

# Benzene Loss from Trityl Cations— A Mechanistic Study

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Triarylmethyl cations eliminate substituted benzene in the gas phase, upon activation. The mechanism of this process has been studied using deuterium labeling, substituent effects, and density functional theory calculations. It is shown that this apparently simple dissociation is in fact a complicated stepwise process that involves several consecutive hydride shifts. The combination of experimental evidence and computational results leads to a clear description of transition states and reaction intermediates. (J Am Soc Mass Spectrom 2006, 17, 730–736) © 2006 American Society for Mass Spectrometry

Triphenylmethane dyes form a very important class of commercial dyes with applications in many fields [1]. Another function of the triphenylmethyl (trityl) groups is their usefulness as labile protecting groups in organic synthesis [2]. The applications of trityl groups are based on their unique ability to form stabilized cations. This is reflected in the relative electrophilicity parameter for trityl cation [3] as well as hydride affinity [4] and  $k_R^+$  values [5]. Trityl cations are generated from alcohols in acidic conditions, but they can also be generated from trityl halides in the presence of alkali metal, alkaline earth metal ions [6], or Lewis acids. A useful tool for the study of ionic species like trityl cations is gas-phase ion chemistry using mass spectrometry. Mass spectrometry has been used to understand dissociation kinetics and mechanisms of gas-phase molecular ions. Fragmentation pathways of molecular ions are determined using tandem mass spectrometry (MS/MS) isotopic labeling and molecular orbital calculations that provide valuable information. Owing to its general importance to synthetic organic chemistry, a large body of knowledge on the chemistry of cationic aromatic compounds, like alkylbenzenium ions and benzyl cations has been accumulated in the past four decades. For example, the production of  $C_7H_7^+$  from toluene molecular ion is one of the most extensively studied reactions in the field of gas-phase ion chemistry [7]. Other studies concentrate on protonation, ion-neutral complex formation, and H/D exchange processes in aromatic systems. See for example [8] and references cited therein.

Electron ionization spectra of several trityl compounds were recorded by Shupe and Berlin [9]. The authors show several typical fragmentation pathways,

the most abundant being the formation of a trityl cation. Another characteristic of these EI spectra is the presence of an ion at  $m/z$  165 that corresponds to the loss of 78 Da from the trityl cation of  $m/z$  243. The authors suggest that the resulting ion of  $m/z$  165 is a 9-fluorenyl cation. It is also known that benzhydryl cations can afford an analogous ion by the loss of  $H_2$  [10]. The loss of molecular hydrogen is supported by the presence of a metastable ion.

Triphenylmethane has also been studied with negative chemical ionization, showing an abundant  $[M - H]^-$  ion. Upon high-energy collisional activation, two major dissociation processes occur, involving the losses of  $C_2H_4$  and  $C_6H_6$  neutral fragments. The authors suggest that the loss of  $C_6H_6$ , a benzene ring, results in the formation of a 9-fluorenyl anion. Isotopic labeling experiments indicate extensive hydrogen-deuterium scrambling within this process [11].

Modern desorption techniques enable the generation of stable trityl cations under relatively mild conditions. In the present work, we studied the characteristic loss of benzene or substituted benzene molecules from trityl cations. A detailed mechanism for the formation of 9-fluorenyl cation is proposed and supported by experimental work and theoretical calculations.

## Results and Discussion

Protonated trityl alcohols eliminate water readily affording trityl cations, under chemical ionization, atmospheric pressure chemical ionization, or electrospray ionization (ESI). Cation **1** (Figure 1) and *para*-substituted analogs were generated in the ESI source from the corresponding alcohols in a 0.01 M TFA solution of methanol. The relative stability of the resulting trityl cations is evident by their inefficient reaction with nucleophiles, at least under low pressures, in an FT-ICR cell. For comparison, reactions of analogous benzhydryl and 9-fluorenyl cations with the same nucleophiles

