A New Rearrangement Process in *tert*-Amyl Cation

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Abstract: ^{13}C NMR spectroscopy of the 2-methyl-2-butyl-1-^{13}C cation (^{13}C-labeled *tert*-amyl cation) indicates that interchange of the inside and outside carbons occurs via a barrier of 19.5 ± 2.0 kcal/mol. A plausible mechanism involves hydride migration in the proposed 2-pentyl cation **4** to form 3-pentyl cation **5**. Via the protonated cyclopropane intermediate **6**, which undergoes degenerate corner-to-corner hydride shift, the secondary 3-pentyl cation **5′** with the label shifted to the central carbon atom is formed. The *tert*-amyl cation obtained from **5′** in the reverse process has the ^{13}C label on an inside carbon atom. All intermediates and transition structures were located on the PES theoretically at the MP2/6-31G(d,p) level of theory. The rearrangement rate of the doubly labeled *tert*-amyl cation (methyl-^{13}C-butyl-1-^{13}C cation), followed by means of ^{13}C NMR, revealed that the process that interchanges inside and outside carbons has the highest barrier. Comparison of the initial rates revealed that isotopomer **1e** arises considerably more slowly than other isotopomers, indicating that in the overall rearrangement process transition structure **5-TS** has the highest energy.

Introduction

Obtaining rearranged products in solvolysis reactions has long been considered evidence for 1,2-hydride, methide, and alkide shifts in the carbocations that are intermediates in these reactions. Only extremely rapid rearrangement steps can be seen in this way because the intermediate cations have such short lifetimes. The development of conditions where some of these ions are indefinitely stable has made it possible to detect and measure the rates of a variety of much slower rearrangement processes.

The *tert*-amyl cation (2-methyl-2-butyl cation) has been investigated for more than three decades, in stable solution in superacid,[1−4] as a stable salt,[5] and theoretically.[6,7] Solvolysis studies go back still further. Two rearrangement processes that rapidly interchange chemically different hydrogens have been reported in the stable ion. Changes in the proton NMR line shape with temperature demonstrate interchange of the two types of methyl groups. The mechanism proposed (Scheme 1, pathway I) involves uphill isomerization of the *tert*-amyl cation **1** to the secondary ion **2**, followed by a degenerate Wagner−Meerwein 1,2-methide shift, proceeding through the protonated dimethyl-cyclopropane structure **3**. A 1,2-hydride shift then returns to

the rearranged tertiary ion **1′**. The measured barrier was 15.4 kcal/mol. A second, slower, process that exchanges the methylene protons and methyl protons was subsequently observed, and its barrier was found to be 18.8 kcal/mol.[8] The mechanism proposed for the second process was corner-to-corner proton migration in the protonated dimethylcyclopropane **3** through the transition structure **3-TS** to form the secondary unbranched cation **4** (Scheme 1, pathway II). The energies of stationary points along reaction pathways I and II were calculated at the MP4SDTQ(FC)/6-31G(d,p)//MP2(FC)/6-31G(d,p) level. The optimized geometries of the "open" secondary 3-methyl-2-butyl cation **2** and the 1,3-protonated *trans*-1,2-dimethylcyclopropane (edge-protonated cyclopropane **3-TS**) were located as the transition-state structures for pathway I and pathway II, respectively. The calculated energy barriers (15.2 and 18.5 kcal/mol, respectively) are in close agreement with the experimental results.

