shifts of the alkylated adducts from TSB into the corresponding ions protonated ipso to the $SiMe_3$ group. The results, i.e., $k_i = 1.6 \times 10^9$ s^{-1} at 310 K and $E_i^{\ddagger} \approx 9.5$ kcal mol^{-1}, represent the first experimental evaluation of the kinetic parameters of proton 1,2-shifts within gaseous arenium ions, generally too fast to be monitored by mass spectrometric techniques, and are in excellent agreement with theoretical and solution-chemistry studies of the model $C_6H_7^+$ ion. The selectivity of the alkylation of TSB and of *m*- and *p*-TST is discussed, particularly as regards direct ipso substitution and the steric hindrance to deprotonation of the ortho-isopropylated adducts.

Introduction

Occurrence of 1,2-shifts of protons in arenium ions was first demonstrated in superacid solutions by Olah and co-workers, who evaluated the activation energy of the process, ~10 kcal mol^{-1}, in $C_6H_7^+$ ions.[1] Subsequently, intramolecular H/D scrambling in gaseous protonated arenes was demonstrated by mass spectrometric techniques,[2,3] an observation soon extended to polycyclic systems,[4] e.g., up to 21 protons were reported to undergo scrambling via interannular and intrannular processes in gaseous protonated tetrabenzylmethane within the 10^{-5}-s time scale of mass spectrometric experiments.[5]

On the basis of indirect evidence from the temperature dependence of proton-transfer equilibria, it was further suggested that certain gaseous arenium ions undergo extremely fast (10^{12} s^{-1}) intramolecular proton migration, characterized by remarkably low barriers to 1,2-shifts, e.g., below 5.5 kcal mol^{-1} in gaseous $C_6H_7^+$ ions.[6,7] Such a value is considerably lower than the ones experimentally measured in solution,[1] and obtained from ab initio calculations, ranging from 20 kcal mol^{-1} at the STO-31 G level of theory[8] to 8–10 kcal mol^{-1} at the MP 2/6-31G** level.[9]

Direct kinetic study of such fast processes is hardly amenable to mass spectrometric techniques, whose time scale, typically 10^{-5} s, has allowed to establish only a *lower limit*, 10^6 s^{-1}, of the rate constants of proton 1,2-shifts in gaseous arenium ions.[4,5] Furthermore, it is difficult to define the "temperature" of the excited and thermally nonequilibrated ions formed under mass spectrometric conditions.

The above difficulties can be overcome, at least in principle, by resorting to the radiolytic technique, characterized by extremely short sampling times and by a pressure range up to several atmospheres, which allows the charged species to be more nearly thermalized.[10] In particular, previous mass spectrometric, radiolytic, and theoretical studies suggest that the $SiMe_3$ group can represent a useful probe to investigate proton migration within gaseous arenium ions exploiting its unique features, in the first place the ability of the ring carbon bearing the $SiMe_3$ group to act as an effective proton sink, owing to its enhanced basicity, leading to formation of the ipso-substituted isomer. Moreover, once the latter is formed, its deprotonation or desilylation can selectively be accomplished upon reaction with an appropriate gaseous nucleophile.[11-13]

On the basis of the above premises, this study is aimed at evaluating the rate of intramolecular proton migration within gaseous arenium ions containing the $SiMe_3$ group and the orienting properties of the latter in electrophilic substitution processes promoted by gaseous cations.

Experimental Section

Materials. The gases were research-grade samples from Matheson Gas Products, Inc., whose stated purity exceeded 99.9 mol %, and were used without further purification. The chemicals were obtained from commercial sources or prepared according to standard procedures. When appropriate, their identity was established by NMR and mass spectrometry and their purity checked by GC. The TSB and TST samples were purified by preparative GC, using a 5-m-long column packed with C 20 M on KOH-washed Supelcoport.

Mass Spectrometric Measurements. The spectra were recorded on a Hewlett-Packard 5892A quadrupole instrument, or a VG Micromass ZAB-2F magnetic spectrometer operated in the CI mode, by using C_3H_8 as the reactant gas, at a source temperature of 60 °C and in the pressure range from 0.5 to 1.0 Torr, as measured by a Bourdon-type mechanical gauge (Hewlett-Packard) or a MKS Baratron Model 221A capacitance manometer (Micromass ZAB-2F).

Radiolytic Reactions. The preparation of the gaseous samples was carried out by using a greaseless vacuum line, as described in earlier reports.[10-13] The irradiations were performed in a 220 Gammacell (Nuclear Canada Ltd.) fitted with a thermostated cell, to a total dose of 10^4 Gy, at a dose rate of 5×10^3 Gy h^{-1}.