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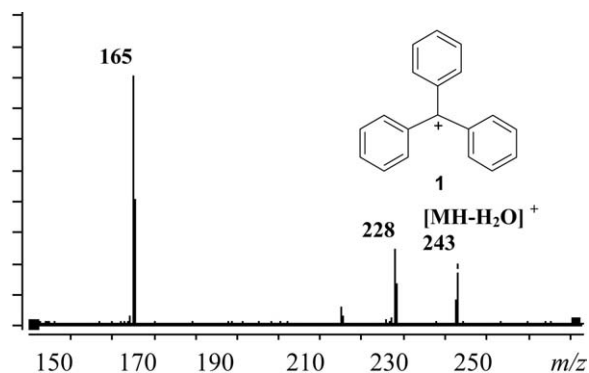
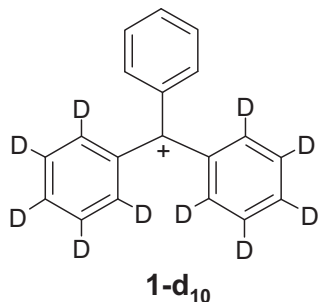


Figure 1. CID spectrum of trityl cation 1.

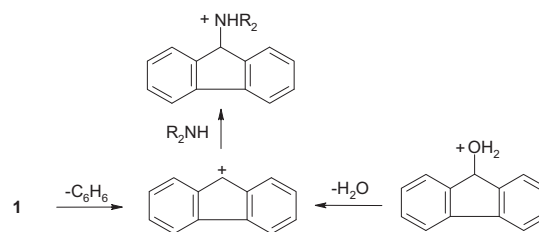
were carried out under similar conditions [12]. Nevertheless, despite this apparent stability towards association, it is found that **1** dissociates under relatively low-energy, affording a cationic product of  $m/z$  165 that corresponds to the loss of benzene. This process occurs under collision induced dissociation (CID) but can also be initiated in the source by increasing the voltage at the electrospray capillary (Figure 1). It is noteworthy that analogous diphenylmethyl cations also generate product ions of  $m/z$  165, by the loss of two hydrogen atoms.

As mentioned above, the loss of benzene from trityl cation was proposed to involve the formation of 9-fluorenyl cation (Scheme 1) [9, 10]. Before delving any further into the dissociation mechanism of **1** it was essential to support this proposal by comparison of the CID behavior of this product ion with that of 9-fluorenyl cation produced directly from 9-fluorenone (Scheme 1). However, the two ions do not dissociate under the experimental conditions chosen for this study (both in an FTICR and in a triple stage quadrupole mass spectrometer). Therefore, instead of CID spectra comparison, ion-molecule association reactions of these two cations with amines were investigated. To follow the reaction of these two ions under identical conditions, deuterium labeled **1-d<sub>10</sub>** was prepared.



This approach has been previously used by Nibbering and coworkers to distinguish between benzyl and tropylium cations [13].

The elimination of benzene, upon activation of cation **1-d<sub>10</sub>** involves the losses of  $C_6H_5D$ ,  $C_6D_5H$  or  $C_6D_6$ , affording ions of  $m/z$  174, 170, and 169, respectively,



Scheme 1. Proposed formation of 9-fluorenyl cation from both cation **1** and 9-fluorenone.

while the mass of unlabeled 9-fluorenyl cation is 165 Da. In the presence of pyrrolidine (4.5 exp-9 mbar) the relative abundances of all parent ions decrease with time, affording four product ions at  $m/z$  245, 241, 240, and 236 (Figure 2). Figure 3 shows the decrease in the relative intensity of two precursor ions as a function of time, the 9-fluorenyl cation of  $m/z$  165 and one of the labeled products of  $m/z$  170. The two pseudo first-order rate constants are proportional to the measured slopes that are  $-0.49$  ( $R^2 = 0.9990$ ) and  $-0.48$  ( $R^2 = 0.9976$ ), respectively, for the reaction with pyrrolidine. Reactions of the two cations of  $m/z$  165 and 170 that were carried out with benzylamine afford slopes of  $-0.31$  ( $R^2 = 0.9948$ ) and  $-0.32$  ( $R^2 = 0.9854$ ) for the two cations. These values are within our experimental error and support the notion that these are identical cationic structures. Consequently, we conclude that the product ion of  $m/z$  165 is indeed 9-fluorenyl cation (Scheme 1).

The favored loss of benzene from **1** must involve either considerable rearrangement of the dissociating cation before benzene loss or a stepwise loss of two radicals. Three initial processes that were considered for the reaction under study are illustrated in Scheme 2. Routes (b) and (c) are rearrangement processes of **1** and both involve cyclization. Route (a) is the dissociation of a C—C bond to form a complex between phenyl radical and a diphenylmethylene radical cation. DFT calculations at the B3LYP/6-31G(d) level were employed to assess the viability of each process.

