

Internal Solvation Effects on the Reactivity of  $\alpha,\omega$ -Diphenylalkanes toward  $\text{Me}_3\text{C}^+$  IonsMaria Elisa Crestoni,<sup>\*,†</sup> Simonetta Fornarini,<sup>†</sup> and Dietmar Kuck<sup>‡</sup>*Dipartimento degli Studi di Chimica e Tecnologia delle Sostanze Biologicamente Attive, Università "La Sapienza", P.le A. Moro 5, I-00185 Roma, Italy, and Fakultät für Chemie der Universität Bielefeld, D-33501 Bielefeld, Germany**Received: June 10, 1994; In Final Form: October 17, 1994*<sup>⊗</sup>

The reactivity of  $\alpha,\omega$ -diphenylalkanes ( $1 \leq n \leq 4$ ) toward  $\text{Me}_3\text{C}^+$  ions has been investigated with the radiolytic technique at 720 Torr, at temperatures of 47 and 120 °C. The intramolecular isotopic discrimination of  $\text{Me}_3\text{C}^+$ , favoring attack at the unlabeled ring of  $\text{C}_6\text{H}_5(\text{CH}_2)_2\text{C}_6\text{D}_5$  by a factor of 1.5 at 120 °C, contrasts with the lack of intermolecular isotopic discrimination, reflected by the same reactivity toward  $(\text{C}_6\text{H}_5\text{CH}_2)_2$  and  $(\text{C}_6\text{D}_5\text{CH}_2)_2$ . Competition experiments show an appreciably higher reactivity of  $\text{Ph}(\text{CH}_2)_n\text{Ph}$  ( $n = 2-4$ ) relative to toluene and diphenylmethane (DPM), but, when  $\text{Ph}(\text{CH}_2)_n\text{Ph}$  ( $n = 3, 4$ ) or  $(3-\text{CH}_3\text{C}_6\text{H}_4)(\text{CH}_2)_2\text{C}_6\text{H}_5$  compete with  $\text{Ph}(\text{CH}_2)_2\text{Ph}$ , relative reactivities level off. The lack of substrate selectivity, in contrast to an intramolecular discrimination in the *tert*-butylation of  $(3-\text{CH}_3\text{C}_6\text{H}_4)(\text{CH}_2)_2\text{C}_6\text{H}_5$  of a factor of 2, together with the related variation of kinetic isotope effects, points out the kinetic role of the collision complex **1** from  $\text{Me}_3\text{C}^+$  and diphenylalkanes. The additional ("spectator") ring of the higher homologues  $\text{Ph}(\text{CH}_2)_n\text{Ph}$  ( $n = 2-4$ ) prevents dissociation of **1**, making its formation irreversible and causing *tert*-butylation to occur at the encounter rate, in contrast to DPM, whose second ring appears essentially inert. Experiments involving substitution by  $\text{Me}_3\text{Si}^+$  at 120 °C show that this electrophile attacks preferably the unlabeled ring of  $\text{C}_6\text{H}_5(\text{CH}_2)_2\text{C}_6\text{D}_5$  by a factor of 1.5, consistent with the 1.4 times higher reactivity toward  $(\text{C}_6\text{H}_5\text{CH}_2)_2$  with respect to  $(\text{C}_6\text{D}_5\text{CH}_2)_2$ . In this case, the isotopic discrimination is traced to the competition between desilylation and deprotonation of intermediate *ipso*-silylated arenium ions.

## Introduction

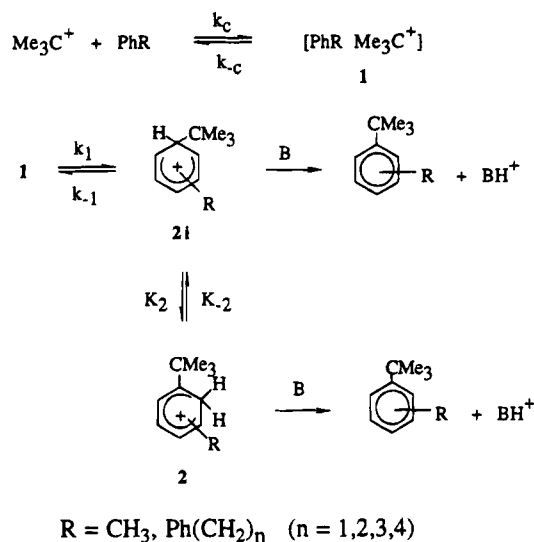
Despite the wealth of data and the sustained interest in the understanding of the multistep sequence of electrophilic aromatic substitution,<sup>1,2</sup> significant mechanistic facets have not yet been fully ascertained. Whereas direct experimental evidence testifies the existence of  $\sigma$ -complex intermediates, providing detailed information on their structure and energetics,<sup>2,3</sup> the existence and the features of a  $\pi$ -complex intermediate in the reaction coordinate are far less defined and have been the object of a long-standing debate.<sup>2,4</sup> In the gas phase the occurrence of noncovalent interactions in purely electrostatically bound ion-neutral complexes has been inferred from studies of unimolecular decomposition<sup>5-7</sup> and alkyl side chain isomerization<sup>8,9</sup> of certain alkybenzenium ions. Strong evidence for the kinetic role of a noncovalent encounter complex<sup>10</sup> in electrophilic aromatic substitution comes from studies performed in solution<sup>11,12</sup> and in the gas phase,<sup>13</sup> implying its rate-determining formation when positional but not substrate selectivity is observed. In some cases transient formation of a chelate-type adduct by interaction of the cation with a suitable electron-rich substituent has been invoked to account for anomalously high *ortho* substitution.<sup>14,15</sup> The environmental effects involved in condensed phase, such as ion-pairing and solvation interactions, affect the nature and the reactivity of the ionic electrophile and prevent the development of generalized reaction models, which accounts for the growing interest in gas-phase approaches aimed at establishing the intrinsic properties of unsolvated ionic species. Among these methodologies, the radiolytic technique<sup>16,17</sup> allows the ionic reagent to be generated in the gas phase and to be completely thermalized by multiple unreactive collisions with the dense bath gas (up to atmospheric pressure)<sup>18</sup>

