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Rearrangements of $[C_6H_7Si]^+$ Cations. A Radiochemical and Quantum Chemical Study

Igor S. Ignatyev,[†] **Tom Sundius,***[‡] **T. A. Kochina,**[§] **V. V. Avrorin,**[†] **and E. N. Sinotova**[†]

Department of Chemistry, Radiochemistry Laboratory, St. Petersburg State University, Universitetskaiy pr. 26, 198504 St. Petersburg, Russia, Department of Physics, University of Helsinki, P.O. Box 64, FIN-00014 Helsinki, Finland, and Laboratory of Organosilicon Compounds and Materials, Institute for Silicate Chemistry of RAS, Makarov nab. 2, 199034 St. Petersburg, Russia

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Nucleogenic cations were formed by β-decay of phenylsilane tritiated at ortho- and para-positions of the benzene ring as well as at the silyl group and the products of their reactions with methyl *tert*-butyl ether were analyzed by radiochromatography. We found that the *o*-silatolyl cation was isomerized into the silabenzyl cation while the *p*-silatolyl cation was not. Furthermore, the silabenzyl cation was not converted into other isomers. The potential energy surface of the $C_6H_7Si^+$ system was constructed by B3LYP and MP2 methods using an aug-cc-pVDZ basis set. Theory predicts the low barrier for *o*-silatolyl−silabenzyl isomerization but high barriers for hydride shifts in the ring from para to meta- to ortho-isomers. It seems that nascent nucleogenic ions have enough internal energy to overcome the ortho-to-benzyl barrier but not enough to cross over the hydride-shift barriers. Theory also confirms that the isomerization of the silabenzyl cation to the $[C_6H_6 \cdot SiH]^+$ complex takes place in one step with a 62 kcal mol^{-1} barrier, whereas that to either the global minimum $[C_6H_7 \cdot Si]^+$ or the silatropylium ion involves multisteps with 69−80 kcal/mol barriers. In addition, we find that the barrier of interconversion between the $[C_6H_6 \cdot SiH]^+$ complex and one of the low-lying $[C_6H_7 \cdot Si]^+$ complexes is only 29 kcal/mol.

Introduction

It is well-known from experiments and theory that the two most stable $C_7H_7^+$ isomers are the benzyl and tropylium ions with the latter being the global minimum of the system.[1] In the case of $C_6SiH_7^+$, the two silicon analogs were reported to be observed from the electron impact of phenylsilane.[2,3] The authors have proposed that, by analogy with the $C_7H_7^+$ system, the seven-membered ring silatropylium cation is more stable than the silabenzyl cation. However, high-level theoretical studies[4] have shown that the silatropylium ion lies 9 kcal/mol higher in energy.[5]

Moreover, the silabenzyl cation is not the global energy minimum on the $C_6H_7Si^+$ potential energy surface. Nicolaides and Radom[5,6] have found that the methylcyclopentadienylsilicon cation denoted $[C_5H_4CH_3 \cdot Si]^+$ is the global energy minimum and proposed this complex rather than the silatropylium ion as a candidate for the second (unreactive) isomer observed by Beauchamp and co-workers.[2] However, Jarek and Shin[7] revealed that in the collision activated experiment the major dissociation products from the unreactive species were SiH^+ with a loss of C_6H_6 and $C_6H_5Si^+$ with a loss of H_2. These findings allowed the authors to conclude that the second unreactive isomer is the $[C_6H_6 \cdot SiH]^+$ complex. Meanwhile, quantum chemical studies[5] have shown that this $[C_6H_6 \cdot SiH]^+$ complex is ca. 10 kcal/mol less stable than the silabenzyl cation.

More recently, Choe[8] has shown that the main channel for the fragmentation of metastable $C_6H_7Si^+$ ions is the elimination of H_2. He has also pointed out the role of the $[C_6H_6 \cdot SiH]^+$ complex in the process of the H_2 loss and located the transition states for this reaction as well as for the $[C_6H_6 \cdot SiH]^+$ to silabenzyl cation interconversion.[8]

In comparison with both the benzyl and tropylium ions less attention was paid to tolyl cations. The first experimental studies revealed a different order of stability for *m*- and *p*-tolyl cations.[7,9]

The MINDO/3 study[10] has shown that the *p*-tolyl cation is less stable than the other two isomers and high-level ab initio calculations[11,12] have confirmed the relative stability of isomers ascending in the order ortho−meta−para. The similar order of isomer stabilities has been predicted for silatolyl cations.[13]

Interconversions between the tolyl isomers may occur through hydride shift. Classical barrier heights for hydride shift as well as for this isomerization of nucleogenic phenyl and tolyl cations were subjects of previous works.[14−20] Experimentalists presume that hydride shifts may occur in free phenyl cations,[14−16,19] to the contrary, theory[17,18,20] predicts that the intrinsic potential internal energy of the nascent nucleogenic ion is not high enough to overcome the barrier for these shifts.