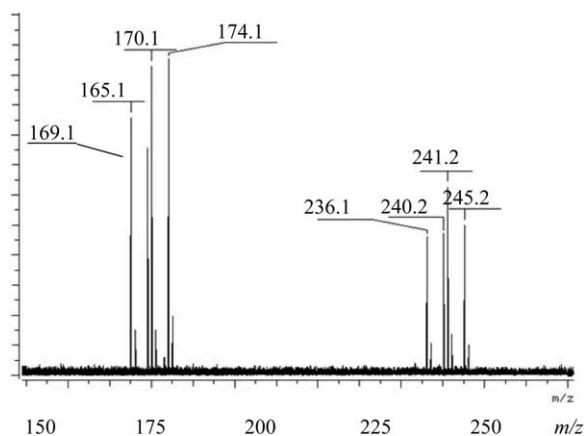
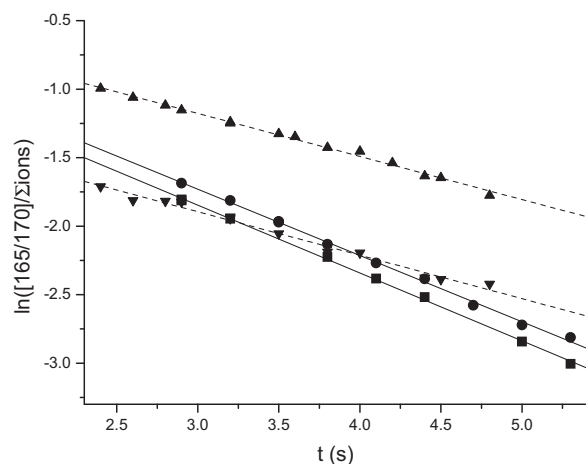


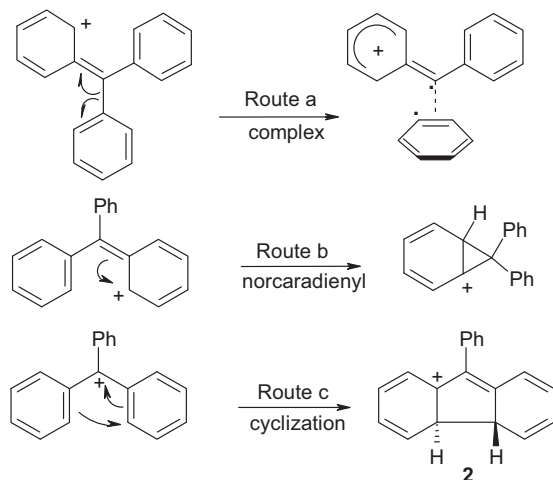
Figure 2. Ion-molecule reactions of the deuterium labeled cations generated during CID of **1-d<sub>10</sub>** ( $m/z$  169, 170, and 174) and 9-fluorenyl cation ( $m/z$  165), with pyrrolidine.



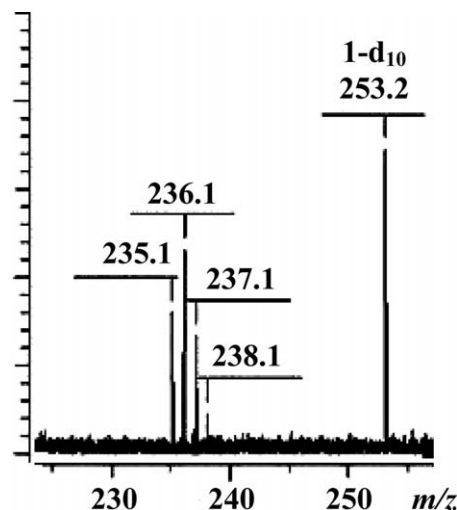
**Figure 3.** Pseudo first-order kinetics in the reaction of deuterium labeled cation generated during CID of **1-d<sub>10</sub>** (*m/z*170) with pyrrolidine (filled circles), benzylamine (filled triangles), reaction of 9-fluorenyl cation with pyrrolidine (filled squares), and benzylamine (filled inverted triangles).