Similar mechanisms for formation of protonated cyclopropanes and corner-to-corner proton shifts (pathway II) have been proposed in other stable secondary carbocations. The interchange of the methyl hydrogens with the ring hydrogens in the methycyclopentyl cation and migration of a ^{13}C label from the methyl into the ring can be rationalized through a similar mechanism. Scrambling of the hydrogens and carbons in the 2-butyl cation is also considered to occur through corner-to-corner proton shifts in a protonated cyclopropane intermediate.[9]

If the secondary 2-pentyl cation **4** is formed in pathway II, it would be expected to rapidly and reversibly rearrange to the

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Scheme 1

Pathway I

Pathway II

Pathway III
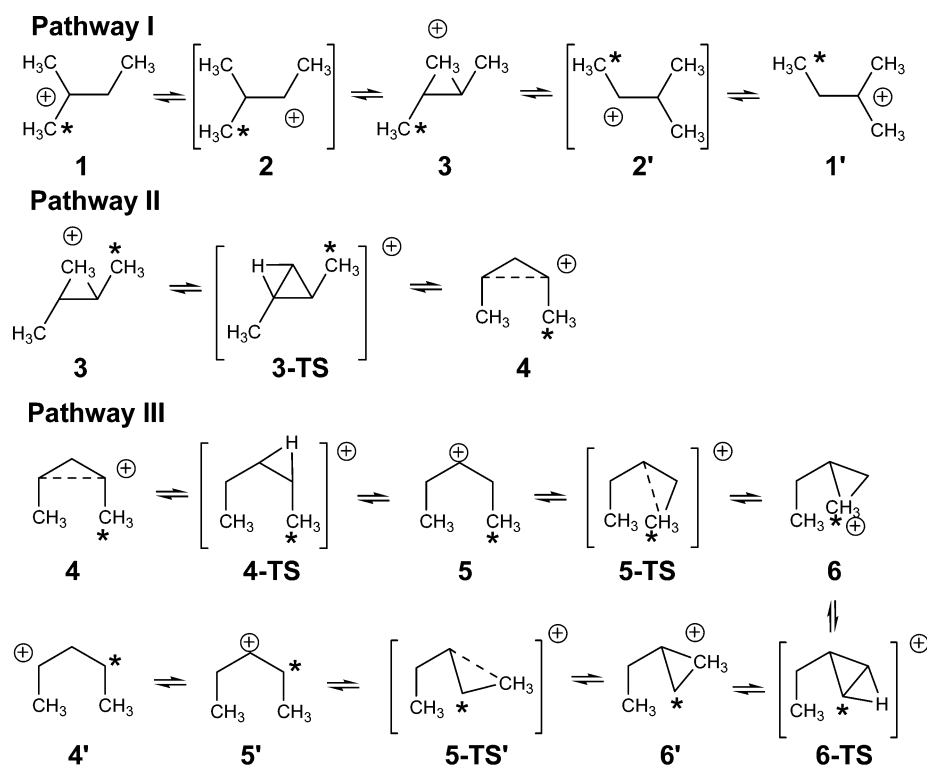
3-pentyl cation **5**, since 1,2-hydride shifts that are not uphill typically have very low barriers. For example, cyclopentyl cation shows a single sharp proton peak even at low temperatures. Furthermore, since the 3-pentyl cation is a secondary cation similar to those mentioned above, it should also undergo rearrangement through a protonated cyclopropane intermediate and a corner-to-corner proton shift, in a manner similar to that of *sec*-butyl cation.

The two processes previously reported (pathways I and II) do not interchange the two inside carbons of *tert*-amyl with the three methyl carbons. However, if the 3-pentyl cation **5** is formed, its rearrangement would be expected to interchange these carbon atoms. To see whether this scrambling process occurs, we labeled a methyl group with [13]C. We report here observing its rearrangement to the inside carbon positions by means of ^{13}C NMR spectroscopy. Theoretical calculations concerning the pathway are also described.