The analysis of the radiolytic products was carried out by GC using a Hewlett-Packard 5890 A, or a Dani 3800 chromatograph, equipped with FID detectors, on the following columns: (i) a 30-m-long, 0.32-mm i.d. fused-silica capillary coated with a dimethylpolysiloxane (SPB-1) stationary phase from Supelco Co., operated from 50 to 180 °C; (ii) a 15-m-long, 0.53-mm i.d. fused-silica wide-bore, capillary, coated with a 5% diphenyl- + 94% dimethyl- + 1% vinylpolysiloxane (SPB-5) stationary phase from Supelco Co., operated from 40 to 160 °C; (iii) a 50-m-long, 0.20-mm i.d. capillary, coated with a cross-linked methyl

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Table I. Gas-Phase Reaction of (Trimethylsilyl)benzene (TSB) with Radiolytically Formed i-$C_3H_7^+$ Ions

system composition (Torr)^a		absolute yields of products (G_{+M})^b				relative yields (%)		
TSB	additives	PhH	Ph-i-Pr	i-$PrC_6H_4SiMe_3$	total yield	PhH	Ph-i-Pr	i-$PrC_6H_4SiMe_3$ (o:m:p)
1.12		0.46	1.81	0.11	2.38	19	76	5 (6:76:18)
0.86	NEt_3: 0.21	0.48	1.02	0.37	1.87	26	54	20 (2:61:37)
1.06	0.48	0.19	0.95	0.54	1.68	11	57	32 (3:57:40)
0.71	0.77	0.19	0.51	0.51	1.21	16	42	42 (2:53:45)
1.10	1.38	0.17	0.44	0.58	1.19	15	35	50 (2:53:45)
1.11	2.74	0.13	0.22	0.40	0.75	17	30	53 (2:53:45)
1.07^d	3.26^d	0.089	0.12	0.19	0.40	22	30	48 (3:57:40)
1.12	5.90	c	0.086	0.30	0.39	c	22	78 (2:49:49)
1.29	9.45	c	0.075	0.25	0.32	c	23	77 (2:49:49)
0.79	c-$C_6H_{10}O$: 0.26	0.38	0.93	0.17	1.48	26	63	9 (3:86:11)
1.12	0.67	0.090	0.83	0.19	1.11	8	75	17 (2:86:12)
0.73	1.27	0.11	0.57	0.15	0.83	13	69	18 (4:84:12)
1.23	3.16	0.030	0.31	0.10	0.44	7	70	13 (2:86:12)
0.89	6.08	0.030	0.13	0.054	0.21	14	62	24 (4:85:11)
1.08	9.36	c	0.084	0.033	0.12	c	72	28 (c:87:13)
0.81	$Me_2N(CH_2)_2OH$: 0.45	0.09	0.74	0.46	1.29	7	57	36 (3:66:31)
0.91	1.66	0.13	0.40	0.33	0.86	15	46	39 (3:66:31)
0.81	5.54	0.02	0.14	0.13	0.29	7	48	45 (3:67:30)

[a] Reactions carried out at 37.5 °C. All gaseous systems contained C_3H_8 (750 Torr) and O_2 (10 Torr). [b] See text. [c] Not detectable. [d] Propane pressure 3040 Torr.

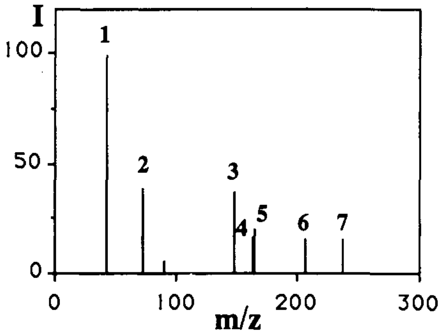


Figure 1. C_3H_8 CI mass spectrum of p-TST (M): 1, $C_3H_7^+$; 2, $Si(CH_3)_3^+$; 3, $(M - CH_3)^+$; 4, M^+; 5, $(M + H)^+$; 6, $(M + C_3H_7)^+$; 7, $(M + Si(CH_3)_3)^+$.

silicone (PONA) stationary phase from Hewlett-Packard Co., operated from 50 to 180 °C.

The identity of the products was confirmed by GC/MS, using a HP 5970 B mass-selective detector from Hewlett-Packard Co. The quantitative analyses were carried out by the internal-standard technique, using ethylbenzene as the reference compound.

Results

Chemical Ionization (CI) Mass Spectra. CI spectra of (trimethylsilyl)benzene (TSB) and p-(trimethylsilyl)toluene (p-TST) have been recorded by using as the reactant gas C_3H_8, the bulk component of the radiolytic systems. The major ion detected is $SiMe_3^+$, $m/z = 73$, whose formation cannot be traced to direct ionization of the aromatic molecules. In fact, the most abundant fragments in their electron impact (EI) spectra are instead those deriving from the loss of a methyl group, which are but minor peaks in the C_3H_8 CI spectra. As a consequence, formation of $SiMe_3^+$ must be traced to processes promoted by the i-$C_3H_7^+$ reactant ions, i.e., to protodesilylation and alkyldesilylation, both energetically allowed (vide infra). The CI spectra, especially those recorded at high C_3H_8 pressures and at low temperatures, display additional peaks that are mechanistically informative, despite their relatively low intensity. Of particular note is the formation of alkylated adducts, $(M + C_3H_7)^+$, and of silylated adducts, $(M + SiMe_3)^+$, as illustrated in Figure 1 that reproduces a typical CI spectrum of p-TST recorded in C_3H_8 at 0.6 Torr and 60 °C.

Radiolytic Reactions. The experiments are based on the γ irradiation of gaseous systems containing C_3H_8 as the bulk component, in the presence of small amounts of O_2, used as a radical scavenger, of the aromatic substrate and of a gaseous base, i.e., triethylamine, cyclohexanone, or 2-(dimethylamino)ethanol. The composition of the irradiated systems, the absolute and relative yields of the products from TSB, and their isomeric composition are given in Table I. The absolute yields of the products are expressed by the G_{+M} values, i.e., the number of molecules formed per 100 eV. The internal consistency of the G values is satisfactory, with standard deviations below 10%, while their absolute accuracy is affected by dosimetric problems and by other sources of systematic errors, leading to a cumulative uncertainty estimated around 30%. The salient features can be itemized as follows.

