

Theoretical study of carbon atom scrambling in benzenium ions with ethyl or isopropyl groups

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ABSTRACT: Carbon atom scrambling is observed in benzenium ions in the mass spectrometer and in isotopic labeling experiments in the methanol-to-hydrocarbons reaction over acidic zeolites. We have shown plausible scrambling mechanisms in ethyl- and isopropylbenzenium ions and various intramolecular interconversion reactions that may take place in alkylbenzenium ions. Quantum chemical Density Functional Theory (DFT) modeling at the B3LYP/cc-pVTZ//B3LYP/6-311G(d,p) level of theory has been carried out to investigate carbon atom scrambling reactions in ethyl- and isopropyl(methyl)benzenium ions. A total of 85 stationary points have been calculated (48 minima and 37 transition states). The carbon atom scrambling reactions start with an initial ring expansion of the benzenium ions to a seven-membered ring. The seven-membered ring may rearrange and at a later stage re-contrast to the original benzenium species, albeit with some atoms interchanged, i.e. there has been atom scrambling.

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KEYWORDS: carbon atom scrambling; DFT study; benzenium ions; alkylbenzenium ions; methanol-to-hydrocarbons; hydrocarbon pool mechanism; benzene ring expansion

INTRODUCTION

Recent research on the methanol-to-hydrocarbons (MTH) reaction over acidic zeolites^{1–4} has revealed that alkenes are formed via an indirect mechanism type, termed the ‘hydrocarbon pool mechanism’.^{5–21} According to this mechanism an adsorbed hydrocarbon complex continually adds methanol/dimethyl ether and splits off alkenes. Figure 1 shows a schematic view of the mechanism. Different organic species may constitute the hydrocarbon pool. Methylbenzenes are probably the most important reaction centers in the MTH reaction.^{8,9,13,14} Details on the mechanism for formation of small alkenes from these hydrocarbon species are still debated.

Two main reaction mechanisms for alkyl chain formation on aromatic rings have been proposed. One is based on intramolecular isomerizations of a cationic methylbenzenium species and is often referred to as the ‘paring reaction’.²² In this reaction, the methylbenzenium rearrangements take place via ring contractions and expansions that eventually lead to an alkyl chain on the

benzenium ring. Previously we have used quantum chemical modeling to investigate the various intramolecular reactions that methylbenzenium ions may undergo to form higher alkyl chains.^{23,24}

Another explanation for alkyl chain formation on benzenium species is the side-chain methylation mechanism. It was first proposed by Mole *et al.* to explain the co-catalytic role of toluene in the MTH reaction over zeolite H-ZSM-5.²⁵ In the side-chain methylation mechanism, an alkyl group on an alkylbenzenium ion is deprotonated so that an exocyclic double bond is formed. This double bond subsequently may be methylated so that a higher alkyl chain is formed. The alkyl chain subsequently may be split off as an alkene. Sassi *et al.*¹⁷ suggested that side-chain methylations are important pathways for ethene and propene formation over zeolite H-Beta. The mechanism is illustrated schematically in Fig. 2, which is taken from Arstad *et al.*²⁶ They used quantum chemical methods to model the main features of the side-chain methylation mechanism. Seiler *et al.*²¹ used *in situ* NMR techniques, and obtained evidence that side-chain methylation is an important pathway for alkene formation in the MTH reaction over zeolite H-ZSM-5.

During the last decade, several isotopic labeling studies of the MTH reaction have been published where [¹³C]methanol was co-reacted with other hydrocarbons.^{5,6,7,9,11,16,17} In these experiments, it was observed

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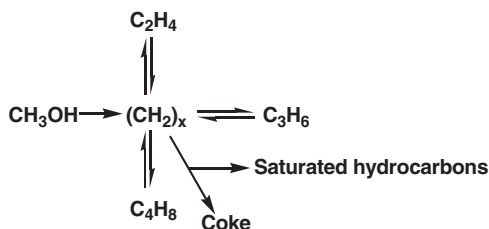