Route (a) was examined here by calculation of the energy of cation **1** while increasing the bond length of the dissociating C—C bond. This bond length was increased up to 2.45 Å while all other geometrical parameters were optimized. This simple bond cleavage is found to be highly endothermic with a barrier that exceeds 80 kcal mol<sup>-1</sup>. It is therefore concluded that Route (a) is unlikely to occur.

Route (b) is a cyclopropyl carbinyl cation rearrangement; however, it was not possible to locate a minimum geometry for the resulting norcaradienyl cation. This is in accordance with the calculated results of Smith and Hall [14], who showed that this norcaradienyl cation is a transition-state in the rearrangement of benzyl to tropylium cation at the G2(MP2,SVP) level. They estimate the barrier for the formation of the norcaradienyl cation as 57.8 kcal mol<sup>-1</sup>. This transition-state leads to an unstable cycloheptatrienyl cation that rearranges to a



**Scheme 2.** Three initial reaction steps that were considered for the dissociation of trityl cation **1**.



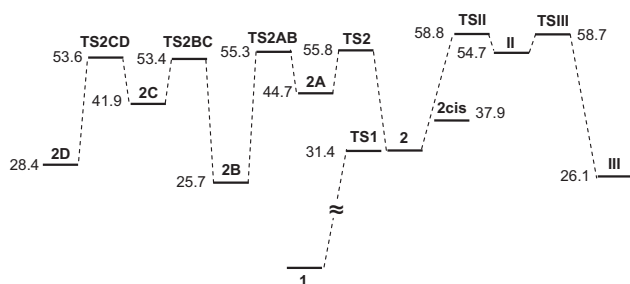
**Figure 4.** Partial CID spectrum of **1-d<sub>10</sub>**, showing H/D exchange during the elimination of methyl.

tropylium cation. It is thus shown that the lowest energy path for rearrangement of benzyl cation to tropylium requires 65.1 kcal mol<sup>-1</sup> and proceeds through a single stable intermediate [14]. Such a mechanism should exhibit hydrogen scrambling in the rearranging cation. Lately, the barrier for benzyl-tropylium cation rearrangement has also been reviewed by Ignatyev and Sundius at the B3LYP/6-31G(d,p) level, and a barrier of 68.8 kcal mol<sup>-1</sup> was estimated [15].

The specific losses of C<sub>6</sub>H<sub>5</sub>D, C<sub>6</sub>D<sub>5</sub>H and C<sub>6</sub>D<sub>6</sub> from deuterium labeled **1-d<sub>10</sub>** also indicates that a norcaradienyl transition-state [Scheme 2, Route (b)] that would rearrange to a tropylium cation is not generated under the experimental conditions of this study. If these were to be formed, H/D scrambling between different positions would be expected. It is worth adding that cation **1** undergoes a competitive, less favored methyl loss (*m/z* 228, Figure A1) [10]. Unlike the benzene elimination under study, methyl loss according to the CID spectrum of deuterium labeled **1-d<sub>10</sub>** occurs with extensive H/D scrambling, and the resulting fragment ions correspond to CH<sub>3</sub>, CDH<sub>2</sub>, CD<sub>2</sub>H, and CD<sub>3</sub> losses, indicating the involvement of a tropylium cation in the process (Figure A).

Finally, Route (c) was also investigated, theoretically, by following the cyclization process. A transition-state for this cyclization was located by decreasing the distance between the two binding carbon atoms while optimizing all other coordinates. This transition-state, TS1, is 1.4 kcal mol<sup>-1</sup> above the energy of **1** (Figure A). A disrotatory cyclization affording a *cis* cyclized product was also considered. However, the energy of this *cis* isomer is 5.4 kcal mol<sup>-1</sup> higher than the energy of the *trans* cyclized isomer **2** and TS1 that lead to the formation of **2**.

Hence, the most reasonable reaction of the three proposed is Scheme 2 is Route (c) that suggests the initial formation of cyclized **2**. The abundance of the fully labeled



**Figure 5.** Schematic potential energy curve corresponding to the reaction steps proposed in Scheme 3. Energies are in kcal mol<sup>-1</sup> with ZPE correction.