prior to a reactive encounter with the aromatic substrate. In the high-pressure range, the excess internal energy gained from the ion-molecule electrostatic interaction by the collision complex can be released to the buffer gas, and the reactivity pattern, driven by thermal activation, becomes comparable with that prevailing in solution. The actual isolation of the neutral end products (together with the use of classical mechanistic probes, such as temperature-dependence studies and isotopic labeling) makes the radiolytic technique a powerful and simplified approach for meaningful comparison with solution chemistry studies.

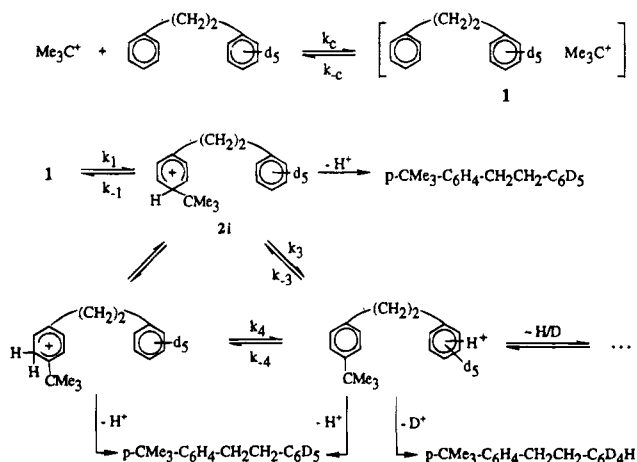
The scope of this study is to gather new insights into the potential energy surface of aromatic substitution by the gaseous  $\text{Me}_3\text{C}^+$  ion, a mild electrophile whose reactivity toward arenes has been the focus of detailed investigations<sup>19-21</sup> (Scheme 1). Recently, new aspects have emerged from consideration of the kinetic features of the gas-phase *tert*-butylation of toluene and of  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$  (DPE), i.e. relative reactivities and their H/D kinetic isotope effect (KIE).<sup>21</sup> The finding of an overall KIE in the *tert*-butylation of toluene,<sup>20</sup> measured by a  $k_{\text{C}_7\text{H}_8}/k_{\text{C}_7\text{D}_8}$  ratio of 1.5 at 120 °C, has been ascribed to the role of the *ipso*-substituted arenium ion **2i**. The  $\sigma$ -complex may isomerize to **2** via 1,2-H(D) shift or back-dissociate to the collision complex **1** (or even to the free reactants). The observation of an interannular H/D discrimination during the attack of  $\text{Me}_3\text{C}^+$  on the  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{C}_6\text{D}_5$  (DPE-*d*<sub>5</sub>) molecule,<sup>21</sup> by a factor of 1.5 at 120 °C, points out that also *tert*-butylation of DPE is endowed with some reversible character (Scheme 2). Since methyl and  $\beta$ -phenylethyl groups have a similar activating power, the observation of a higher *tert*-butylation rate of DPE than of toluene ( $k_{\text{DPE}}/k_{\text{toluene}} = 2.9$ , at 120 °C) can be rationalized only by considering the kinetic role of the collision complex **1**. The presence of a second phenyl ring ("spectator" ring) in the DPE molecule can in fact be envisioned as a factor that favors

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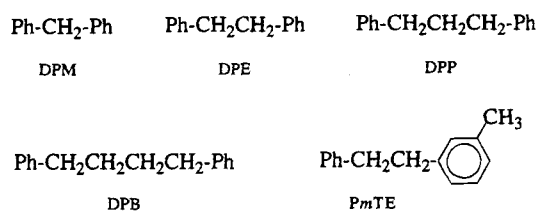
## SCHEME 1



## SCHEME 2



## CHART 1



the formation of ion **1** by trapping  $\text{Me}_3\text{C}^+$  in a better solvated (and hence more stable) complex, as compared to the analogous ion **1** originating from toluene. In this perspective, ions **1** from DPE should not be prone to easy dissociation, i.e.  $k_{-c} < k_1$ , rendering *tert*-butylation irreversible. On this basis, the present work is aimed at verifying whether (and to what extent) the "spectator" phenyl ring decreases the tendency of  $\text{Me}_3\text{C}^+$  to escape from collision complex **1** in the series of  $\alpha,\omega$ -diphenylalkanes containing one to four methylene units. The effects of such more effective complexation are expected to reduce, and eventually suppress, those features that characterize *tert*-butylation as a selective and reversible reaction. Chart 1 illustrates the selected substrates and the abbreviations used for their identification.