Figure 1. Schematic description of the hydrocarbon pool mechanism from Ref. 5

that there is an exchange of carbon atoms between the methyl groups and the ring carbons in methylbenzenes and methylnaphthalenes. An appealing explanation for these observations involves methylbenzenium rearrangements via ring expansions/contractions and the formation of alkyl chains that are eliminated as alkenes. These intramolecular reactions will necessarily incorporate carbon atoms from methyl groups into the benzenium ring when the alkyl chains are formed. Mass spectrometric studies of ethene elimination from xylenium ions²⁷ and our two previous papers^{23,24} on the methylbenzenium rearrangement mechanisms demonstrate this.

Sassi *et al.*¹⁷ proposed an additional model for the carbon atom scrambling involving hydride transfer from neutral alkylbenzenes and the formation of tropylium ion-type species, where ring and alkyl carbons scramble through a series of contractions/expansions.

As described above, the side-chain methylation mechanism was set forth to explain alkyl chain formation on methyl arene reaction centers. If this reaction path is important, scrambling reactions taking place in the alkylbenzenium species that are formed by the side-chain methylation might explain the observation that carbon atoms from the benzene ring appear in the alkene products. In as early as 1985 there was a discussion between Pines and Mole on this issue.²⁸ Hence, a more detailed insight into carbon atom scrambling reactions in ethyl- or isopropyl(methyl)benzenium species may contribute to a more comprehensive understanding of the MTH reaction. On this background, we have performed a quantum chemical study of such scrambling reactions. Protonated ethylbenzene, protonated isopropylbenzene, 1-ethyl-4,4-dimethylbenzenium, 1-isopropyl-4,4-dimethylbenzenium,

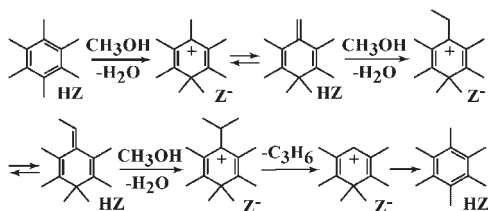


Figure 2. Side-chain methylation mechanism for propene formation in the MTH reaction (HZ represents the zeolite) from Ref. 26

1-ethyl-3,4,4,5-tetramethylbenzenium, 1-isopropyl-3,4,4,5-tetramethylbenzenium, 1-ethyl-2,3,4,4,5,6-hexamethylbenzenium and 1-isopropyl-2,3,4,4,5,6-hexamethylbenzenium ions were used as starting points. All these species may be formed after protonation or methylation (by a methyl cation) of a neutral alkylbenzene molecule.

Over the years much work has been devoted to the study of protonated alkylbenzenes, in solution and in gas phase. An early study of the benzenium ion and monalkylbenzenium ions in solution was carried out by Olah *et al.*²⁹ Most work that has a direct bearing on this work has, however, been carried out in the mass spectrometer and relates to monomolecular reactions in isolated molecules, i.e. reaction systems relevant to the reactions we study in this paper. Comprehensive reviews have been published.^{30–33}

COMPUTATIONAL DETAILS

All computations were carried out using the Gaussian 98 program package.³⁴ The structures were first optimized at the B3LYP/6-31G(d) level of theory, and then re-optimized at the B3LYP/6-311G(d,p) level of theory to investigate the basis set effects. The geometry changes with the larger basis set were marginal and the energies also were very similar. Analytical frequencies were calculated at the B3LYP/6-311G(d,p) level of theory using the geometries found at the same level of theory. It was ensured that the transition states had one, and only one, imaginary frequency and that the minima had none. Zero-point energy corrections were obtained from the frequency calculations. Single-point energies were finally calculated at the B3LYP/cc-pVTZ level. All reported energies are thus calculated at the B3LYP/cc-pVTZ//B3LYP/6-311G(d,p)+ZPE level and given in kJ mol^{-1} . Single-point energies obtained with the B3LYP functional and cc-pVTZ basis sets give good reaction energies for related systems, even for non-isodesmic reactions.²⁶ Furthermore, intrinsic reaction coordinate (IRC) calculations, as implemented in Gaussian 98, were performed to ensure that the transition states connected the desired minima. To minimize numerical noise, which may impair convergence in the geometry optimizations, the ‘ultrafine’ grid was chosen for the numerical integration scheme in all calculations.