C<sub>13</sub>D<sub>9</sub><sup>+</sup> ion in the CID spectrum of **1-d**<sub>10</sub> (not shown) is roughly half than the sum of the two other ions, C<sub>13</sub>H<sub>4</sub>D<sub>5</sub><sup>+</sup> and C<sub>13</sub>H<sub>5</sub>D<sub>4</sub><sup>+</sup>, as expected statistically. However, the abundance of C<sub>13</sub>H<sub>4</sub>D<sub>5</sub><sup>+</sup> is higher than that of C<sub>13</sub>H<sub>5</sub>D<sub>4</sub><sup>+</sup>, indicating an H/D isotope effect of 1.17 considering the <sup>13</sup>C natural abundance. This is a small isotope effect even for energetic conditions that may be the result of several consecutive hydrogen shifts before or during the rate determining step of this reaction.

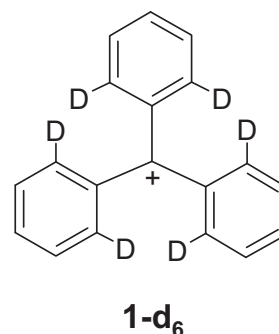
The cyclization of **1** is characterized by a transition-state **TS1** that is of the same energy as the cyclized product **2** (31.4 kcal mol<sup>-1</sup> above the energy of **1**). The reversed ring opening, transforming **2** back to the trityl cation **1**, occurs without barrier and, therefore, the formation of **2** must in effect be followed by a hydride shift. Thus, two possible 1,2 hydride shifts that give rise to structures **II** and **2A** (Scheme 3, Figure 5) were considered. Calculations shown that **II** and **2A** are generated through transitions states **TSII** and **TS2** at 58.8 and 55.8 kcal mol<sup>-1</sup> (higher than trityl **1**), respectively. Intermediate structure **II** is unstable (54.7 kcal mol<sup>-1</sup>) forming intermediate **III** (26.1 kcal mol<sup>-1</sup>) readily. Alternatively, **2A** can further rearrange into **2B**, **2C**, and **2D** that are 25.7, 41.9, and 28.4 kcal mol<sup>-1</sup> less stable than **1**, respectively (Scheme 3, Figure 5).

Structure **2D** can further generate **3** through **TS3**

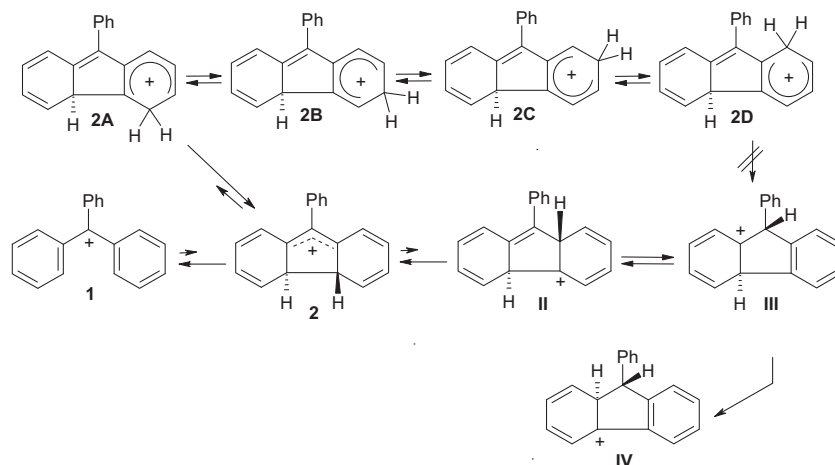
(46.1 kcal mol<sup>-1</sup> higher than **1**). Other hydride rearrangements that follow involve the formation of additional intermediates **4**, **5**, and **6** at 15.5, 15.1, and 23.5 kcal mol<sup>-1</sup>, respectively. The final calculated dissociation product is ion-neutral complex **7** that is 12.0 kcal mol<sup>-1</sup> less stable than trityl cation **1**. Scheme 4 and Figure 6 show the calculated structures and relative energies of **4**, **5**, and **6** that are formed from **3**, indicating that this part of the reaction path occurs in the same manner regardless of the initial process undertaken (i.e., **II** versus **2A**).

The first proposed reaction path, through cations **II**, **III**, and **IV** should not involve H/D scrambling within the hydrogen atoms in each phenyl ring. According to this proposed mechanism (Scheme 3 and 4) only *ortho* hydrogen atoms are eliminated within the benzene moiety.