Table II. Gas-Phase Reaction of (Trimethylsilyl)benzene (TSB) with Radiolytically Formed $(CH_3)_2F^+$ Ions

system composition (Torr)^a		absolute yields of products (G_{+M})^b		relative yields (%)	
TSB	additives	PhMe	$MeC_6H_4SiMe_3$	PhMe	$MeC_6H_4SiMe_3$ (o:m:p)
1.75	NEt_3: 1.09	0.44	0.24	35	65 (18:64:18)
2.33	c-$C_6H_{10}O$: 1.50	0.29	0.24	45	55 (19:62:19)

[a] Reactions carried out at 37.5 °C. All gaseous systems contained CH_3F (750 Torr) and O_2 (10 Torr). [b] See text.

(i) The products identified are benzene, cumene, and isomeric i-propyl(trimethylsilyl)benzenes.

(ii) The *absolute* yields decrease monotonically with the concentration of added bases, irrespective of their nature.

(iii) The yields of alkylated products display a peculiar behavior, being quite low in the absence of added bases, then raising gradually to a maximum value, and eventually declining as the base concentration is increased. Among the bases, NEt_3 and c-$C_6H_{10}O$ are the most and respectively the least effective in enhancing the yields of alkylated products, whereas $Me_2N(CH_2)_2OH$ has an intermediate efficiency.

(iv) There is very little substitution ortho to the $SiMe_3$ group.

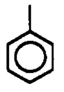
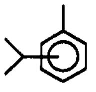
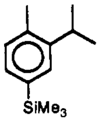
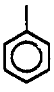
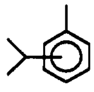
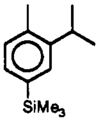
(v) Raising the pressure of C_3H_8 from 1 to 4 atm has remarkably little effects on the yields and the composition of the products.

In order to evaluate the reactivity of TSB relative to benzene, competition experiments have been performed by using C_6D_6 as the reference substrate, in view of the fact that C_6H_6 is one of the products from $C_6H_5SiMe_3$.

The apparent $k_{TSB}/k_{C_6D_6}$ ratio, measured at 750 Torr and 37.5 °C, in the presence of NEt_3 (1.9–5.4 Torr), is 1.0 ± 0.1 if one considers only the alkylation process. If however the overall reactivity of TSB is taken into account by considering both alkylation and alkyldesilylation, the $k_{TSB}/k_{C_6D_6}$ ratio increases to 1.4 ± 0.04.

Table II illustrates the methylation of TSB by $(CH_3)_2F^+$ ions from the radiolysis of CH_3F. Apart from the fact that no C_6H_6 is formed, consistent with the inability of $(CH_3)_2F^+$ to promote

Table III. Gas-Phase Reaction of *p*-(Trimethylsilyl)toluene (*p*-TST) with Radiolytically Formed i-$C_3H_7^+$ Ions

	system composition (Torr)[a]		absolute yields (G_{+M})[b]				relative yields (%)		
t (°C)	*p*-TST	additives			 SiMe3	total yield		 (o:m:p)	 SiMe3
37.5	1.01		1.59	1.37	0.039	3.00	53	46 (63:30:7)	1
37.5	1.00	NEt$_3$: 0.38	0.76	0.78	0.21	1.75	43	45 (51:33:16)	12
	1.06	1.17	0.29	0.37	0.24	0.90	32	41 (38:41:21)	27
	0.99	4.33	0.10	0.11	0.12	0.33	30	33 (27:46:27)	37
100	1.20	0.91	0.59	0.57	0.085	1.25	47	46 (59:28:13)	7
37.5	1.18	Me$_2$N(CH$_2$)$_2$OH: 0.50	0.54	0.43	0.11	1.08	50	40 (52:34:14)	10
	0.94	0.88	0.38	0.45	0.21	1.04	37	43 (38:45:17)	20
	1.23	4.67	0.085	0.15	0.090	0.32	26	46 (38:44:18)	28
100	1.01	1.01	0.32	0.43	0.045	0.80	40	54 (60:28:12)	6
37.5	0.92	c-C$_6$H$_{10}$O: 0.30	0.95	1.13	0.045	2.12	45	53 (59:30:11)	2
	1.05	0.97	0.44	0.52	0.022	0.98	45	53 (58:30:12)	2
	1.01	6.26	0.091	0.11	0.0083	0.21	43	52 (52:32:16)	2
100	0.95	0.92	0.84	0.61	0.064	1.46	56	40 (63:26:11)	4

[a] All systems contained C_3H_8 (750 Torr) and O_2 (10 Torr). [b] See text.

protodesilylation, the major difference with respect to isopropylation is the much higher extent of substitution ortho to the $SiMe_3$ group.

The isopropylation of *p*-TST has also been investigated in order to gather more direct information on the mechanism of alkyldesilylation. The results, summarized in Table III, show that a mixture of isomeric cymenes is formed, significant yields of *m*-, and even of *o*-cymene, being obtained together with *p*-cymene.

This indicates that, in addition to direct ipso substitution, alkyldesilylation can be promoted by alkylation at unsubstituted positions, followed by proton migration to the ring carbon bearing the $SiMe_3$ group, which eventually leads to the loss of the latter. The process is not suppressed by gaseous bases, at least within the concentration range investigated, and is considerably enhanced at higher temperatures.