RESULTS

The scrambling reactions studied in the present work start with a ring expansion of the alkylbenzenium ions. We have shown earlier that ring expansion of a methylbenzenium species is more facile if it may be considered to start with a 1,3-hydrogen shift from a methyl group that has another hydrogen or methyl group on the same ring carbon atom,²³ e.g. a *gem*-dimethyl group or an

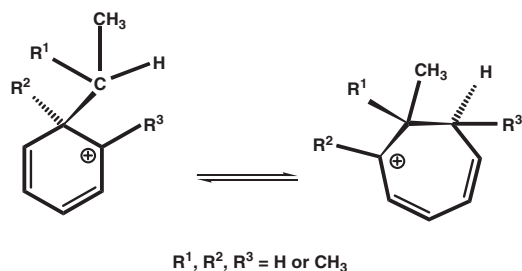


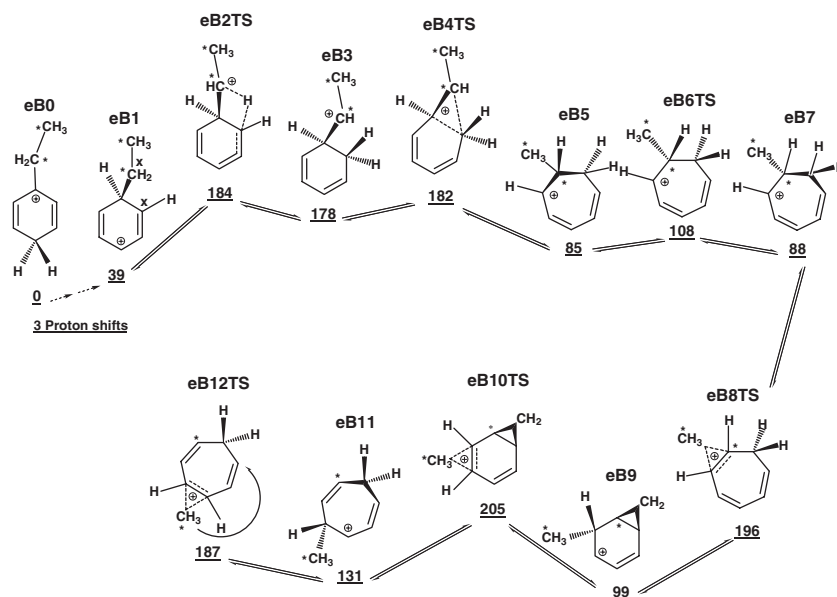
Figure 3. Structures of the species that can most easily expand to a seven-membered ring and contract to a six-membered ring

ipso-protonated methylbenzene. In accordance with this finding, all ring expansions in the present work start with a 1,3-hydrogen shift in an ion having the structure element shown in the left part of Fig. 3. In all but one case the species with R^2 in *para*-position relative to the alkyl group have the lowest energies; for this reason they have been taken as the initial species and all energies are given relative to these initial species. The initial species are labeled with a set of letters and a zero (**xxx0**). The hydrogen or methyl shifts leading to the ring-expanding structure from the initial species are facile and are therefore not detailed. The carbon atoms in the original alkyl chain are marked with asterisks (*) to make it easier to keep track of the atoms as the reactions proceed. In the reaction schemes only a selection of the many possible reaction paths that may lead to carbon atom scrambling are shown. We cannot rule out the possibility that other reaction paths may be more efficient for bringing about the scrambling.