The study has been extended to aromatic substitution by an analogous planar cation, the gaseous  $\text{Me}_3\text{Si}^+$  ion,<sup>22</sup> where the ability of the  $\text{Me}_3\text{Si}$  group to enhance the basicity of the *ipso*

**TABLE 1: Gas-Phase Reaction of  $\text{Me}_3\text{X}^+$  ( $\text{X} = \text{C}, \text{Si}$ ) Ions with DPE- $d_5$  and PhMe/PhMe- $d_8$  or DPE/DPE- $d_{10}$  Mixtures**

system composition (Torr) <sup>a</sup>					$\text{Me}_3\text{C}$ -substitution products			
substrate	triethyl-amine	bulk gas	temp (°C)	reactant ion: $\text{Me}_3\text{X}^+$	isomers		$k_{\text{H}}/k_{\text{D}}^b$	
					<i>meta</i>	<i>para</i>	<i>meta</i>	<i>para</i>
DPE- $d_5$ , 0.4		690	47	X = C	44	56	1.7	1.4
DPE- $d_5$ , 0.4	0.5	690	47	X = C	44	56	1.5	1.3
DPE, 0.6								
DPE- $d_{10}$ , 0.6	0.4	680	120	X = C	60	40	1.0	1.1
DPE- $d_5$ , 0.6	0.4	660	120	X = C	60	40	1.5	1.6
PhMe, 0.9								
PhMe- $d_8$ , 0.9	0.3	700	120	X = C	53	47	1.4	1.5
DPE, 0.5								
DPE- $d_{10}$ , 0.6	0.9	690	120	X = Si	30	70	1.4	1.4
DPE- $d_5$ , 1.6	0.8	700	120	X = Si	27	73	1.5	1.5

<sup>a</sup> All gaseous systems contained  $\text{O}_2$  (10 Torr). The bulk gas was  $i\text{-C}_4\text{H}_{10}$  ( $\text{X} = \text{C}$ ) or a 35/1 mixture of  $\text{CH}_4/(\text{CH}_3)_3\text{Si}$ . <sup>b</sup>  $k_{\text{H}}/k_{\text{D}} = ([\text{PH}][\text{SD}])/([\text{PD}][\text{SH}])$ , where  $\text{P}_\text{H}$  and  $\text{P}_\text{D}$  are the products of the attack at the unlabeled ( $\text{S}_\text{H}$ ) and the deuterated ( $\text{S}_\text{D}$ ) substrate or ring.

carbon,<sup>23</sup> due to electronic factors, is the key difference with respect to the  $\text{Me}_3\text{C}$  group.

## Experimental Section

**Materials.**  $i\text{-C}_4\text{H}_{10}$ ,  $\text{CH}_4$ , and  $\text{O}_2$  were research-grade (99.98 mol %) gases from Matheson Gas Products Inc. DPE- $d_5$ , PmTE, DPP, and DPB were prepared as described in ref 24;  $(\text{C}_6\text{D}_5\text{-CH}_2)_2$  (DPE- $d_{10}$ ) has been obtained by oxidative coupling of  $\text{C}_6\text{D}_5(\text{CH}_2)_2\text{MgBr}$ .<sup>24c</sup> Their identity and purity were established by GC-MS and NMR spectrometry. All other chemicals used were purchased from commercial sources.

**Radiolytic Reactions.** The gaseous samples were prepared according to standard vacuum procedures in sealed Pyrex vessels (250 mL). Since the competition experiments required a precise knowledge of the relative amounts of the reactants, carefully weighed combinations were prepared, as stock amounts from which the desired quantity for each experiment was taken, and a long equilibration time (5–10 h) was allowed for complete vaporization of the reactants. The irradiations, which were run to less than 1% substrate conversion into products, were performed in a 220 Gammacell (Nuclear Canada Ltd.) at a total dose of  $1 \times 10^4$  Gy, at the rate of ca.  $2 \times 10^4$  Gy  $\text{h}^{-1}$ . The radiolytic products were extracted by repeated freeze-thaw cycles with ethyl acetate and analyzed by GC-MS using the following columns mounted on a Hewlett-Packard 5890 gas chromatograph in series with a Model 5970B mass-selective detector: (i) a 30-m-long, 0.25-mm-i.d. polyethylene glycol (Supelcowax 10) bonded-phase column (0.25- $\mu\text{m}$  film thickness) from Supelco Co.; (ii) a 50-m-long, 0.20-mm-i.d. fused silica capillary column, coated with a 0.50- $\mu\text{m}$  cross-linked methyl-silicone film (PONA column from Hewlett-Packard); (iii) a 100-m-long, 0.25-mm-i.d. silica column coated with a 0.50- $\mu\text{m}$  film of nonpolar-bonded methyl silicone (Petrocol column from Supelco Co.).