Remarkably, only the isomer alkylated ortho to the methyl group could be detected, irrespective of the nature and concentration of added bases, whereas a specific search failed to reveal any products alkylated ortho to the $SiMe_3$ group.

The isopropylation of *m*-TST has been studied in a limited number of irradiations in C_3H_8 at 750 Torr and 37.5 °C. The products identified are toluene, isomeric cymenes, and *i*-propyl(trimethylsilyl)toluenes. As noted in the case of *p*-TST, the alkylation yields are very low ($G = 0.1$) in the absence of added bases and increase in the presence of moderate concentrations of the latter, e.g., in the presence of Et_3N (4.0 Torr), the *G* value raises to 0.28.

The composition of cymenes, 56% ortho, 20% meta, and 24% para in the absence of added bases, passes to 25% ortho, 22% meta, and 53% para in the presence of Et_3N. While the results are less straightforward than those concerning *p*-TST, they support the view that alkyldesilylation can be promoted by attack to ring positions other than the one bearing the $SiMe_3$ group.

Alkylating Cations. Gaseous i-$C_3H_7^+$ is formed both in the CI ion source and in the radiolytic systems from the ionization of propane, either directly or via fast hydride ion abstraction from C_3H_8 by the primary fragment ions, e.g., $C_2H_5^+$, $C_3H_5^+$, n-$C_3H_7^+$, etc. Extensive mass spectrometric and radiolytic studies indicate that i-$C_3H_7^+$ is the only significant charged reactant formed and that its *G* value is ca. 3 in the pressure range of interest to this work.[14-16]

As to the methylation reaction, $(CH_3)_2F^+$ is obtained from the ionization of gaseous CH_3F via a sequence of fast ion–molecule reactions, well-established by extensive mass spectrometric studies.[17]

In the radiolytic systems, i-$C_3H_7^+$ and $(CH_3)_2F^+$ ions undergo many unreactive collisions with the parent molecules and are therefore fully thermalized before their reactive encounter with the aromatic molecules.

Ionic Nature of the Reaction. A preliminary problem invariably encountered in the application of the radiolytic technique to gas-phase ion chemistry is to ascertain the ionic origin of the relevant products, excluding contributions from radical and/or excited-molecule processes.

In the present case, the problem does not arise at all, as long as the alkylation process is concerned, in that *little or no alkylated products are formed unless a strong gaseous base is present in the system.* This finding underlines the role of deprotonation as a necessary link in the chain of reactions yielding the alkylated products and is inconsistent with alkylation mechanisms other than those involving the intermediacy of gaseous arenium ions.

More generally, the following considerations argue for the ionic nature of the reactions of interest. First, all irradiations are performed in the presence of O_2, an effective radical scavenger, at concentrations much higher than those of the aromatic substrate. Second, all charged reactants and intermediates invoked in the ionic alkylation have directly been detected in the CI mass spectra of the same systems studied by the radiolytic technique. Further evidence is provided by the depression, and the eventual suppression, of the products yields caused by addition of increasing concentrations of gaseous bases capable of intercepting the charged reactants. Moreover, the dependence of the total yield of products on the concentration of added base has been found to follow a trend consistent with a simple kinetic model envisaging the competition of the aromatic substrate, S, with the base, B, for the charged electrophile. According to such a model, the total absolute yield *G* at any concentration of base is given by

$$G = rG_0$$

where G_0 is the yield in the absence of added bases and $r = k_S[S]/(k_S[S] + k_B[B])$.

Taking $k_S \approx k_B$, as expected for a highly reactive and indiscriminate electrophile such as i-$C_3H_7^+$, one obtains an excellent fit with the experimental trend, as illustrated in Figure 2, that refers to the reaction of TSB with i-$C_3H_7^+$ in C_3H_8 at 750 Torr and 37.5 °C in the presence of variable concentrations of different bases. It should be noted that under the assumption that $k_S \approx k_B$, the ratio *r* expresses simply the mole fraction of the substrate with respect to all nucleophiles present in the system. As a whole,

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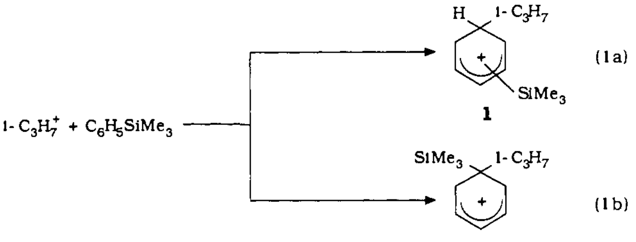
the above considerations provide compelling evidence for the ionic character of all processes studied, i.e., protodesilylation and alkyldesilylation, in addition to alkylation.

Discussion

Alkylation vs Alkyldesilylation. Any mechanistic model of the alkylation process must provide in the first place a reasonable explanation of the peculiar features of the reaction outlined in the previous section, i.e., the unusual dependence of the yields on the nature and the concentration of added bases. A satisfactory rationalization of the radiolytic results, consistent with the evidence from CI mass spectrometry and from previous studies, can be based on the following scheme.