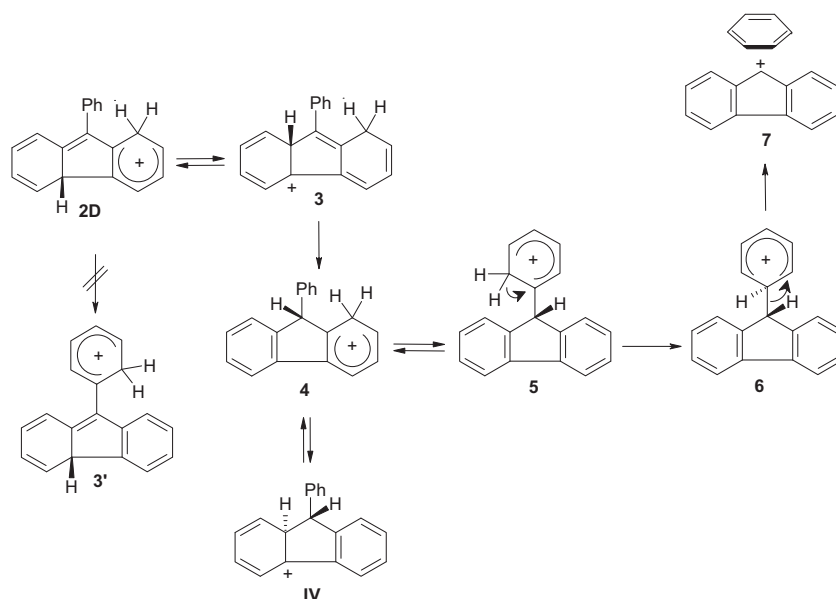
Also noteworthy is that the formation of intermediate **II** through **TSII** is higher in energy than the alternative formation of **2A** through **TS2** by 3.0 kcal mol<sup>-1</sup>. The labeled model **1-d**<sub>10</sub> cannot reveal whether H/D exchange within the phenyl rings occurs.



Hence, deuterium labeled **1-d**<sub>6</sub> was prepared to gain deeper insight into the mechanism and learn whether **II** or the rearranged structures **2A**, **2B**, **2C**, and **2D** are



**Scheme 3.** Two proposed hydride shifts giving rise to: (1) rearranged structures **2A**, **2B**, **2C**, and **2D**, or (2) cation **II** that rearranges into the more stable **IV**.



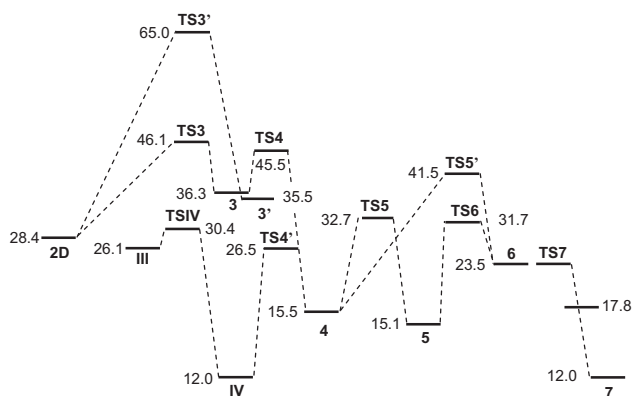
**Scheme 4.** Possible reaction steps following the rate determining step. The barrier for the formation of 3' is 65 kcal mol<sup>-1</sup>; it is therefore presented as an unreasonable step.

generated. Indeed, the CID spectrum of **1-d<sub>6</sub>** contains abundant ions at *m/z* 168 and 169, corresponding to the losses of C<sub>6</sub>H<sub>3</sub>D<sub>3</sub> and C<sub>6</sub>H<sub>4</sub>D<sub>2</sub>, respectively, with an *m/z* 169/168 ion ratio of 1.80 (spectrum not shown). This supports the formation of **2A**, **2B**, **2C**, and **2D** that rearrange back and forth and thus induce H/D exchange only in each ring but not between the three phenyl rings. It has already been noted that by comparison of the statistically expected ion ratio in **1-d<sub>10</sub>** and the experimental results, an H/D isotope effect of 1.17 is derived. In the case of **1-d<sub>6</sub>** the expected statistical 169/168 ion ratio is 1.5 and, therefore, the derived H/D isotope effect is 1.20 as indeed observed.