## Results

The composition of the irradiated systems and the positional and substrate selectivity of the gaseous  $\text{Me}_3\text{X}^+$  ( $\text{X} = \text{C}, \text{Si}$ ) ions are summarized in Tables 1 and 2. The reactions, carried out at nearly atmospheric pressure, are already well-known processes, whose ionic character is ensured by the presence of a large excess (10 Torr) of  $\text{O}_2$  as an effective radical scavenger. The absolute radiochemical yields, expressed by their  $G_{+\text{M}}$  value ( $\mu\text{mol J}^{-1}$ ), are found to be close to the known  $G_{+\text{M}}$  values of the reactant cations and decrease with the concentration of any added base/nucleophile, as consistent with the ionic origin of

**TABLE 2: Gas-Phase Reactions of Ph<sub>2</sub>(CH<sub>2</sub>)<sub>n</sub> (n = 1, 2, 3, 4) and Toluene with Me<sub>3</sub>C<sup>+</sup> Ions**

system composition (Torr) <sup>a</sup>			<i>tert</i> -butylation product of S <sub>1</sub> (P <sub>1</sub> ) and S <sub>2</sub> (P <sub>2</sub> )				apparent <sup>b</sup> k <sub>1</sub> /k <sub>2</sub>
substrates		triethyl-amine	P <sub>1</sub>		P <sub>2</sub>		
S <sub>1</sub>	S <sub>2</sub>		<i>meta</i>	<i>para</i>	<i>meta</i>	<i>para</i>	
DPE, 0.5	PhMe, 0.7	0.4	66	34	46	54	4.5
DPE, 0.4	PhMe, 0.8	2.2	54	46	36	64	4.6
DPP, 0.7	PhMe, 0.8	0.4	34	66	45	55	4.7
DPP, 0.3	PhMe, 0.8	2.0	26	74	38	62	4.1
DPP, 0.6	PhMe, 1.0	0.2	31	69	49	51	6.1 <sup>c</sup>
DPP, 0.3	DPE, 0.3		49	51	69	31	1.0
DPP, 0.4	DPE, 0.4	0.3	35	65	60	40	1.0
DPE, 0.3	<i>Pm</i> TE, 0.3		60	40	59 <sup>d</sup>	41 <sup>d</sup>	1.0 <sup>e</sup>
DPE, 0.4	<i>Pm</i> TE, 0.4	0.5	61	39	63 <sup>d</sup>	37 <sup>d</sup>	1.0 <sup>f</sup>
DPE, 0.4	<i>Pm</i> TE, 0.5	3.2	54	46	55 <sup>d</sup>	45 <sup>d</sup>	1.1 <sup>g</sup>
DPE, 0.4	DPB, 0.5	0.4	61	39	43	57	1.0
DPE, 0.4	DPM, 0.4		68	32	68	32	1.9
DPE, 0.4	DPM, 0.4	0.3	62	38	56	44	2.2

<sup>a</sup> All gaseous systems contained O<sub>2</sub> (10 Torr) as a radical scavenger and *i*-C<sub>4</sub>H<sub>10</sub> (700 Torr) as the bulk gas and were submitted to  $\gamma$ -radiolysis at 120 °C. <sup>b</sup>  $k_1/k_2 = ([P_1][S_2])/([P_2][S_1])$ . <sup>c</sup> 50 Torr MeCl added to the gaseous system. <sup>d</sup> *meta* and *para* values are for *tert*-butylation at the unsubstituted phenyl ring of *Pm*TE. <sup>e</sup> Alkylation at the *m*-Me substituted ring yields a 100% *tert*-butylated product at position 5, which is 2.0 times more abundant than the substitution products at the unsubstituted ring. <sup>f</sup> The *m*-Me-substituted ring yields a 100% *tert*-butylation product at position 5, which is 2.4 times more abundant than the overall substitution products at the unsubstituted ring. <sup>g</sup> *tert*-butylation at the *m*-Me-substituted ring yields a 97% substitution product at position 5 and a 3% substitution product at position 4, whose combined yields exceed by a factor of 2.0 those relative to *tert*-butylation of the unsubstituted ring.

the reaction. In accord with previous reports, no *ortho* substitution results from the attack of the charged electrophiles Me<sub>3</sub>X<sup>+</sup> on the selected aromatic substrates. The *meta/para* distribution is markedly influenced by the temperature and the base concentration. Except where specifically noted, reactions were run in the presence of NEt<sub>3</sub>, a strong base (proton affinity (PA) = 232.3 kcal mol<sup>-1</sup>; gas-phase basicity (GB) = 224.5 kcal mol<sup>-1</sup>)<sup>25</sup> able to intercept Me<sub>3</sub>C<sup>+</sup> ions and to efficiently deprotonate alkylated arenium ions. At higher temperature and lower concentration of NEt<sub>3</sub>, a noticeable enhancement of *meta* substitution is apparent. The isomeric composition of products appears to depend on the intrinsic features of the aromatic substrate; for example, at 120 °C, at nearly constant partial pressure of NEt<sub>3</sub> (0.24–0.42 Torr), the *2para/meta* ratio decreases from 3.7 (DPP) to 2.6 (DPB), 2.3 (toluene), 1.6 (DPM), and down to 1.3 (DPE).