The barrier heights for the ring hydride shifts in silatolyl cations are close to those in phenyl and tolyl cations. However, the exocyclic shift of a positive charge or the hydride shift from the SiH_3 group to the positively charged site on the benzene ring have a substantially lower barrier than the corresponding shift from the CH_3 group in tolyl cations.[13] Thus theory predicts that only the *o*-silatolyl cation isomerizes into the silabenzyl cation.[13] Herein we report the experimental data that support this prediction. We also report the energy profiles for the isomerization of the silabenzyl cation into other low-lying isomers. Although the structures of these isomers were predicted earlier,[4−6] the transition states on the pathways to these isomers were not presented before.

Experimental and Theoretical Details

o- and *p*-silatolyl cations were generated by β-decay of tritium atoms in phenylsilane tritiated at the ortho- and para-positions of the benzene ring of phenylsilane:

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* Corresponding author. E-mail: Tom.Sundius@helsinki.fi.

[†] St. Petersburg State University.

[‡] University of Helsinki.

[§] Institute for Silicate Chemistry.

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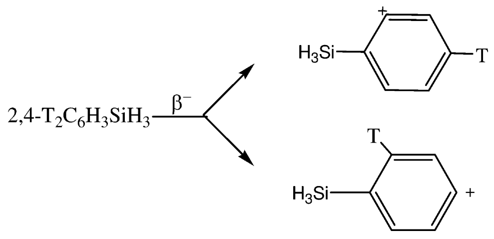


Silabenzyl cations were generated by tritium β-decay of phenylsilane tritiated at the silyl group:

$$PhSiT_3 \xrightarrow{\beta^-} PhSi^+T_2 \qquad (1)$$

Reactions of labeled silatolyl and silabenzyl cations with a substrate (methyl *tert*-butyl ether) yield radioactive products conveniently analyzed by the radiochromatographic technique.[21,22]

The synthesis of phenylsilane tritiated at ortho- and para-positions of the benzene ring $2,4\text{-}T_2C_6H_3SiH_3$ was carried out by a catalytic substitution of halogen with tritium in (2,4-dibromophenyl)trimethoxysilane followed by the reduction of the methoxy derivative using lithium aluminum hydride.[23] The trimethoxy derivative was used as starting material instead of (2,4-dibromophenyl)silane to avoid the replacement of hydrogen atoms in the Si−H bond with tritium. The synthesis of phenylsilane tritiated at the silyl group was done by the reduction of phenyltrichlorosilane with lithium aluminum tritide.[24]

Commercial methyl *tert*-butyl ether was distilled, and its purity was checked by gas chromatography. The reaction mixtures were prepared by introducing 1 mCi of tritiated phenylsilane $2,4\text{-}T_2C_6H_3SiH_3$ or $PhSiT_3$ diluted by xenon to a specific activity at 5 Ci/mol and gaseous methyl *tert*-butyl ether at pressure of 10 Torr into an evacuated and carefully outgassed 20 mL vessel. The mixtures were stored in the dark at room temperature for 1−2 months. After the storage period, the ampules were opened and their contents were analyzed using the “Tzvet” gas chromatograph equipped with a running proportional counter. Before the chromatographic analysis of products, the gaseous contents were condensed at −196 °C and the walls were rinsed with a suitable solvent.

The tritiated products of reactions were identified by comparing their retention times with those of authentic reference compounds under identical chromatographic conditions. A 2 m long column (2 mm in diameter) packed with 5% Silicon SE-30 on Inerton-AW was used.

Relative yields of products were determined as the ratio of activity of each product to the combined activity of all products identified.

o- and *p*-methoxyphenylsilanes used as reference compounds were prepared correspondingly from *o*- and *p*-bromoanisoles and trichlorosilane followed by the reduction of their chloro derivatives with $LiAlH_4$.[25] Phenylmethoxysilane was synthesized as described in the literature.[26]

Geometries of all of the stationary points have been fully optimized and characterized by harmonic vibrational frequency calculations using the B3LYP,[27,28] hybrid density functional method, and frozen-core second-order Møller−Plesset perturbation theory (MP2).[29] The basis sets used were the Dunning correlation-consistent aug-cc-pVDZ basis sets.[30,31] The inclusion of diffuse functions is determined by the role of hydride shifts in rearrangements of the discussed system. All the methods and basis sets were used as implemented in the Gaussian03 program.[32] The IRC[33,34] path following method for the descent from the barrier top was employed to locate energy minima, which are connected by a particular transition state.