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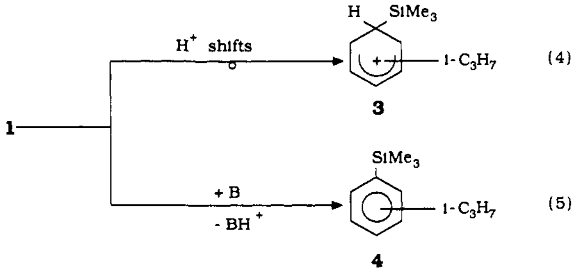
The electrophilic addition yields isomeric arenium ions excited by the considerable exothermicity of the reaction, estimated in excess of 50 kcal mol^{-1}.[18]

Unless collisionally deactivated, the excited adducts can undergo fragmentation, e.g., the overall alkyldesilylation process is exothermic by ca. 23 kcal mol^{-1}, whereas the overall protodesilylation process is nearly thermoneutral. Whereas reactions 2 and 3 can

$$i\text{-}C_3H_7^+ + C_6H_5SiMe_3 \rightarrow C_6H_5\text{-}i\text{-}C_3H_7 + SiMe_3^+ \quad (2)$$

$$i\text{-}C_3H_7^+ + C_6H_5SiMe_3 \rightarrow C_3H_6 + C_6H_6 + SiMe_3^+ \quad (3)$$

play a role in CI mass spectrometry, they seem quite unlikely at the much higher pressures typical of the radiolytic experiments. Consistent with the results of previous studies pointing to the enhanced basicity of the ring carbon bearing the $SiMe_3$ group,[13] the arenium ions **1**, unless deprotonated by a base of sufficient strength, are expected to rearrange via consecutive proton shifts into the corresponding ipso-substituted isomer.



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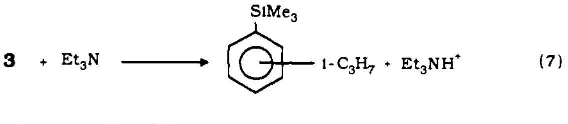
All bases employed in this study, i.e., Et_3N, $c\text{-}C_6H_{10}O$, and $Me_2N(CH_2)_2OH$, can react exothermically according to eq 5. However, once **3** is formed, its fate depends on the nature of the base(s) present in the gaseous system, in that oxygenated bases such as H_2O, $c\text{-}C_6H_{10}O$, etc. act as efficient desilylating reagents, e.g., according to the exothermic process leading to alkyldesilylation

$$3 + c\text{-}C_6H_{10}O \rightarrow i\text{-}C_3H_7C_6H_5 + (c\text{-}C_6H_{10}O\cdot SiMe_3)^+ \quad (6)$$

whereas trimethylamine reacts as a deprotonating agent, according to the process



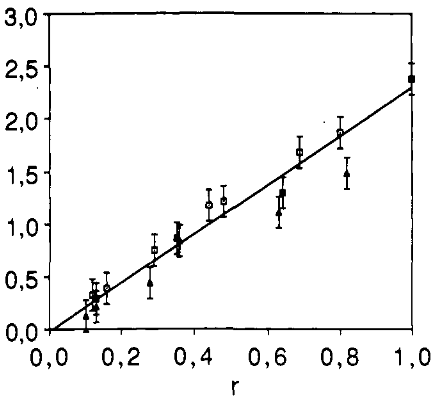


Figure 2. Dependence of the total absolute yields of products from the reaction of $i\text{-}C_3H_7^+$ with TSB on r = [TSB]/([TSB] + [B]): (▣) B = Et_3N, (▲) B = $c\text{-}C_6H_{10}O$, (■) B = $Me_2N(CH_2)_2OH$.

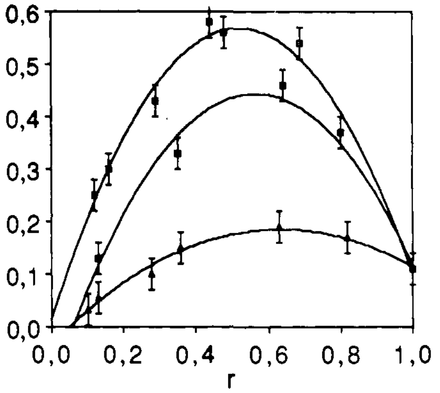


Figure 3. Dependence of the absolute yields of the products from the alkylation of TSB by $i\text{-}C_3H_7^+$ on r: (▣) B = Et_3N, (▲) B = $c\text{-}C_6H_{10}O$, (■) B = $Me_2N(CH_2)_2OH$.

The scheme outlined in eqs 4–7 accommodates the otherwise puzzling features of the radiolytic results.

In the absence of added bases, the inefficiency of process 5 allows extensive isomerization of **1** into **3**, which subsequently is desilylated by traces of water, or of other bases too weak to accomplish deprotonation (eq 5), that are present as trace impurities in the gaseous system or are formed from its radiolysis.

Small concentrations of strong bases *enhance* the absolute alkylation yields by deprotonating arenium ions before their isomerization into **3** and, in the case of Et_3N, by deprotonating, rather than desilylating, any ions **3** formed. Of course, such effects are counterbalanced by the interception of the $i\text{-}C_3H_7^+$ reactant by the base, a factor that tends to depress the absolute alkylation yields and becomes predominant at high concentrations of bases, thus accounting for the peculiar maximum that characterizes the curves of Figure 3.