The results of the competitive *tert*-butylation of the DPE/DPE-*d*<sub>10</sub> and C<sub>7</sub>H<sub>8</sub>/C<sub>7</sub>D<sub>8</sub> pairs are reported in Table 1, which gives the apparent  $k_H/k_D$  ratios (values are derived from the relative yields of unlabeled and deuterated products, normalized by the amounts of the respective substrates). As observed previously, the rate of alkylation of the DPE-*d*<sub>5</sub> rings is different, the substitution at the unlabeled one being favored at 47 °C by a factor of 1.7, which decreases to 1.5 in the presence of added base as well as at elevated temperature (120 °C). A comparable  $k_H/k_D$  ratio (1.5) is measured in the competitive alkylation of C<sub>7</sub>H<sub>8</sub>/C<sub>7</sub>D<sub>8</sub>. The intermolecular isotopic discrimination between DPE and DPE-*d*<sub>10</sub> vanishes under similar experimental conditions (that is, at 120 °C and with 0.30–0.45 Torr of added NEt<sub>3</sub>), where a  $k_H/k_D$  value equal to 1.0 is observed. The final entries in Table 1 illustrate the competitive trimethylsilylation of the C<sub>6</sub>H<sub>5</sub> and C<sub>6</sub>D<sub>5</sub> rings in the molecule of DPE-*d*<sub>5</sub> and of the DPE/DPE-*d*<sub>10</sub> mixture studied at 120 °C, in the presence of 0.8–0.9 Torr of NEt<sub>3</sub>. The clear bias toward trimethylsilylation of the unlabeled ring of DPE-*d*<sub>5</sub>, reflected in a value of the intra-

molecular  $k_H/k_D$  ratio of 1.5, remains unchanged when the isotopic discrimination originates from an intermolecular competition, as demonstrated by the comparable  $k_{DPE}/k_{DPE-d_{10}}$  ratio of 1.4.

The first entries in Table 2 show the results of competition experiments aimed at evaluating the reactivity of  $\alpha,\omega$ -diphenylalkanes, Ph(CH<sub>2</sub>)<sub>n</sub>Ph, *n* = 1–4, relative to a comparably activated aromatic substrate (toluene), toward Me<sub>3</sub>C<sup>+</sup> ions at 120 °C. The appreciably higher reactivity of DPE and of DPP with respect to toluene is shown by  $k_S/k_T$  ratios of 4.5 and 4.7, respectively, in the presence of ca. 0.4 Torr of NEt<sub>3</sub>. With increasing base concentration (2.0–2.2 Torr of NEt<sub>3</sub>) the relative reactivities of DPE and DPP are still similar, both substrates reacting about 4 times faster than toluene.

When the apolar *i*-C<sub>4</sub>H<sub>10</sub> bulk gas is in part replaced by the polar MeCl, the gaseous environment allows a better “solvation” of the reactant Me<sub>3</sub>C<sup>+</sup> ions. Thus, the addition of 50 Torr of MeCl to the bulk *i*-C<sub>4</sub>H<sub>10</sub> gas brings about an increase of the  $k_{DPP}/k_{\text{toluene}}$  ratio from 4.7 to 6.1.

The  $k_{DPE}/k_{DPM}$  ratio (2.2) provides an indirect comparison of DPM with toluene. DPM appears to react twice as fast as toluene at similar base concentration. When the competition involves DPE vs Ph(CH<sub>2</sub>)<sub>n</sub>Ph (*n* = 3–4) and vs *Pm*TE under comparable conditions, the substrate selectivity vanishes; that is, all investigated  $\alpha,\omega$ -diphenylalkanes display the same reactivity when allowed to directly compete for the electrophile. The alkylation at the methylated ring of *Pm*TE, twice as fast as at the unsubstituted phenyl ring, occurs only at position 5 (100%) in the presence of 0.47 Torr at NEt<sub>3</sub>, changing to 97% substitution at position 5 and 3% substitution at position 4 when the amount of NEt<sub>3</sub> is increased to 3.2 Torr.