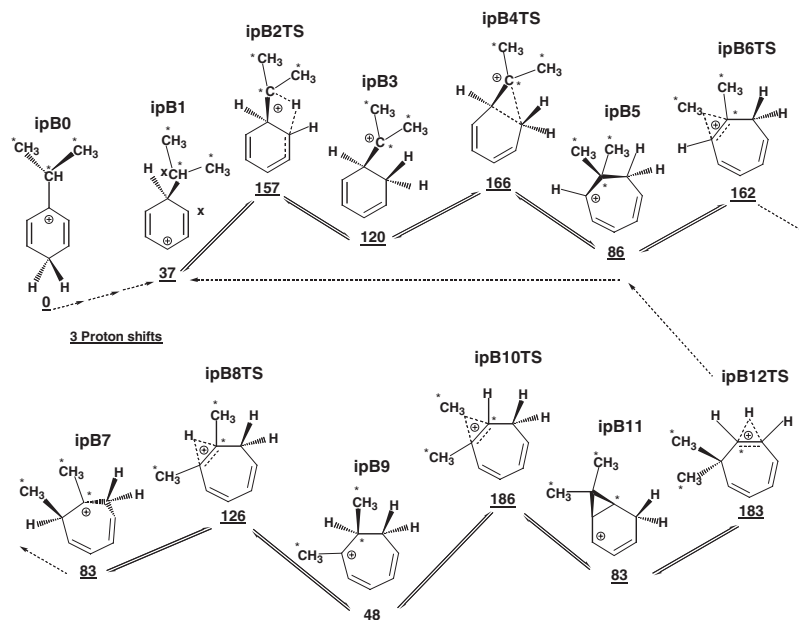
Carbon atom scrambling in protonated ethylbenzene

Scheme 1 shows a reaction path for carbon atom scrambling in protonated ethylbenzene. Protonation in the *para*-position relative to the ethyl group gives the most stable species, **eB0**. Protonation of ethylbenzene on the ring carbon that carries the ethyl group (**eB1**) is 39 kJ mol^{-1} less stable than **eB0**. The first eight species in Scheme 1 are taken from our earlier study of protonated xylenes,²³ where a rearrangement sequence that transforms dimethylbenzenium to ethylbenzenium was studied. The first step is a 1,3-hydrogen atom shift from the ethyl group onto the ring carbon atom in *ortho*-position to the ethyl group, **eB2TS**. The product is **eB3**, which via **eB4TS** may form the seven-membered ring, **eB5**. The energy differences between **eB2TS**, **eB3** and **eB4TS** are very small. We cannot, on the basis of the computed results, rule out the possibility that the reaction from **eB1** to **eB5** is a one-step process.

To obtain an interchange between the carbon atoms in the alkyl group and the benzenium ring, the two carbon atoms in the ethyl group (marked by asterisks) must be separated from each other, i.e. there must be a methyl group migration in **eB5** before the alkyl chain is reformed. A (facile) conformational change of **eB5**, via **eB6TS** to **eB7**, is necessary before the methyl group can migrate to the adjacent ring carbon atom. The first 1,2-methyl shift is shown as **eB8TS**. The resulting species, **eB9**, is bicyclic. The same methyl group that moved in **eB8TS** may migrate further, to form **eB11**. The transition state **eB12TS** leads to formation of the enantiomer of **eB11**. Following the same reaction series backwards, an



Scheme 1. Carbon atom scrambling in protonated ethylbenzene. The energies (kJ mol^{-1}) are given below each structure, and are relative to that of **eB0** (see text)



Scheme 2. Carbon atom scrambling in protonated isopropylbenzene. The energies (kJ mol^{-1}) are given below each structure, and are relative to **ipB0** (see text)

enantiomer of **eB5** results. When **eB5** reconstructs to **eB1**, the atoms marked by an 'x' in **eB1** are interchanged. The step from **eB1** to **eB3** has the highest barrier of any elementary reaction in Scheme 1 at $(184 - 39 =) 145 \text{ kJ mol}^{-1}$. The highest energy in Scheme 1 is found in **eB10TS**, at 205 kJ mol^{-1} above **eB0**.