Results and Discussion

The monolabeled *tert*-amyl alcohol (2-methyl-2-butanol-1-^{13}C) was prepared via the Grignard addition of [^{13}C]methyl iodide to the methyl ethyl ketone. Dilabeled *tert*-amyl alcohol [2-(methyl-^{13}C)-2-butanol-1-^{13}C] was obtained from the ethyl propionate and the [^{13}C]methyl iodide also by Grignard reaction. The stable carbocation solution was prepared from the alcohol via the molecular beam method in SbF$_5$/SO$_2$ClF.[10]

^{13}C NMR spectroscopy of the monolabeled isotopomer (125 MHz) showed a decrease of the signal due to the (methyl) carbons (8.6 and 43.4 ppm) and the appearance of "inside" [13]C signals (56.2 and 334.6 ppm) (Figure 1), indicating that interchange of the outside and inside carbons occurs. The
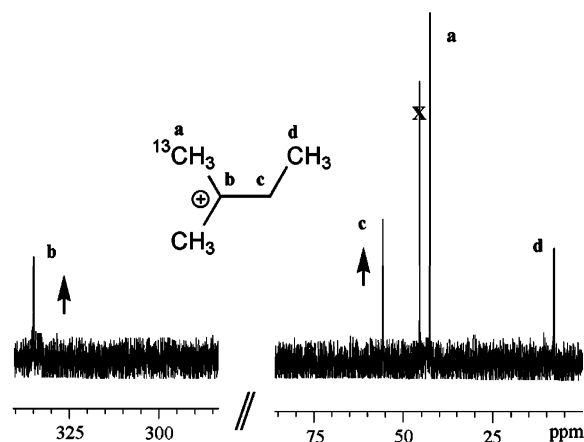
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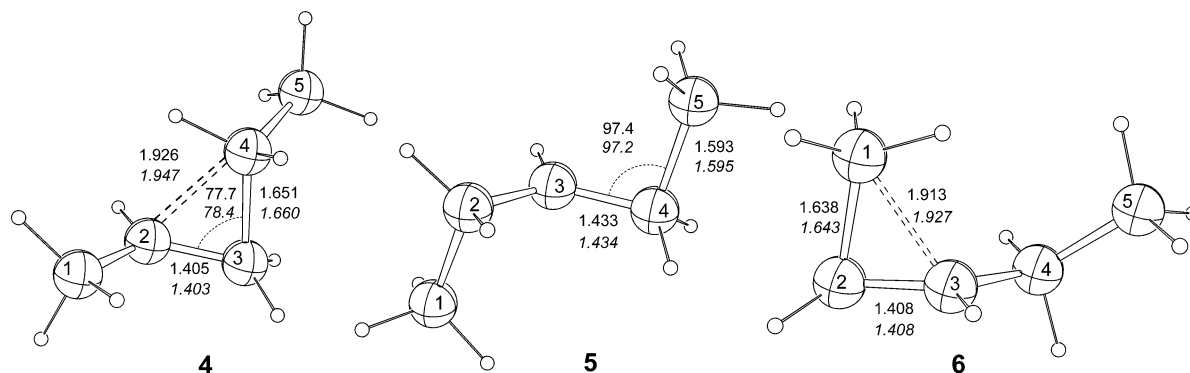

Figure 1. ^{13}C NMR spectrum (125 MHz) of the ^{13}C-labeled *tert*-amyl cation **1** in SbF$_5$/HF at −9 °C. The methyl signal of the *tert*-butyl cation is denoted as X.

rearrangement rate constants were calculated from the increasing fractions of the isotopomers having the ^{13}C label on the inside carbons (data obtained from the peak heights). The following first-order rearrangement rates were obtained: $(9.0 \pm 0.4) \times 10^{-4}$ s^{-1} (−9 °C), $(2.0 \pm 0.1) \times 10^{-3}$ s^{-1} (−4 °C), and $(6.0 \pm 0.4) \times 10^{-3}$ s^{-1} (5 °C). Since only one of the three outside methyl groups was labeled in the starting compound, the observed rate of moving to the inside is only one-third the total rate of the overall process. However, since the process is first order, the half-life and rate constants are not affected. Thus, from the rearrangement rate, the barrier for the interchange of the inside and outside carbons was found to be $E_a = 19.5 \pm 2.0$ kcal/mol.