TABLE 1: Relative Yields of Labeled Products of the Reactions $[SiC_6H_7]^+$ Ions with Methyl *tert*-Butyl Ether

cation	labeled product	relative yield (%)
$H_3SiC_6H_3T^+$	$p\text{-}H_3SiC_6H_4OCH_3$	44 ± 5
	$o\text{-}H_3SiC_6H_4OCH_3$	22 ± 3
	$C_6H_5SiH_2OCH_3$	34 ± 4
$(C_6H_5)T_2Si^+$	$C_6H_5SiH_2OCH_3$	100

Results and Discussion

The source of the studied cations is phenylsilane $C_6H_5SiH_3$ labeled by tritium in different positions. When tritium is placed into the ortho- and para-positions of the benzene ring, the $C_6H_3T_2SiH_3$ molecule is a source of silyl-substituted phenyl (silatolyl) cations with a localization of the positive charge at the corresponding carbon atoms. Likewise, phenylsilane with tritium in the silyl group is the source of phenyl-substituted silylium (silabenzyl) cations. The plausible migration of the cationic center was studied by considering reactions of nucleogenic cations with methyl *tert*-butyl ether. For this experiment the reactive mixtures of studied nucleophiles and phenylsilane tritium-labeled at Si as well as in the ortho- and para-positions of the benzene ring have been prepared. Taking into account the equal probability of the tritium atom decay in both positions, we expect an equal amount of two isomers of the nucleogenic silatolyl cations.

The observed tritiated products of the gas-phase reactions of the cations $[SiC_6H_7]^+$ with CH_3OtBu and their relative yields are presented in Table 1. All observed products are formed by the unimolecular decomposition of the cation−methyl *tert*-butyl ether complexes for which the elimination of $t\text{-}Bu^+$ cation is the most favorable channel. In the absence of isomerization, one may expect equal yields of para- and ortho-isomers of $H_3SiC_6H_4OCH_3$. However, the data presented in Table 1 suggest that yields of these isomers are substantially different. While the yield of the para-isomer is close (within the error bar) to 50%, the yield of ortho-isomer drops to 22%. Moreover, $C_6H_5SiH_2OCH_3$ appears with the 34% yield. This molecule is obviously the product of the unimolecular decomposition of the silatolyl cation adduct. Note that the reduction in ortho-isomer yield roughly equals the increase in $C_6H_5SiH_2OCH_3$ yield. These data clearly indicate that more than the half of nucleogenic *o*-silatolyl cations are isomerized into silabenzyl cations.

On the other hand, when hydrogen atoms in the silyl group of phenylsilane are substituted by tritium and the silabenzyl cation is formed as a result of β-decay, the only observed product of the ion−molecule reaction is $C_6H_5SiH_2OCH_3$, which is the product of *tert*-butyl cation elimination from the adduct. This fact shows that no isomerization of silabenzyl cation occurs.

To rationalize these experimental findings, we studied the potential energy surface of the $C_6H_7Si^+$ system by quantum chemical methods.

The isomerization from the *o*-silatolyl to silabenzyl cation and that from the *p*- to *o*-silatolyl cation have been characterized in our previous publication.[13] Here we revisited stationary points on these paths at a higher theoretical level. Barrier heights for other isomerization processes in this system have not been predicted in previous theoretical works except for the transition state for the silabenzyl−$[C_6H_6 \cdot SiH]^+$ complex rearrangement proposed by Choe.[8]

The equilibrium structure of the *p*-silatolyl cation (**1**) and stationary points for its isomerization into the ortho-isomer (**3**)