The different efficiency of the bases, clearly illustrated in the figure, is traced to their different reactivity toward ions **3**. Oxygenated compounds, although sufficiently basic to perform deprotonation, selectively remove the $SiMe_3$ group, as demonstrated in the specific case of $c\text{-}C_6H_{10}O$[19] by high-pressure and ion cyclotron resonance (ICR) mass spectrometry.[12,13,18]

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(18) All thermochemical data taken from (a) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, N. G. *J. Phys. Chem. Ref. Data, Suppl.* **1988**, 17. The heat of formation of $PhSiMe_3$ reported, −21 kcal mol^{-1}, is an estimate owing to the lack of reliable experimental data. Other estimates, based on the group increment method, give instead −25 kcal mol^{-1} and ab initio calculations at the STO-3G level −26.6 kcal mol^{-1}: cf. ref 13. We use the value of −25 kcal mol^{-1}. The ΔH° value of reaction 1a is a lower limit obtained by taking the binding energy of $SiMe_3^+$ to cumene equal to that of toluene, reported by (b) Wojtyniak, A. C. M.; Stone, J. A. *Int. J. Mass Spectrom. Ion Processes* **1986**, *74*, 89.

(19) It should be noted that the proton affinity of $c\text{-}C_6H_{10}O$, 201.4 kcal mol^{-1}, see ref 18a, is sufficiently high to allow exothermic deprotonation of **3**.

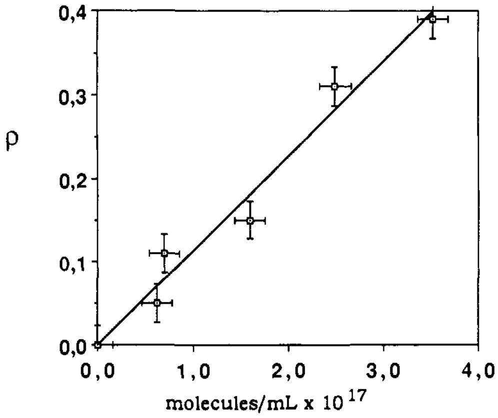


Figure 4. Dependence of the ratio ρ of alkylated to alkyldesilylated products from TSB on the concentration of added c-$C_6H_{10}O$.

Consequently, in the presence of c-$C_6H_{10}O$, formation of **3** is the rate-determining step of the alkyldesilylation process, because any **3** formed is bound to undergo deprotonation. The above-cited studies show that Et_3N accomplishes instead deprotonation of the ipso-silylated adduct, at least in the case of the model $C_6H_6SiMe_3^+$ ion. To the extent to which such behavior can be extended to ions **3**, sufficiently high concentrations of Et_3N can be expected to suppress alkyldesilylation in favor of alkylation. In fact, Table I shows that, at the highest Et_3N pressure used (9.45 Torr), alkylated products predominate over cumene by a factor of 3.3. As a comparison, a ratio as low as 0.34 is measured in the presence of 9.34 Torr of *i*-$C_6H_{10}O$, under otherwise similar conditions.

It is tempting to trace the intermediate efficiency of the bidentate $Me_2N(CH_2)_2OH$ reactant to the intramolecular competition for ions **3** between the Me_2N and the OH nucleophilic centers, leading respectively to alkylation and to alkyldesilylation. This point deserves however further investigation.

Evaluation of the Isomerization Rate. The results discussed in the previous section, expecially those concerning the systems containing c-$C_6H_{10}O$, suggest the possibility of evaluating the rate of conversion of arenium ions **1** into the corresponding ions **3**. In fact, if one assumes that c-$C_6H_{10}O$ deprotonates arenium ions before their conversion into **3** and reacts with the latter exclusively by removing the $SiMe_3$ group,[13] then the ratio ρ of the yields of alkylated and of desilylated products is given simply by $\rho = k_B[B]/k_i$, where [B] is the concentration of c-$C_6H_{10}O$, k_B the bimolecular rate constant of the deprotonation reaction, and k_i the unimolecular rate constant of the $\mathbf{1} \rightarrow \mathbf{3}$ isomerization. To test the validity of the above assumptions, the dependence of ρ on [B] has been investigated over a wide range of c-$C_6H_{10}O$ concentrations. The results, illustrated in Figure 4, are consistent with the assumptions made, showing a linear dependence of ρ on [B], with a zero intercept and a correlation coefficient of 0.99.

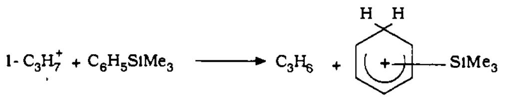
Unless sterically hindered, deprotonation of the arenium ions by c-$C_6H_{10}O$ can reasonably be assumed to proceed with unit collision efficiency, like most exothermic proton-transfer processes on n-type nucleophiles,[20] i.e., $k_B \approx k_{\text{collision}}$. From the value of the latter, calculated according to the ADO model to be 1.8×10^{-9} cm^3 $molecule^{-1}$ s^{-1},[20] one eventually derives $k_i = 1.6 \times 10^9$ s^{-1} at 310 K.

The rate constant derived in this way does not refer to a specific proton 1,2-shift within a single arenium ion, since alkylation (eq 1) gives a mixture of isomeric ions **1** whose isomerization to **3** can require, in general, several proton 1,2-shifts. The k_i constant is rather the weighed average of the individual rate constants of the slowest step in each of the sequences of proton 1,2-shifts required to convert the various isomers **1** into the corresponding isomer **3**.