The experiment presented above clearly demonstrates the existence of both the 2-pentyl cation **4** and the 3-pentyl cation **5**. It should be noted that the methyl and methylene hydrogens

Figure 2. MP2/6-31G(d,p)-optimized geometries of carbocations involved in pathway III (MP2/6-31G(d)-calculated geometry parameters are in italics), bond lengths in angstroms and bond angles in degrees.

could exchange without going to the 2-pentyl cation. Once the protonated cyclopropane derivative **3** is formed**,** exchange of the hydrogens could occur by two successive corner-to-corner proton migrations. A proton could move to C-2, and the proton which was initially there could move back. However, exchange of the inside and outside carbon atoms can only happen if the protonated cyclopropane **6** is formed, and this can arise only from the 3-pentyl cation. The 3-pentyl cation, in turn, can be obtained only by a hydride shift from the 2-pentyl cation.

A plausible mechanism consistent with the new result is presented in Scheme 1, pathway III. The first step is the hydride migration in the secondary cation **4**, and formation of the secondary cation **5**. The next step is the formation of the protonated cyclopropane **6** that undergoes a degenerate corner-to-corner proton shift. Reopening the cyclopropane ring gives **5′**, which is the isotopomer of **5** with the label shifted to the central carbon atom. This ion can return to a *tert*-amyl cation by the reverse of the process that formed the unbranched ion, but now the ^{13}C label is on an inside carbon atom.

We performed quantum chemical calculations using the Gaussian 94 program suite[11] to study these proposed intermediates. All structures were fully optimized (in the specified symmetry) at the Møller−Plesset perturbation theory. The ab initio calculations were performed using frozen core (FC) second-order MP2 perturbation correction and fourth-order MP4(SDTQ) theory with single, double, triple, and quadruple substitutions.[12] The standard split valence and polarized 6-31G(d) basis set was employed in the geometry optimizations and frequency calculations. For comparison, we also carried out calculations with the larger basis set 6-31G(d,p). A vibrational analysis was performed at the same level of theory (except for MP4 calculations) to determine the zero-point vibrational energy (ZPE) and to characterize each stationary point as a minimum (NImag = 0) or transition-state structure (NImag = 1). The optimized MP2/6-31G(d,p) geometries were subjected to single-point energy calculations at the MP4 level; thus, our final level is MP4(SDTQ)/6-31G(d,p)//MP2/6-311G(d,p), which is comparable to the

Table 1. Relative Energies (kcal/mol) for Stationary Points Located along Pathway III[a]

cation	MP2/6-31G(d)	MP2/6-31G(d,p)	MP4/6-31G(d,p)//MP2/6-31G(d,p)
1	0	0	0
4	10.3	9.8	11.1
	(11.7)	(11.2)	(12.5)
4-TS	17.5	16.2	16.6
	(19.3)	(17.6)	(17.9)
5	12.7	12.6	12.8
	(13.6)	(13.6)	(13.8)
5-TS	12.7	12.7	12.9
	(13.7)	(13.7)	(13.9)
6	11.8	11.5	12.6
	(13.1)	(12.7)	(13.8)
6-TS	21.6	19.8	21.9
	(22.5)	(20.6)	(22.8)

[a] The relative energies with ZPE included are given in parentheses.

calculated results obtained by Farcasiu and Norton.[6] Corrections for ZPE (not scaled) are included in the calculated energies.

The relative energies are given in kcal/mol with respect to the most stable corresponding isomer **1** and are listed in Table 1. For minimum structures **4**−**6** only the most stable conformers were considered.