In conclusion of this part, both the experimental results and theoretical calculations support a reaction path that involves the formation of cation **2**, which in turn rearranges back and forth into **2A**, **2B**, **2C**, and **2D**. The formation of **2D** through the former intermediates

is the endothermic part of the reaction (Figure A5). Hence, intermediate cations **4**, **5**, and **6** are all generated with lower barriers, while the final ion-neutral product **7** is 12.0 kcal mol<sup>-1</sup> above the cationic starting material **1** (Figure A6).

An electronic substituent effect on this process was investigated with cations **8–15**. The proposed mechanism (Scheme 4, Figure A5) suggests that positive charge is developing away from the eliminated benzene ring during rate determining steps. According to this proposal, an electron withdrawing group should enhance the process, resulting in higher abundance of ions that correspond to the loss of C<sub>6</sub>H<sub>5</sub>X, where X is an electron withdrawing group. On the other hand electron donating groups should have the opposite effect, giving rise to more abundant loss of C<sub>6</sub>H<sub>6</sub>. CID experiments were carried out on each of the substituted trityl cations and the results are summarized in Table 1.  $[M - C_6H_6]^+ / [M - C_6H_5X]^+$  are corrected according to the statistical abundance of phenyl and substituted phenyl rings (in brackets). Clearly elimination of substituted C<sub>6</sub>H<sub>5</sub>X is



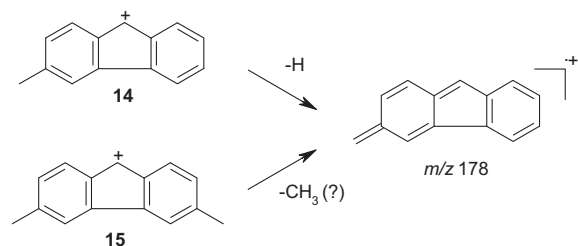
**Figure 6.** Schematic potential energy curve corresponding to the reaction steps proposed in Scheme 4. Energies are in kcal mol<sup>-1</sup> with ZPE correction.

**Table 1.** Elimination of benzene versus substituted benzene in the CID of cations **8–14**

	<i>para</i> Substituents	Mass of parent ion	$[M - C_6H_6]^+ / [M - C_6H_5X]^+$
<b>14</b>	CH <sub>3</sub> , H, H	257	3.5* (1.7)
<b>9</b>	OCH <sub>3</sub> , OCH <sub>3</sub> , H	303	0.43 (0.86)
<b>8</b>	OCH <sub>3</sub> , H, H	273	1.44 (0.72)
<b>10</b>	F, H, H	261	0.90 (0.45)
<b>11</b>	F, F, H	279	0.11 (0.22)
<b>12</b>	CF <sub>3</sub> , H, H	311	0.28 (0.14)
<b>13</b>	CF <sub>3</sub> , CF <sub>3</sub> , H	379	0.0 (–)

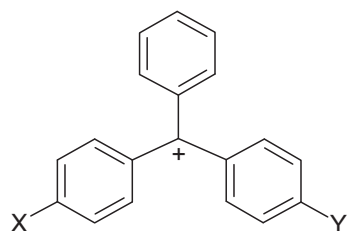
\*The  $[M - C_6H_6]^+$  product ion of **14** undergoes consecutive H loss that was considered as well.





**Scheme 5.** Formation of cation radical in the CID spectra of methyl substituted cations **14** and **15**

always favored over the elimination of  $C_6H_6$ . One exception is the methyl substituted **14** that undergoes preferential elimination of  $C_6H_6$ . However, as will be discussed further, methyl substituted **14** afford both closed-shell and radical product ions and the  $[M - C_6H_6]^+ / ([M - C_7H_8]^+ + [M - C_7H_9]^+)$  ion ratio is 3.5 (without any correction). It seems that the methoxy groups in **8** and **9** are not necessarily acting as electron donating groups and, therefore, the corrected  $[M - C_6H_6]^+ / [M - C_6H_5X]^+$  ion ratio is smaller than 1. This is due to the formation of intermediate structures **2B** and **2D**, in which the positive charge is not conjugated to the substituent X that consequently exhibits mainly an inductive effect. Nevertheless, the more electron withdrawing *para* substituents (i.e.,  $CF_3$ ) enhance the loss of substitute benzene as expected. This is consistent with the above proposed mechanism.