Despite its composite nature, the k_i value derived from the radiolytic experiments provides otherwise inaccessible information on the rate of proton shifts within gaseous arenium ions. In fact, the k_i values *exceeds by almost 3 orders of magnitude* the previously reported limit of the 1,2-shifts rate constant, which clearly reflects the insufficient time resolution of the mass spectrometric techniques employed.[4,5] On the other hand, our results fail to support the "dynamic" model that envisages extremely fast proton shifts occurring with rate constants as high as 10^{12} s^{-1},[6,7] although such a model could not necessarily extend to the arenium ions investigated.

It is worth noting that the rate of $\mathbf{1} \rightarrow \mathbf{3}$ isomerization is *lower* by a factor of 30 than the rate of collision with the molecules of the bath gas in C_3H_8 at 4 atm.[20] Therefore, it is reasonable to assume that the isomerizing ions are thermally equilibrated with the bath gas and hence that their reaction obeys thermal kinetics. Using the preexponential factor $A = 10^{15.9\pm1.5}$ measured for thermal 1,2-shifts of protons with $C_6H_7^+$ ions in superacid solutions,[1] one can estimate the activation energy of the gas-phase isomerization of ions **1**, $E^* \approx 9.5$ kcal mol^{-1}. Within the obvious limitations arising from the use of a preexponential factor that refers to a different arenium ion, $C_6H_7^+$, studied in a different environment, the estimated value of ca. 9.5 kcal mol^{-1} is in accord with the results of the most accurate ab initio calculations concerning the proton shifts in $C_6H_7^+$, and with the experimental measurements in superacid solutions.

Protodesilylation Process. Formation of benzene and toluene, major ionic products from the reaction of *i*-$C_3H_7^+$ with TSB and respectively with *m*- and *p*-TST, is likely to involve, in addition to ipso attack, preliminary protonation of the aromatic substrate, e.g.



(8)

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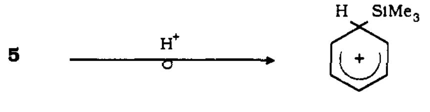
$\Delta H° = -14.7$ kcal mol^{-1},[18] followed by intramolecular isomerization of the ipso-substituted arenium ion and eventually by desilylation upon reaction with a nucleophile present in the systems.



(9)

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It should be noted that even the weakest among such nucleophiles, i.e., water, can react with ion **6** according to the process

$$\mathbf{6} + H_2O \rightarrow C_6H_6 + Me_3SiOH_2^+ \qquad (10)$$

whose exothermicity, ca. 6 kcal mol^{-1}, corresponds to the difference of the bonding energy of $SiMe_3^+$ to water and to benzene.[18] The sequence 8–10 is consistent with the effects of added bases, in particular with the suppression of the protodesilylation process caused by high concentrations of Et_3N, which is known to selectively deprotonate the ipso-substituted ion **6**, yielding again TSB, the starting material. Formation of benzene via the direct reaction **3** is unlikely at the high pressures typical of the radiolytic systems, as suggested, inter alia by the observation that the benzene yields are not depressed when the C_3H_8 pressure is raised from 1 to 4 atm.

Selectivity and Orientation. As expected for a highly reactive and indiscriminate electrophile such as free *i*-$C_3H_7^+$, the alkylation lacks substrate selectivity, e.g., $k_{TSB}/k_{C_6D_6} = 1$, a situation frequencyl occurring in gas-phase aromatic substitution by the lower carbenium ions.[10] Passing to orientation, it should be noted that the isomeric composition of the isopropylated products does not reflect in general the positional selectivity of the electrophile, in that the population of primary arenium ions **1** can profoundly be affected by secondary processes, leading in particular to desilylation. Discussion of the positional selectivity of the reaction must therefore be restricted to those systems that contain relatively high concentrations of Et_3N, where alkyldesilylation is largely suppressed and where the isomeric composition of the products most

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(20) Su, T.; Bowers, M. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press, New York, 1979; Vol. 1, p 83.

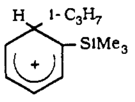
faithfully reproduces the initial orientation.

Two experimental features are salient: First, even at Et_3N pressures in the range of 5–10 Torr, which entirely suppress protodesilylation, alkyldesilylation still occurs with a relative yield of ca. 20%. In the same systems, the isomeric composition of the products is characterized by a remarkably low extent (2%) of substitution ortho to the $SiMe_3$ group.

There are several ways to account for the inability of Et_3N to prevent alkyldesilylation as efficiently as protodesilylation. A first explanation can be based on the occurrence of direct ipso substitution. Whereas direct protonation of the ring position bearing the $SiMe_3$ group yields ion **6**, whose reaction with Et_3N does not lead to desilylation, direct ipso isopropylation (eq 1b) gives instead ion **2**, which can only be desilylated by Et_3N, yielding cumene. According to this view, the fraction of alkyldesilylation that cannot be suppressed by Et_3N reflects the extent of ipso alkylation of TSB.

Independent evidence for the role of ipso alkylation is provided by the significant proportions (20–27%) of *p*-cymene from the isopropylation of *p*-TST in the presence of Et_3N, although it could be argued that the methyl group of *p*-TST specifically activates the carbon bearing the $SiMe_3$ group.