The secondary 2-pentyl cation **4**, which is formed from the cation **3** (pathway II), is calculated to be 12.5 kcal/mol less stable than the starting *tert*-amyl cation **1**. The 3-pentyl cation **5**, obtained by hydride shift in **4**, is an additional 1.3 kcal/mol higher in energy than the cation **4**. Cation **5** has C_2 symmetry in which the C1−C2 and C4−C5 bonds are aligned parallel to the formally vacant π-orbital at the C3 carbocation center, each on one side of the carbon skeleton "plane" (Figure 2). The formation of **5** is followed by ring closure, yielding the corner-protonated ethylcyclopropane **6**. This interconversion of **5** to **6** (the calculated energy barrier is only 0.1 kcal/mol) occurs via the partially bridged transition-state structure **5-TS** (Figure 3) characterized by one imaginary frequency (−70 cm^{−1}), which corresponds to the three-membered ring closure process **5** → **6**. We have located two more rotamers for the protonated cyclopropane **6** obtained by the rotation around the C3−C4 bond axis, and the relative energy difference between the most stable (**6**) and the least stable is only 0.8 kcal/mol. The methyl-bridged structure **6** undergoes a degenerate corner-to-corner hydride shift via the edge-protonated ethylcyclopropane cation **6-TS** to yield an equivalent structure, **6′**. The most important energy minimum structures are presented in Figure 2, while the most important transition structures are presented in Figure 3.

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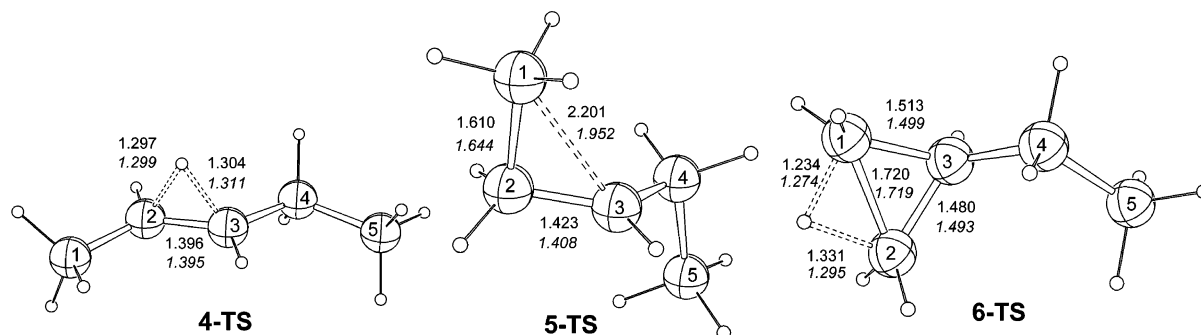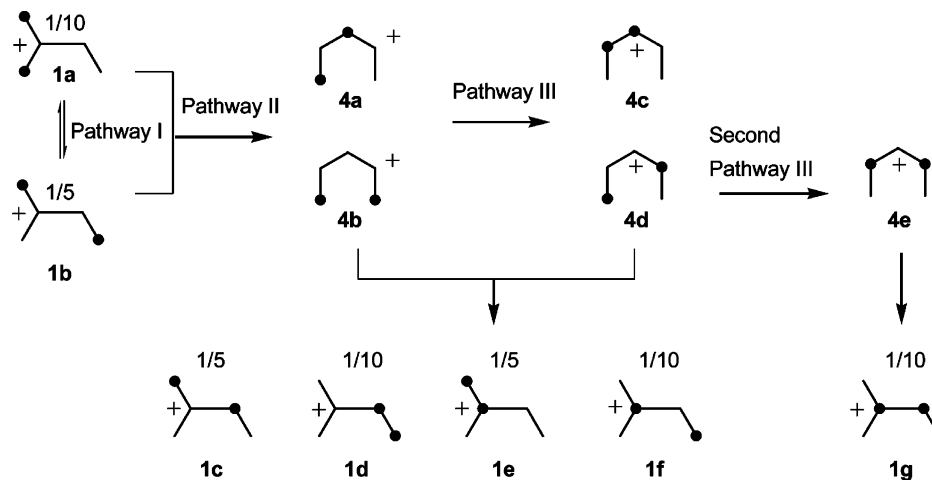(12) Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244.

Figure 3. MP2/6-31G(d,p)-optimized geometries of transition-state structures involved in pathway III (MP2/6-31G(d)-calculated geometry parameters are in italics), bond lengths in angstroms and bond angles in degrees.