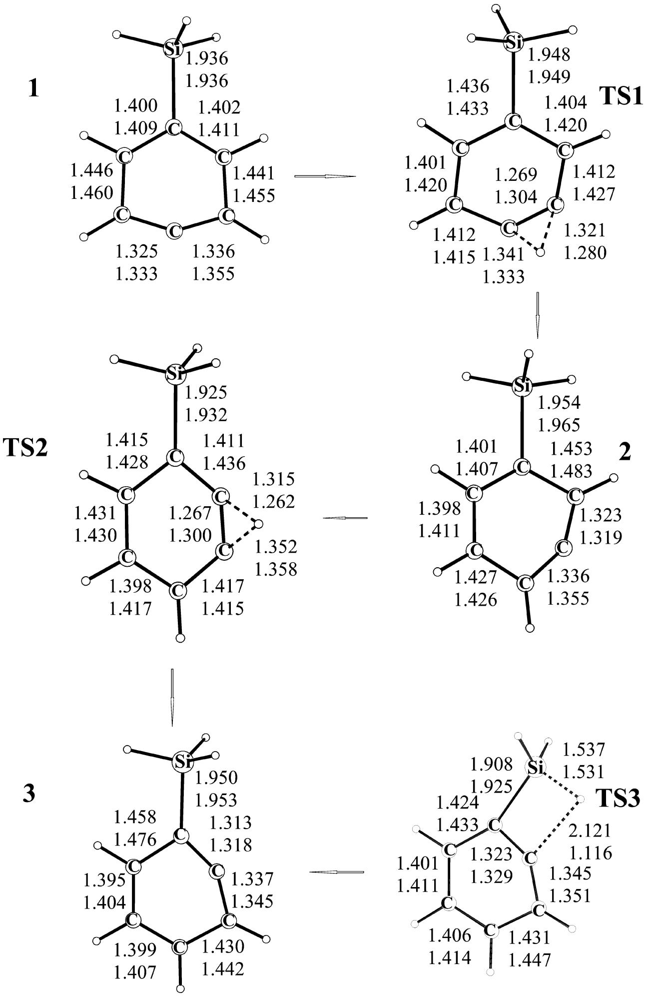


Figure 1. Equilibrium geometries (bond lengths in Å) of stationary points for the transformation of *p*-silatolyl cation into silabenzyl cation obtained at the B3LYP (upper figures) and MP2 levels of theory.

TABLE 2: Relative Energies (ΔE_e and $\Delta E_0 = \Delta E_e$ + ZPVE) in kcal/mol of Stationary Points on the Isomerization Path from the *p*-Silatolyl Cation (1) to the Silabenzyl Cation (4) Obtained by B3LYP and MP2 Methods with the aug-cc-pVDZ Basis Set

	B3LYP		MP2	
structure no.	ΔE_e	ΔE_0	ΔE_e	ΔE_0
1	0	0	0	0
TS1	47.0	44.7	38.8	37.3
2	−4.0	−3.4	−4.8	−4.1
TS2	45.5	43.3	37.6	36.3
3	−10.5	−9.6	−11.3	−10.2
TS3	−2.2	−1.7	−1.8	−1.3
4	−59.6	−54.7	−64.0	−59.0

are presented in Figure 1. Of the silatolyl isomers both **1** and **3** have symmetry elements; they belong to the $C_s$point group. Substitution of a hydrogen atom in the phenyl cation by the silyl group brings about a small effect on the electronic structure of the ring, especially in the case of the para-isomer **1**. When the silyl group is drawn closer to a positive charge center in the meta-isomer (**2**) and ortho-isomer (**3**), not only the ring structure destorts from the symmetry of phenylsilane but also the positive charge character shifts from the ring to silicon. Consequently, the barrier height of the ring hydride shift (**TS1** and **TS2**) decreases slightly, although they do not differ substantially from the corresponding value in the phenyl cation (compare MP2 values in Table 2 with the value of 40.1 kcal/mol for the barrier in the phenyl cation[19]). The deformation energy, i.e., the energy of geometry relaxation from the nascent nucleogenic ion structure (phenylsilane structure in our case) to the equilibrium structure of the ion, calculated as a difference between total energies of a cation in these two structures, is 34.0 and 39.4 kcal/mol for the *o*-silatolyl cation at the B3LYP and MP2 levels, respectively. For the para-isomer these values are slightly lower, i.e., 29.0 and 34.6 kcal/mol, respectively. This difference reflects the aforementioned increase of the ring distortion in the ortho-isomer. Since this energy is usually considered as the main source of the excess energy of nucleogenic ions which allows them to surpass isomerization barriers,[21] one may conclude that the deformation energy of the *p*-silatolyl cation is not high enough to isomerize to an ortho-isomer (to pass through **TS1** and **TS2** barriers). In contrast, the deformation energy in the *o*-silatolyl cation substantially exceeds the **TS3** barrier height, thus undergoing a facile isomerization to the silabenzyl cation (**4**, Figure 2).

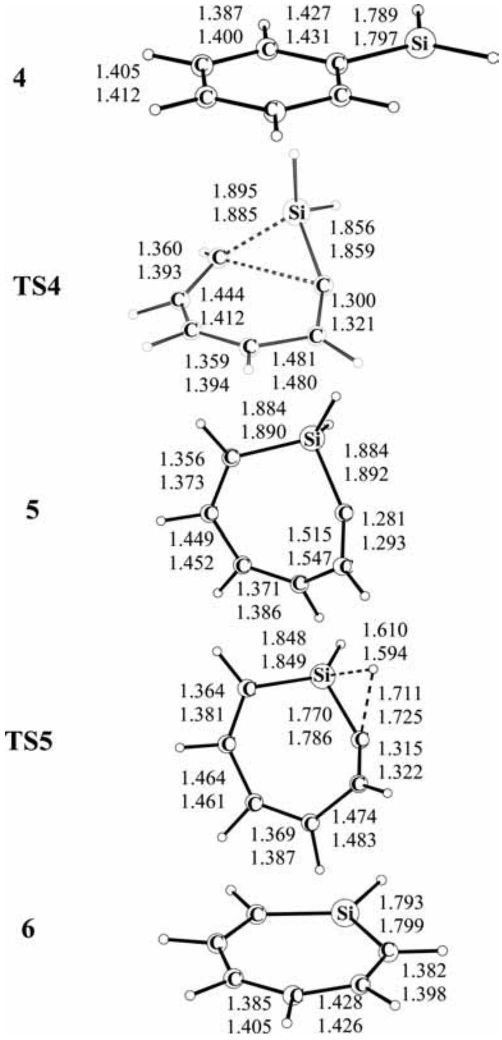


Figure 2. Equilibrium geometries (bond lengths in Å) of stationary points for the transformation of silabenzyl cation into silatropylium cation obtained at the B3LYP (upper figures) and MP2 levels of theory.