An alternative explanation proceeds from the remarkably low extent of isopropylation ortho to the $SiMe_3$ group of TSB, which cannot be traced to steric hindrance to the $i\text{-}C_3H_7^+$ attack, since other gaseous cations of comparable size, such as $(CH_3)_2F^+$ and $CH_3O^+(H)NO_2$, give significant proportions of ortho-substituted isomers, respectively, 18% (Table II) and 37%.[21] Steric factors could instead hinder the subsequent deprotonation of the arenium ion **8** formed via a fast, energetically favored[13] proton 1,2-shift from the primary adduct **7**. The steric compression arising from the coplanarity of the $SiMe_3$ and of the $i\text{-}C_3H_7$ substituent in the deprotonated product **9** could affect the selectivity in the Et_3N reaction in favor of desilylation, inverting the bias in favor of deprotonation noted in the sterically unhindered arenium ion **6**.[22]



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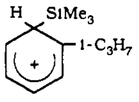

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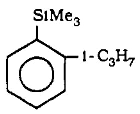

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Such interpretation takes into account the ability of Et_3N to bind to $SiMe_3^+$, demonstrated by ICR spectrometry,[13] and has the advantage of accounting both for the failure of Et_3N to suppress alkyldesilylation as efficiently as protodesilylation and for the remarkably low extent of substitution ortho to the $SiMe_3$ group, a feature noted as well in the alkylation of *p*-TST. In this connection, we note that steric hindrance to deprotonation has previously been reported in the gas-phase isopropylation of crowded arenes.[23]

A clear-cut decision between the explanations outlined above of the failure of Et_3N to entirely suppress alkyldesilylation cannot at present be made, especially since they are not mutually exclusive. It can only be asserted with a sufficient degree of confidence that the desilylated products still detectable in the presence of 5–10 Torr of Et_3N arise from the direct attack on the carbon bearing the $SiMe_3$ group and/or from the alkylation of the ortho positions. It follows that the combined extent of ipso and ortho substitution of TSB by $i\text{-}C_3H_7^+$ should amount to ca. 20%.

Acknowledgment. This work was supported by the Italian Consiglio Nazionale delle Ricerche (CNR) and by the Ministero della Università e della Ricerca Scientifica e Tecnologica (MURST). We thank M. Speranza for useful discussions.

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(21) Attinà, M.; Cacace, F.; Ricci, A. *Gazz. Chim. Ital.* **1989**, *119*, 217.

(22) The postulated dependence of the deprotonation/desilylation branching ratio in the Et_3N reactivity on the nature of the arenium ion is not unprecedented, e.g., there is evidence that $Me_2N(CH_2)_2OH$, which acts exclusively as a desilylating reagent toward 6, see refs 11 and 12, can deprotonate, as well as desilylate, ions 3.

(23) Aliprandi, B.; Cacace, F.; Cipollini, R. *Radiochim. Acta* **1982**, *32*, 1072.

Gas-Phase Proton-Transfer Reactions between Alkoxide Anions

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Abstract: Reaction efficiencies for proton transfer between alkoxide anions and neutral alcohols have been measured in an ion cyclotron resonance spectrometer, using a competition kinetics technique. The efficiencies for identity proton-transfer reactions are measurably less than 0.5, which is the simple statistical prediction for a thermoneutral reaction with no energetic barrier. In addition, the trend in reaction efficiencies for exothermic proton transfers is consistent with the presence of a substantial Marcus intrinsic barrier. An energetic barrier of this magnitude is not consistent with a surface which is believed to have little or no barrier. The results are consistent, however, with recent quasi-classical trajectory calculations which show that efficiencies for reactions on a barrierless surface can be slower than expected.

I. Introduction

While sophisticated equilibrium studies have significantly enhanced our understanding of the thermodynamics that govern gas-phase proton-transfer reactions,[1] the corresponding kinetics are less well characterized. Certain characteristics are known to decrease reaction rates, including charge delocalization and steric hindrance.[2] For example, gas-phase proton transfers involving delocalized carbanions are often slow, occurring on only a small fraction of ion–molecule collisions.[2a,b] These rate decreases have been attributed to considerable energetic barriers on the potential

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(1) For example, see: (a) McMahon, T. B.; Kebarle, P. *J. Am. Chem. Soc.* **1985**, *107*, 2612. (b) Larson, J. W.; McMahon, T. B. *J. Phys. Chem.* **1984**, *88*, 1083. (c) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1984**, *106*, 517. (d) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1983**, *105*, 2944. (e) Yamdagni, R.; Kebarle, P. *J. Am. Chem. Soc.* **1971**, *93*, 7139. (f) Caldwell, G.; Rozeboom, M. D.; Kiplinger, J. P.; Bartmess, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 4660.

(2) (a) Han, C.-C.; Brauman, J. I. *J. Am. Chem. Soc.* **1989**, *111*, 6491. (b) Meyer, F. K.; Pellerite, M. J.; Brauman, J. I. *Helv. Chem. Acta* **1981**, *64*, 1058. (c) Farneth, W. E.; Brauman, J. I. *J. Am. Chem. Soc.* **1976**, *98*, 7891. (d) Lias, S. G.; Shold, D. M.; Ausloos, P. *J. Am. Chem. Soc.* **1980**, *102*, 2540. (e) Jasinski, J. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1980**, *102*, 2906. (f) Meot-Ner, M. *J. Am. Chem. Soc.* **1982**, *104*, 5. (g) Rakshit, A. B.; Warneck, P. *J. Chem. Phys.* **1981**, *74*, 2853.

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