Scheme 2 *ᵃ*

ᵃ The fractions are the amounts expected at statistical equilibrium assuming no equilibrium isotope effects.

According to quantum chemical calculations carried out at the MP4/6-31G(d,p)//MP2/6-31G(d,p) level of theory, **6-TS** (-195 cm^{-1}) represents the transition-state structure for the overall rearrangement process of the *tert*-amyl cation, since it is 0.7 kcal/mol less stable than **3-TS**. However, these differences are rather small. Experimental data suggest also that pathway III proceeds via a slightly higher barrier than pathway II (18.8 vs 19.5 kcal/mol), but because of the experimental error, this result is ambiguous. Therefore, we performed an experiment with doubly labeled amyl cation (structure **1a**, Scheme 2) to decide which is the rate-determining rearrangement in the cation.

Let us consider how the content of the mixture of doubly labeled *tert*-amyl cations depends on the barriers for processes II and III. If the proton migration in the protonated cyclopropane **6** were the rate-determining process (pathway III), only one closure of **6**, proton migration, and reopening could occur before going back to the *tert*-amyl cation via pathway II. In other words, only one exchange of the inside and outside carbons would take place. All possible rearrangements of the doubly labeled cation **1a** are presented in Scheme 2. Starting from the doubly labeled *tert*-amyl cation **1a**, isotopomer **1b** would arise via the lowest barrier (pathway I). Thus, from the initial mixture **1a**/**1b** two isotopomers of 2-pentyl cations would be formed, **4a** and **4b**. After one rearrangement cycle according to process III, besides isotopomers **4a** and **4b**, the formation of **4c** and **4d** would also occur. From all possible 2-pentyl cations four additional different isotopomers would arise, which are **1c**−**1f**, so the overall mixture would contain isotopomers **1a**−**1f**. However, if the barrier to the formation of **6** were lower than

that of **3**, before going back to the *tert*-amyl cation via pathway II, multiple rearrangements according to pathway III would occur. In that case besides **4a**−**d**, the formation of **4e** (from **4d**) would happen. From **4e** the *tert*-amyl cation **1g** having the inside carbon atoms labeled would be formed at the same rate as cations **1c**−**1f**. On the other hand, if pathway III were rate determining, as is suggested by kinetic data carried out with monolabeled isotopomer and by theoretical calculations, in the early stages of the reaction only **1a**−**1f** would be formed, as predicted above. The formation of **1g** would occur in the later stages of the reaction and slower than the formation of other isotopomers. The overall process is presented in Scheme 2, in which the fractions in certain isotopomers in the final equilibrium are given above the isotopomer structure.