Experimental data discussed above do not indicate any further isomerization of the silabenzyl cation to other low-lying isomers, although there are more stable isomers in this system. For instance, the existence of a complex between silicon and the methyl-substituted cyclopentadienyl moiety has been predicted earlier by Nicolaides and Radom.[5,6] Two other low-lying isomers

TABLE 3: Relative Energies (ΔE_e and $\Delta E_0 = \Delta E_e +$ ZPVE) in kcal/mol of Stationary Points on the Isomerization Path from to Silabenzyl Cation (4) to Other Low-Energy Isomers Obtained by the B3LYP and MP2 Methods with the aug-cc-pVDZ Basis Set

	B3LYP		MP2	
structure no.	ΔE_e	ΔE_0	ΔE_e	ΔE_0
4	0	0	0	0
TS4	65.7	62.8	73.0	70.1
5	62.7	60.0	64.2	61.8
TS5	77.3	74.2	83.1	80.0
6	7.4	9.2	10.2	12.0
TS6	67.4	64.6	71.5	68.7
7	32.3	30.1	33.0	30.4
$C_6H_5Si^+ + H_2$	36.1	31.7	36.6	31.9
TS7	53.1	51.2	54.0	52.2
TS8	64.0	61.8	63.4	61.5
8	12.2	13.4	7.0	8.4
$C_6H_6 + HSi^+$	63.3	62.0	64.5	62.9
TS9	38.9	39.4	36.3	37.2
9	10.7	14.5	−0.1	4.1
TS10	79.0	79.4	72.8	73.0
10	−16.0	−12.8	−29.4	−26.0
$Si + C_5H_4CH_3^+$	138.8	138.4	151.7	151.6
$Si^+ + C_5H_4CH_3$	116.8	116.3		

with energy levels higher than silabenzyl cation were also found at the potential energy surface of the $C_6H_7Si^+$ system. However, the mechanism of the isomerization from the silabenzyl cation into these isomers has not been not revealed.

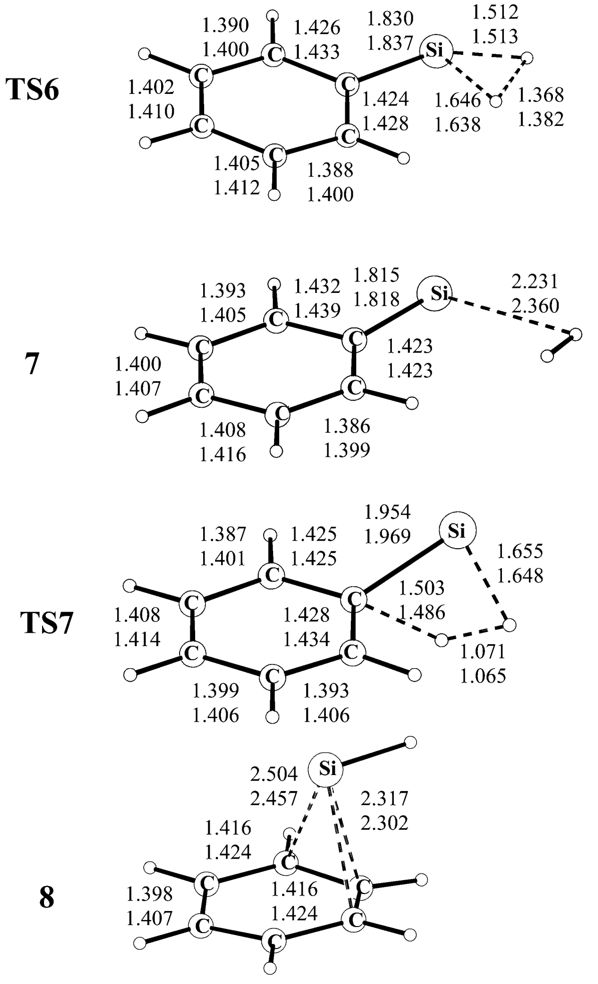


Figure 3. Equilibrium geometries (bond lengths in Å) of stationary points for the transformation of silabenzyl cation into the $[C_6H_6\cdot SiH]^+$ complex obtained at the B3LYP (upper figures) and MP2 levels of theory.