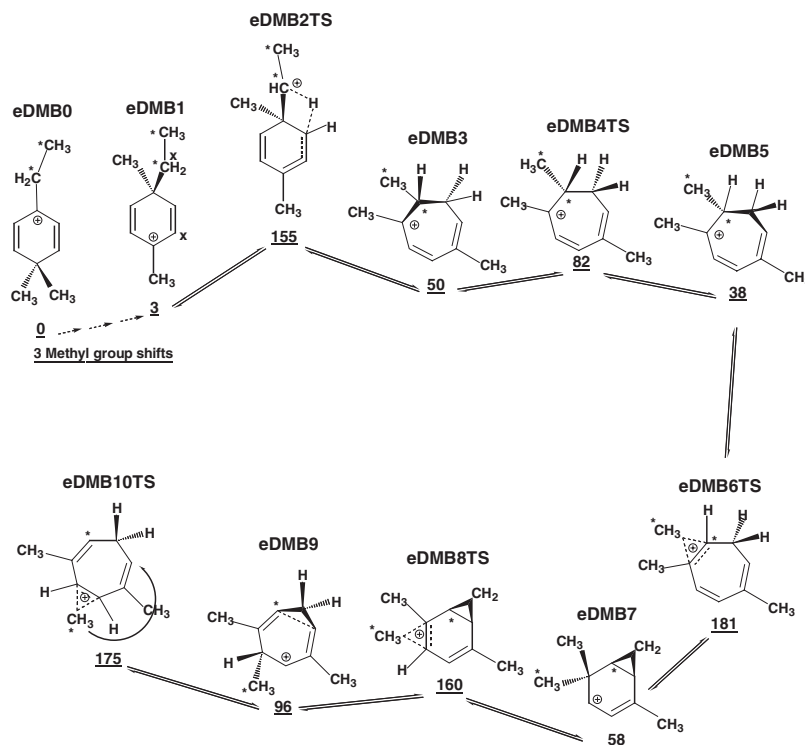
Carbon atom scrambling in protonated isopropylbenzene

Scheme 2 shows a possible reaction path for carbon atom scrambling in protonated isopropylbenzene. The ring expansion starts with a 1,3-hydrogen shift in an *ipso*-protonated isopropylbenzene, **ipB1**, which is 37 kJ mol^{-1} less stable than **ipB0**. The barrier for the transition state, **ipB2TS**, is $(157 - 37 =) 120 \text{ kJ mol}^{-1}$, and the resulting minimum is **ipB3**. In contrast to the ring expansion of ethylbenzenium where **eB3** hardly represented a stable state, **ipB3** is a clearly stable precursor to the expansion step. This difference between ethyl- and isopropylbenzenium ions is found in all the cases we have studied, **ipB3** may react further via transition state **ipB4TS** to form a seven-membered ring, **ipB5**, which may in turn undergo several different reactions by hydrogen or methyl migrations around the ring. In contrast to the case of **eB5**, where a change of conformation was required before a methyl shift could take place, there is a *gem*-dimethyl group in **ipB5**, so one of the methyl groups has the needed axial conformation. Scheme 2 shows an example of a possible reaction path that will re-form an isopropylbenzenium ion and interchange a carbon atom in the alkyl chain with a ring carbon atom.

To contract the seven-membered ring and re-form an isopropyl group, the atomic configuration $-\text{C}(\text{CH}_3)_2-\text{C}(\text{H})_2-$ (as it is in **ipB5**) must be present. The following series of elementary steps will give such a configuration, but with an interchange of atoms. After the formation of **ipB5**, the next step is a methyl group migration to the neighboring ring carbon atom to give **ipB7** via **ipB6TS**. The methyl shift may be followed by a hydrogen shift via **ipB8TS** to **ipB9**, so that the net effect is an interchange of the methyl groups and the hydrogen atoms. After yet another (anticlockwise) methyl shift to **ipB11** and a hydrogen shift (also anticlockwise) via **ipB12TS**, the structure **ipB5** is re-formed, but now the carbon atom from the isopropyl group (marked with the asterisk) is part of the methylene group, and not the *gem*-dimethyl groups. When **ipB5** now re-contracts to **ipB1** the carbon atoms in the positions marked 'x' in **ipB1** are interchanged. The transition state **ipB10TS** is the species with the highest energy in the scheme. The step from **ipB9** to **ipB10TS** has the highest barrier of the elementary steps at $(186 - 48 =) 138 \text{ kJ mol}^{-1}$.