- |                                  |                                  |
|----------------------------------|----------------------------------|
| <b>8</b> X=H; Y=OCH <sub>3</sub> | <b>12</b> X=H; Y=CF <sub>3</sub> |
| <b>9</b> X=Y=OCH <sub>3</sub>    | <b>13</b> X=Y=CF <sub>3</sub>    |
| <b>10</b> X=H; Y=F               | <b>14</b> X=H; Y=CH <sub>3</sub> |
| <b>11</b> X=Y=F                  | <b>15</b> X=Y=CH <sub>3</sub>    |

A special case is the 4-methyl system **14** that affords a 3-methyl fluorenyl cation of  $m/z$  179 by benzene elimination. This ion, in turn, eliminates a hydrogen atom, generating a radical cation of  $m/z$  178. The same is observed in the CID spectrum of **15** (not shown) that contains two methyl substituents (Scheme 5). The formation of radicals from stable closed-shell ions, even at low energies, is unique, but known for several systems [16]. The driving force for a hydrogen loss, in this case, is the relative stability of the resulting conjugated, ionized system, namely the low ionization potential of the corresponding neutral.

## Conclusions

Trityl cations undergo a specific elimination of benzene and/or substituted benzene that is almost their exclusive course of dissociation. This process occurs through an initial electrocyclic cyclization, followed by several hydride shifts. It is shown that the operative mechanism allows complete scrambling between different hydrogen atoms of each phenyl ring. However, there is no exchange between hydrogen atoms at different rings. By combining experimental data and DFT calculations, a detailed and substantiated mechanism is formulated.

## Experimental

### Synthesis

Triarylcarbinols that are the precursors of cations **8–12** and **14–15** were prepared by the reactions of corresponding *para*-substituted phenylmagnesium bromides and substituted benzophenones. Triarylcarbinols that are the precursors of cations **13**, **1-d<sub>10</sub>**, and **1-d<sub>6</sub>**, were prepared by the reactions of the corresponding *para*-substituted phenylmagnesium bromides with methyl benzoate.

Bromobenzene-2,6-d<sub>2</sub> and benzoic-2, 6-d<sub>2</sub> methyl ester were prepared according to a known procedure [17–20]; additional spectral information, and <sup>1</sup>NMR, <sup>13</sup>C NMR, and HRMS data for alcohols that are precursors for cations **1-d<sub>6</sub>**, **1-d<sub>10</sub>**, and **8–15**, as well as energy (Hartrees, with ZPE correction) and Cartesian coordinates for all optimized structures can be found in the Supplementary Material section, which can be accessed in the electronic version of this article.

### Mass spectrometry

All ESI/FTICR experiments were carried out using Bruker BioAPEX III 47e FTICR spectrometer (Bruker Analytical Systems, Inc., Billerica, MA) equipped with a 4.7 T superconducting magnet, an external source (Apollo ESI Source), and an infinity analyzer cell. Samples were dissolved in CH<sub>3</sub>OH (0.01 mg/mL) and introduced into the ESI source at a flow rate of 0.2  $\mu$ L min<sup>-1</sup>. Ions were detected using the broadband detection mode covering a mass range from 50 to 2000 u. Typically, eight individual transients were accumulated to improve the signal-to-noise ratio. Precursor ions were isolated using a series of “shot” swept frequency ejection pulses of 1000  $\mu$ s duration to eject all other ions and avoid activation of precursor ions. A pulsed valve introduced the argon collision gas before ion activation. With the pulsed valve open for 20 ms a peak pressure of  $\sim 2 \times 10^{-7}$  mbar was obtained. The precursor ions were excited using a variable amplitude off-resonance excitation pulse.

## Calculations

All the calculations were carried out using Gaussian 98 package of programs [21]. All the molecules under this study were optimized at the B3LYP/6-31G(d), hybrid density functional level of theory. For the study of each step, a potential energy surface scan was employed. When necessary, transition states were verified by carrying out an intrinsic reaction coordinate (IRC) calculation [22], in which the imaginary mode for the transition-state is followed in both the forward and reverse directions. Starting materials, products and transition states were analyzed using analytical frequencies calculations.

## Acknowledgments

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