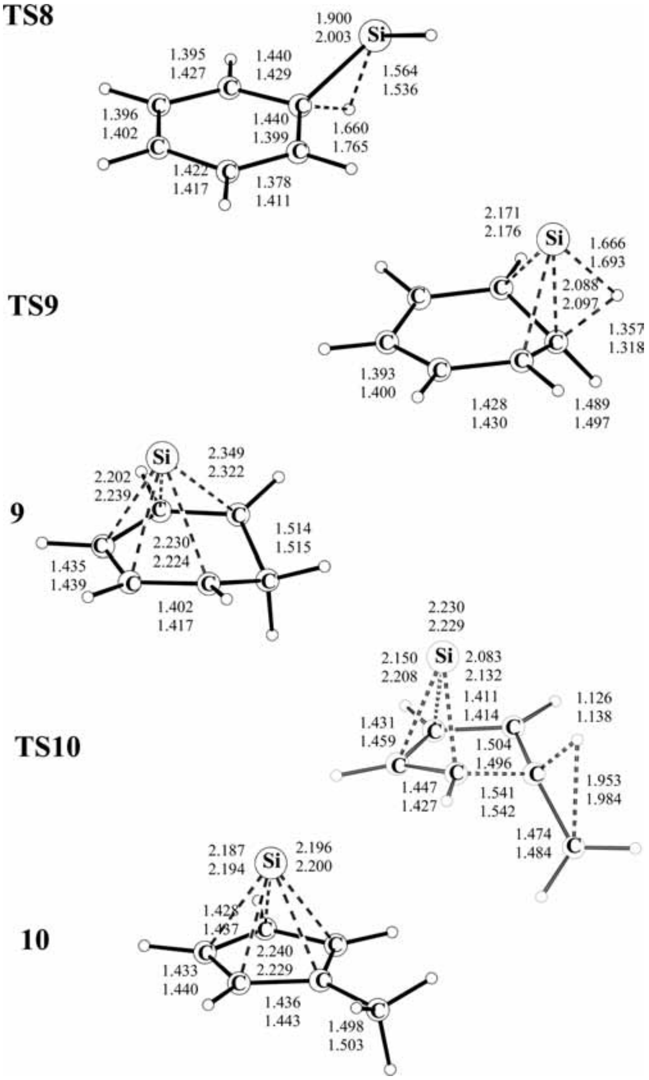


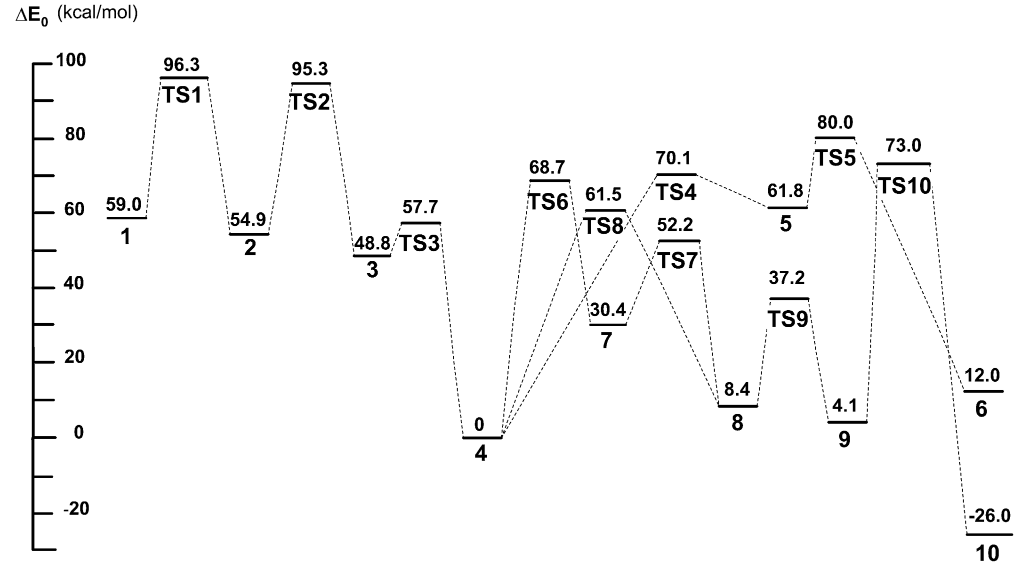
Figure 4. Equilibrium geometries (bond lengths in Å) of the transition state (**TS8**) for the direct conversion of silabenzyl cation into the $[C_6H_6\cdot SiH]^+$ complex as well as a sequence of stationary points for the transformation from the $[C_6H_6\cdot SiH]^+$ complex to (η^5 -methylcyclopentadienyl)silanium cation obtained at the B3LYP (upper figures) and MP2 levels of theory.