## Discussion

The processes leading to formation of the charged reactants Me<sub>3</sub>X<sup>+</sup> (X = C, Si) upon  $\gamma$ -radiolysis of the gaseous precursors, isobutane and a mixture of CH<sub>4</sub>/(CH<sub>3</sub>)<sub>4</sub>Si (35:1 molar ratio), respectively, are well documented, as a result of extensive mass-spectrometric<sup>26–28</sup> and radiolytic studies.<sup>19,22,29</sup> The processes promoted by the electrophilic attack of the Me<sub>3</sub>C<sup>+</sup> ions on an aromatic substrate can be outlined as a multistep sequence (Schemes 1 and 2), wherein several factors influence the relative rate of individual steps. Following the formation of the collision complex **1**, the intermediate arenium ion **2i** is formed, which can undergo back-dissociation, 1,2-H(D) shift, and/or deprotonation by a base B. In addition to the above reactions, the ions **2i** formed from electrophilic attack of a phenyl ring of Ph(CH<sub>2</sub>)<sub>n</sub>Ph can undergo still another process. In fact, the spectator ring of bicyclic substrates has been shown to perform an active role in the overall scheme, e.g. thermal ( $\beta$ -phenylethyl)arenium ions from DPE-*d*<sub>5</sub> display a significant interannular proton-exchange process ( $k_3$ ,  $k_4$  in Scheme 2). The occurrence of such reactions is indicative of a tendency of the methylene chain to fold, allowing the spectator phenyl ring to approach the arenium ring. By the same arguments, it is conceivable that solvation by the spectator ring can stabilize the collision intermediate **1**, increasing the electron density available to the complexed Me<sub>3</sub>C<sup>+</sup> ion, whose binding energy should therefore exceed the value 12 kcal/mol estimated for the [Me<sub>3</sub>C<sup>+</sup> C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>] collision complex.<sup>30,31</sup> Conceivably, the  $\sigma$ -bonded complex **2** should benefit as well from a stabilizing effect exerted by the spectator ring, attaining an electrostatic stabilization whose extent can be estimated from the proton affinity difference ( $\Delta$ PA) between the selected diphenylalkane and toluene. In the following discussion the influence of the spectator ring will therefore be interpreted as arising from

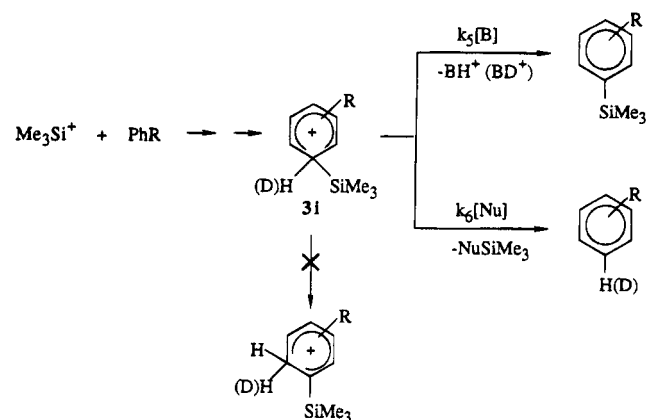
intramolecular electrostatic interactions, a kind of "micro-solvation" effect. Alternatively, one may attempt to analyze the gas-phase reactivity of  $\text{Ph}(\text{CH}_2)_n\text{Ph}$  within the framework of electronic substituent constants, established in solution. However, any specific effects due to differential stabilization of the arenium moiety by the different  $\text{Ph}(\text{CH}_2)_n$  substituents are expected to be small, on the basis of the close similarity of the  $\sigma_p^+$  values of  $\text{PhCH}_2$ , and  $\text{Ph}(\text{CH}_2)_2$  with that of a methyl substituent.<sup>2</sup> Thus, the simple use of substituent parameters, borrowed from solution chemistry, fails to account for the observed reactivity order of  $\text{Ph}(\text{CH}_2)_n\text{Ph}$  toward  $\text{Me}_3\text{C}^+$  ions in the gas phase.

#### H/D Isotopic Discrimination of $\text{Me}_3\text{X}^+$ ( $\text{X} = \text{C}, \text{Si}$ ) Ions.

In order to substantiate the hypothesis of rate-determining formation of **1** from the *tert*-butylation of DPE, the relative reactivity of the DPE/DPE-*d*<sub>10</sub> mixture has been investigated, with the expectation that, should hydron migration take place in a kinetically relevant step of the reaction, this would result in a sizeable KIE. As both the charged reaction intermediate **2i** and ensuing isomeric species are to be deprotonated in order to yield neutral end products, the presence of an efficient proton acceptor such as  $\text{NEt}_3$  has been ensured in these experiments.  $\text{NEt}_3$  fulfills the requisite of performing a fast deprotonation<sup>32</sup> of arenium ions, unaffected by primary KIE,<sup>33</sup> owing to the large difference in basicity between *tert*-butylated substrates ( $\text{GB} \leq 190 \text{ kcal mol}^{-1}$ )<sup>34</sup> and  $\text{NEt}_3$ . The observed  $k_{\text{DPE}}/k_{\text{DPE-}d_{10}}$  ratio of 1.0, at 120 °C, in the presence of  $\text{NEt}_3$  (0.45 Torr), therefore implies that intra- or interannular proton transfer processes do not occur in the rate-determining step of the overall reactive sequence. Such a finding can be evaluated against the sizeable H/D isotopic discrimination associated both to the 1,2-H(D) shift following the *tert*-butylation of toluene<sup>20</sup> and to the interannular hydron migration in DPE-*d*<sub>5</sub>.<sup>21</sup> Such combined information provides crucial mechanistic insight, showing that the spectator ring present in DPE hinders the dissociation of the noncovalent complex **1** into free  $\text{Me}_3\text{C}^+$  and the arene. Referring to the general Scheme 1, the conclusion may be drawn that whenever the structural or electronic features of the arene make  $k_1 > k_{-c}$ , formation of the electrostatic complex **1** becomes irreversible and hence alkylation occurs at the encounter rate. However, the conversion of complex **1** into an *ipso*-substituted arenium ion **2i** is a reversible process, both for toluene and for DPE; that is,  $k_{-1}$  is not negligible with respect to  $k_2$  and to  $k_{\text{B}}[\text{B}]$ . This allows one to detect an otherwise elusive KIE involving an intramolecular hydron migration in the DPE-*d*<sub>5</sub> molecule. The temperature dependence of such KIEs, emerging from the *tert*-butylation of DPE-*d*<sub>5</sub>, is not pronounced or slightly negative. Again, this is as expected from a hydron migration process competing with  $\text{Me}_3\text{C}^+$  detachment from **2i** ( $k_{-1}$ ).<sup>20</sup>