The formation of different isotopomers from the dilabeled **1a**/**1b** cation mixture was followed by ^{13}C NMR at -22 °C. Only formation of the cations in which the labels are adjacent to each other (**1d**, **1e**, and **1g**) can be monitored separately. They have doublets instead of singlets in the carbon spectrum due to ^{13}C$-^{13}$C spin−spin coupling. It turned out that it was convenient to compare the formation of **1d** and **1g**, since the fraction of both isotopomers is equal in the final mixture (1/10) and the coupling constants between C2−C3 (**1g**) and C3−C4 (**1d**) are different. Formation of isotopomer **1d** is seen in the ^{13}C NMR spectrum as the increase of two doublets having the same coupling constant ($J_{C3-C4} = 35.1$ Hz), one centered at 8.6 ppm due to the methyl carbon and the other centered at 56.2 ppm due to the methylene carbon. Formation of isotopomer **1g** in the spectrum is also seen as two doublets with the same coupling
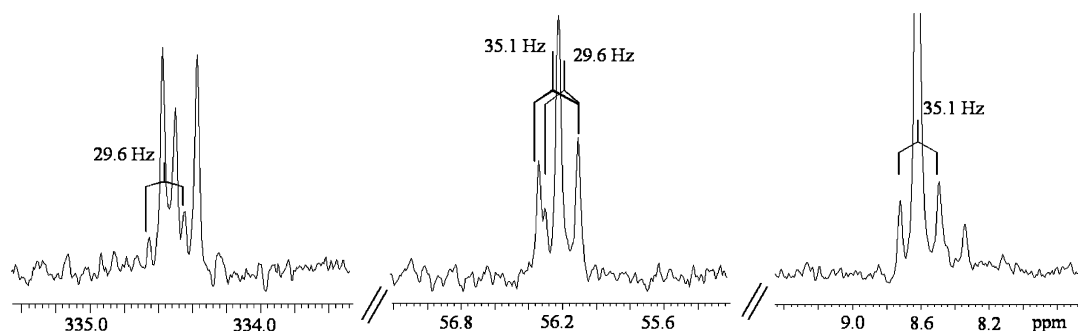
Figure 4. ^{13}C NMR spectrum (125 MHz) of the ^{13}C-dilabeled *tert*-amyl cation **1** in SbF$_5$/HF at -22 °C. The spectrum was taken after 0.5 h. Two corresponding pairs of spin−spin coupling constants are presented for **1d** ($J = 35.1$ Hz) and **1g** ($J = 29.6$ Hz).

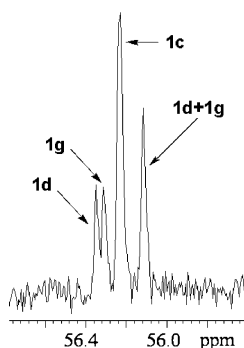**Figure 5.** ^{13}C NMR spectrum (methylene signal) of the ^{13}C-dilabeled *tert*-amyl cation **1** in SbF$_5$/HF at -22 °C. The spectrum was taken after equilibrium was reached.

constant ($J_{C2-C3} = 29.6$ Hz), one centered also at 56.2 ppm due to the methylene carbon and the other centered at 334.6 ppm due to the carbocation center. Thus, direct comparison of the relative ratio of the doublet of **1d** and **1g** at 56.2 ppm enables us to decide which isotopomer is formed more rapidly. Important segments of the spectrum taken in the early stages of rearrangements of the doubly labeled *tert*-amyl cation are presented in Figure 4. Spectra taken in early stages of the reaction clearly revealed that formation of **1d** ($J = 35.1$ Hz) is faster than formation of **1g** ($J = 29.6$ Hz). As shown in Figure 4, after 1/2 h of rearrangement at -22 °C, the height of the peak that corresponds to **1d** is approximately twice as large as the height of the peak that corresponds to **1g** (the upfield signal of the doublet of **1d** overlays the upfield peak of the doublet of **1g**). As expected, at the end of the rearrangement process (after 5 half-lives) after equilibrium is reached, the fractions of both

isotopomers **1d** and **1g** are the same, as is obvious from the spectral region at 55.2 ppm where the peaks that correspond to **1d** and **1g** are equal (Figure 5).

With the above considerations in mind, the experiment with the doubly labeled cation unambiguously shows that the barrier of the new process in the *tert*-amyl cation that interchanges inside and outside carbon atoms proceeds via the protonated cyclopropane transition structure **6-TS** (pathway III, Scheme 1). This is the highest energy transition structure on the pathway. In conclusion, the overall rearrangement in *tert*-amyl cation can be described with three distinct processes: the process that interchanges the methyls (pathway I) proceeds through the lowest barrier (15.4 kcal/mol), the process that interchanges methyl and methylene protons (pathway II) proceeds via a higher barrier (18.8 kcal/mol), and the process that interchanges inside and outside carbons (pathway III) goes through the highest barrier (19.5 kcal/mol).

Supporting Information Available: Precursor and cation preparations, kinetic measurements, and computational data (Cartesian coordinates of optimized structures, absolute energies, ZPE corrections, NImag) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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