Although the tropylium ion is a global energy minimum in the system, ab initio study[4] suggests that the analogous 7-membered silatropylium ion is thermodynamically less stable than the silabenzyl cation. In our previous study[13] the transition states and intermediates on the isomerization path from benzyl to tropylium were located. Admitting the analogous mechanism of isomerization for the silicon substituted system, we obtained the stationary points presented in Figure 2.

Similar to the $C_7H_7^+$ system, the first step of this isomerization is found to be a transformation, which proceeds by bending of the the $C-SiH_2$ moiety toward an adjacent cyclic carbon atom (through **TS4**). This rearrangement forms a 7-membered silacycloheptatrienyl cation (**5**, Figure 2). The shift of hydride from the silicon atom to the neighboring carbon atom of the 7-membered ring (**TS5**) results in the silatropylium ion (**6**). The first step requires substantial energy since both the transition (**TS4**) and the intermediate (**5**) lie high above silabenzyl cation **4** (Table 3). The barrier height of the second transition state **TS5** is only 18 kcal/mol (henceforth MP2 values of ΔE_0 will be cited) above **5** (Table 2).

The collision-induced dissociation study[7] of the two forms of $C_6H_7Si^+$ have shown that the major dissociation products

SCHEME 1: Energy Levels (kcal/mol) of Stationary Points at the $[C_6H_7Si]^+$ Potential Energy Surface



from unreactive species (believed to be the $[C_6H_6{\cdot}SiH]^+$ complex) were SiH^+ with a loss of C_6H_6 and $C_6H_5Si^+$ with a loss of H_2. The latter channel was observed to be the only one for the dissociation of reactive species (unanimously considered to be the silabenzyl cation). Thus the loss of H_2 is one of the low-energy channels for the dissociation of both species.

Since thermochemical characteristics of this channel have not been estimated before, we have located transition states for these transformations. One may assume that the product complex for the H_2 dissociation is the "side-on" complex, the existence of which was revealed for H_3Si^+ [35] and other silylium cations.[36,37] This kind of complex for the silabenzyl cation (**7**, Figure 3) is characterized by the similarity of a $Si{\cdots}H_2$ separation and complexation energy for **7** as well as that for the analogous complex of the methylsilyl cation.[37] The transition state (**TS6**) has a high barrier of 69 kcal/mol, and more importantly, further dissociation with a loss of H_2 requires only 1.5 kcal/mol (Table 3).

We find a transition state **TS7** that connects the H_2 complex **7** with the $[C_6H_6{\cdot}SiH]^+$ complex (**8**). The other transition state **TS8** (Figure 4) described earlier by Choe[8] leads to the complex **8** directly from the silabenzyl cation (**4**). The **TS7** barrier height is only 22 kcal/mol above **7**, but to reach it on the way from the silabenzyl cation, the system needs to cross the **TS6** barrier, which is 69 kcal/mol high (Table 3). The direct way to complex **8** requires crossing the **TS8** barrier (62 kcal/mol). Thus, both paths to the $[C_6H_6{\cdot}SiH]^+$ complex (**8**) from from the silabenzyl cation (**4**) have barriers above 60 kcal/mol but the direct way (through **TS8**) has a slightly lower barrier (Scheme 1). However, our finding of the path for the interconversion between two isomers **7** (H_2 complex) and **8** (SiH complex) may explain the substantial yield of $C_6H_5Si^+$ observed in the collision-induced dissociation of the $[C_6H_6{\cdot}SiH]^+$ complex. The ΔE_0 value for **TS7** is 11 kcal/mol lower than the dissociation limit (Table 3), and it may be argued that the conversion to the H_2 complex is a preferential way of the $[C_6H_6{\cdot}SiH]^+$ complex rearrangement. However, the comparison of the Gibbs free energy values for the $C_6H_6 + HSi^+$ dissociation and **TS7** substantially reduces this preference to 3 kcal/mol due to a higher entropy required for dissociation.

Finally, we describe the path leading to the global minimum of the system, i.e., the $[C_5H_4CH_3{\cdot}Si]^+$ complex (**10**, Figure 4). This complex, the (η^5-methylcyclopentadienyl)silicon cation, was predicted to be the most stable isomer in the $C_6H_7Si^+$ system by Nicolaides and Radom.[5] It possesses C_s symmetry, and its structure may be described as a methylcyclopentadienyl ring capped with silicon. Analogous ring-cap structures were discussed by Jemmis and Schleyer,[38] and their stability was assigned to three-dimensional aromaticity. The high stability of **10** manifests itself also in the large energy of the dissociation of this cation. The dissociation with the loss of the methylcyclopentadienyl cation requires 152 kcal/mol (MP2). Note that this value substantially exceeds that of B3LYP (116.3 kcal/mol, Table 3). The other plausible channel that gives the methylcyclopentadienyl radical and silicon radical cation has slightly lower dissociation energy estimated at the B3LYP level. MP2 values for this channel cannot be estimated since wave functions for both $^2A_2$ and $^2B_1$ states of cyclopentadienyl radical are unstable.[39] We observed this instability also for the methylcyclopentadienyl radical despite its lower symmetry. This makes the UMP2 energy for this species meaningless and the dissociation energy is not shown in Table 2.