The results reported as last entries of Table 1 allow an interesting comparison between *tert*-butylation and trimethylsilylation. The kinetic pattern of  $\text{Me}_3\text{Si}^+$  differs from that of  $\text{Me}_3\text{C}^+$  in that the trimethylsilylated  $\sigma$ -complexes do not undergo back-dissociation. The greater ease of desilylation than of *tert*-butylation of arenes<sup>23b</sup> upon attack of charged reactants and the reluctance of the *ipso* **3i** intermediates to isomerize by 1,2-H(D) shift<sup>20</sup> (Scheme 3) have been ascribed to the enhanced basicity of the trimethylsilylated carbon of the aromatic ring. The effect exerted by the  $\text{SiMe}_3$  group on the thermodynamic basicity of the *ipso* position with respect to that of the adjacent ones makes arenium ions **3i** relatively long lived intermediates. Their fate depends upon the competition between desilylation, by ubiquitous oxygenated nucleophiles, and deprotonation by strong nitrogen bases. In a recent kinetic study the observation of a H/D KIE in the trimethylsilylation of toluene has been

SCHEME 3



reported,<sup>35</sup> its value depending on the strength and the concentration of the added base. Because of the irreversible character of silylation, such a primary KIE cannot derive from a rate-determining hydron transfer, but it rather results from the competition between a deprotonation process which is sensitive to isotopic labeling ( $k_5$ ) and a desilylation process ( $k_6$ ) as shown in Scheme 3. The data in Table 1 support this explanation, since the intramolecular KIE of 1.5 in the silylation of DPE-*d*<sub>5</sub> at 120 °C is approximately equal to the KIE value of 1.4 emerging from the intermolecular DPE vs DPE-*d*<sub>10</sub> competition. In fact, if the factor which controls the silylation is the competition between removal of H/D vs removal of the  $\text{Me}_3\text{Si}$  group in the *ipso*-silylated arenium ion **3i** (Scheme 3), the isotopic composition ( $\text{C}_6\text{D}_5$  vs  $\text{C}_6\text{H}_5$ ) of the spectator ring is irrelevant. If the competition involves exclusively the irreversibly silylated ring position, the same relative reactivity ratio between unlabeled and deuterated rings is expected. This is indeed observed, both for the intra- and intermolecular competition.

**Substrate and Positional Selectivity.** The picture that emerges from the competition experiments summarized in Table 2 provides evidence for the postulated kinetic role of a persistent noncovalent collision complex. All selected diphenylalkanes,  $\text{Ph}(\text{CH}_2)_n\text{Ph}$  ( $n = 2-4$ ) and *PmTE*, appear to react at the same rate; that is, their intermolecular competition is independent of chain length for  $n \geq 2$ . Such behavior is consistent with a kinetic pattern where the barrier to the formation of the  $\sigma$ -complex **2i** ( $E^*$ ) is lower than the barrier to back dissociation ( $E^\circ$ ) of the electrostatically bound adduct **1**. The factors that determine the balance between the two barriers depend on the combination of the effects able to stabilize the charge of the gaseous ions, such as inductive, conjugative, and polarization effects. The outcome of this investigation seems to point out the role of electrostatic interactions in early noncovalent adducts. In those cases where the length of the chain (DPE and *PmTE*,  $n = 2$ ; DPP,  $n = 3$ ; DPB,  $n = 4$ ) allows the approach and the reorientation of the spectator ring, formation of **1** becomes the rate-determining step. In comparing  $\text{Ph}(\text{CH}_2)_n\text{Ph}$  ( $n = 2-4$ ) with an aromatic substrate such as toluene and DPM (which both lack a spectator ring capable of providing additional stabilization to the electrostatic adduct **1**),  $\text{Me}_3\text{C}^+$  ions show again substrate selectivity, favoring the higher ( $n \geq 2$ ) diphenylalkanes. The measured relative rate constants (e.g.  $k_{\text{DPE}}/k_{\text{toluene}} = 4.5$ ;  $k_{\text{DPE}}/k_{\text{DPM}} = 2.2$ ) indicate that the reactions of toluene and DPM are not governed by the collision frequencies ( $k_c$ ); rather, the respective noncovalent complexes **1** may undergo back-dissociation into free reagents, at variance with the corresponding complexes from DPE and DPP. At the same time the  $k_{\text{DPE}}/k_{\text{DPM}} = 2.2$  ratio excludes that polarization effects

may account for the observed reactivity pattern, owing to the comparable polarizability values of DPM and of  $\text{Ph}(\text{CH}_2)_n\text{Ph}$  ( $n = 2-4$ ).

Viewing as a "microsolvation" relationship the interaction of the  $\pi$ -electrons of the diphenylalkane rings with  $\text{Me}_3\text{C}^+$ , it appeared interesting to ascertain whether intermolecular selectivity could be affected by a change of the solvating properties of the bath gas. To this end the  $k_{\text{DPP}}/k_{\text{toluene}}$  ratio was measured in systems containing 50 Torr of MeCl diluted into the bulk gas. In a poorly solvating medium such as pure isobutane gas, the electrophile should be rather sensitive to the stabilizing interactions with the  $\pi$ -rings of the substrate. The same electrophile formed in the MeCl/*i*-C<sub>4</sub>H<sub>10</sub> (1:35 molar ratio) mixtures should benefit from the presence of polar MeCl molecules, which provide better solvation to the  $\text{Me}_3\text{C}^+$  ion.<sup>36</sup> Such interaction reduces the difference between  $E^\circ$  and  $E^*$  and makes the disruption of the  $[\text{Me}_3\text{C}^+ \text{ArH}]$  complex energetically less unfavorable. In agreement with the expected dependence of the  $\text{Me}_3\text{C}^+$  selectivity on the solvating properties of the reaction medium, the toluene reactivity is depressed by the presence of MeCl with respect to DPP ( $k_{\text{DPP}}/k_{\text{toluene}}$  increasing from 4.7 to 6.1), an effect ascribed to the enhanced dissociation of the less stabilized  $[\text{Me}_3\text{C}^+ \text{toluene}]$  collision complex in the better solvating medium.

The existence of a persistent *tert*-butylated complex **1** is also suggested by competition experiments between DPE and PmTE, whose alkylated ring is activated by the electron-releasing effect of the methyl group in the *meta* position. If kinetically determining formation of an early noncovalent complex causes the *tert*-butylation to proceed at the collision limit, a low DPE/PmTE intermolecular selectivity should stand in contrast to a sizeable intramolecular discrimination in the *tert*-butylation of PmTE, where the activation of the two rings roughly matches that of toluene and *m*-xylene. The results show that both arenes react at comparable rates with  $\text{Me}_3\text{C}^+$ , whereas the methylated ring of PmTE is alkylated twice as fast as the unsubstituted one. Such a result provides clear-cut evidence for the coordination hypothesis, since the stability of the electrostatic complex is little affected by methyl substitution (which instead considerably stabilizes the alkylated arenium ion). Such evidence sets definitely the rate-determining formation of **1** as kinetically distinct from the product-controlling step.<sup>37</sup>

In agreement with previous studies on the gas-phase *tert*-butylation of alkylbenzenes, the orientation of the  $\text{Me}_3\text{C}^+$  attack on diphenylalkanes confirms the electrophilic nature of the aromatic *tert*-butylation with a 2*para/meta* ratio exceeding 1.0, a piece of evidence further supported by the effects of changes in temperature and composition of the gaseous systems. In fact, at low base concentration and higher temperature the reaction tends to approach the equilibrium distribution of isomeric arenium ions and *meta* substitution is favored, arising from the most stable arenium ion. A noticeable predominance of *para* substitution is peculiar to DPP, a bias hardly explainable on the basis of different electron-donating power of  $\text{Ph}(\text{CH}_2)_3$  vs  $\text{Ph}(\text{CH}_2)_n$  ( $n = 1, 2, 4$ ) and  $\text{CH}_3$  groups. Such behavior can be explained by the role played by the spectator ring in stabilizing the  $\sigma$ -complex formed from DPP. This arenium ion is favored with respect to both the lower and the higher homologues by the fact that the  $(\text{CH}_2)_3$  chain allows a sandwich-type relationship of the arenium and spectator ring with all staggered conformations at the C-C bonds. The arenium ion from the primary attack of  $\text{Me}_3\text{C}^+$  at a *para* carbon may then show a lower degree of back-dissociation (smaller  $k_{-1}$ ) and a higher activation barrier for the  $2_p \rightarrow 2_m$  isomerization. Such observation points out that the spectator ring may exert an influence both on the

noncovalent complex **1** and on the arenium ion and suggests that stabilizing electrostatic interactions allowed by rotation and folding of the methylene chain outweigh negative entropic terms arising from restricted free rotations.<sup>38</sup>

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