Nevertheless, the high dissociation energy of both channels is obvious and this fact may explain the increased stability of this type of structure. Note that the analogous (η^5-pentamethylcyclopentadienyl)silicon cation has been characterized experimentally.[40]

Transition states en route to **10** are first located in the present work. This path consisting of two steps starts from the $[C_6H_6{\cdot}SiH]^+$ complex (**8**). At first the proton from the HSi^+ moiety shifts to the benzene ring (**TS9**, Figure 4), which results in the formation of **9** formally a five-coordinated cationic complex between Si and cyclohexadienyl or (η^5-cyclohexadienyl)silicon cation. In contrast to **10**, the incorporation of a CH_2 group in the ring distorts the symmetry and decreases its aromaticity. This results in longer SiC bond distances (Figure 4) and a lower stability (Table 3) of **9** compared to **10**. Isomer **9** lies only slightly above the silabenzyl cation **4** (and the MP2 ΔE_e value even lower) but substantially higher in energy than the global minimum, i.e., (η^5-methylcyclopentadienyl)silanium cation (**10**). The transition state (**TS9**) for the transformation from **8** to **9** has a barrier height of only 29 kcal/mol above **8**. However, the next barrier (**TS10**) is much higher. Complex **9** transforms to **10** by breaking the cleavage of a bond between two carbons of the cyclohexadienyl moiety and by hydrogen shift from the cyclic carbon atom to the exocyclic CH_2 group (Figure 4). This complicated rearrangement from the cyclohexadienyl to the cyclopentadienyl structure requires 69 kcal/mol (Table 3).

Thus, although the silabenzyl cation is not a global minimum of the $C_6H_7Si^+$ system, rearrangements to the stable (η^5-methylcyclopentadienyl)silicon cation and other low-energy structures are restricted by high barriers on their paths. This is in agreement with experimental data. Nucleogenic silabenzyl cations, which may possess excess deformation energy of 38.6 kcal/mol (MP2), produce in their reaction with methyl *tert*-butyl ether only one product, which demonstrates the absence of its isomerization.

Conclusions

1. Radiochromatographic identification of the neutral labeled products of reactions of methyl *tert*-butyl ether with nucleogenic *o*- and *p*-silatolyl cations shows that the former cation effectively isomerizes into the silabenzyl cation, while the latter does not. These findings are in agreement with theoretical estimates of classical barriers for hydride shifts in silatolyl cations.

2. No further isomerization was observed for nucleogenic silabenzyl cations.

3. Two isomerization paths from the silabenzyl cation to the $[C_6H_6 \cdot SiH]^+$ complex were found: the first is a direct transformation by hydrogen shift from the SiH_2 group to a carbon atom, while the second proceeds through the $[C_6H_5Si \cdot H_2]^+$ complex. Both paths have barriers as high as 60−70 kcal/mol.

4. Conversion of $[C_6H_6 \cdot SiH]^+$ to $[C_6H_5Si \cdot H_2]^+$ proceeds through a transition state that has an energy close to the $C_6H_6 + SiH^+$ dissociation level. This explains the observation of $C_6H_5Si^+$ along with SiH^+ in the products of collision-induced dissociation of $[C_6H_6 \cdot SiH]^+$.

5. The (η^5-cyclohexadienyl)silicon cation was found to be an intermediate for the isomerization of $[C_6H_6 \cdot SiH]^+$ into the (η^5-methylcyclopentadienyl)silicon cation. The barrier for the first step of this isomerization path is only 29 kcal/mol high, but the transformation from the (η^5-cyclohexadienyl)silicon cation has a 69 kcal/mol barrier.

6. The mechanism of the rearrangement from the silabenzyl cation to the silatropylium ion is similar to that of a two-step benzyl to tropylium isomerization and has a silacycloheptatrienyl cation as an intermediate. Barriers on this path are 70 and 18 kcal/mol high, respectively.

7. Transformations of a nucleogenic silabenzyl cation into the most stable (η^5 -methylcyclopentadienyl)silicon cation as well as into other low-energy isomers require at least 60 kcal/mol.

An excess deformation energy inherent to this cation estimated as 39 kcal/mol is not high enough to cross these barriers.

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Supporting Information Available: Tables with calculated frequencies and rotational constants of the stationary points. This material is available free of charge via the Internet at http://pubs.acs.org.

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