Carbon atom scrambling in 1-ethyl-4,4-dimethylbenzenium ions

Scheme 3 shows a reaction path for carbon atom scrambling in 1-ethyl-4,4-dimethylbenzenium ion, **eDMB0**. The energy difference between the two first species, **eDMB0** and **eDMB1**, is only 3 kJ mol^{-1} . The ring expansion of **eDMB1** to **eDMB3** is, in contrast to the ring expansion in Scheme 2, a one-step process. Similar to the ethylbenzenium case in Scheme 1, a conformational



Scheme 3. Carbon atom scrambling in ethyldimethylbenzenium ions. The energies (kJ mol^{-1}) are given below each structure, and are relative to **eDMB0** (see text)

change is needed where **eDMB3** is transformed to **eDMB5**, so that an axial methyl group is formed that makes a methyl shift to **eDMB7** possible. A further anticlockwise methyl shift gives **eDMB9**, and yet another anticlockwise methyl shift (via **eDMB10TS**) leads to the enantiomer of **eDMB9**. The whole reaction sequence back to **eDMB3** may then take place, where the only difference is that the *CH_3 group is in mirror position relative to the given structures. This species may contract to a six-membered ring, and **eDMB1** is re-formed, albeit with interchange of the two carbon atoms marked with an 'x' in **eDMB1**. The first expansion step, whereby **eDMB3** is formed, has the highest barrier (152 kJ mol^{-1}) in this sequence of steps, and **eDMB6TS** has the highest energy, 181 kJ mol^{-1} .

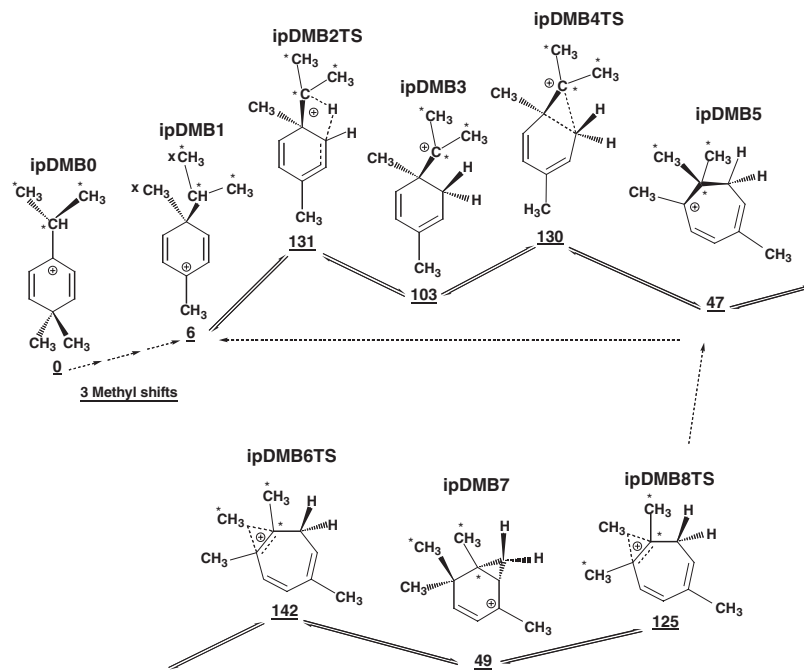
Carbon atom scrambling in 1-isopropyl-4,4-dimethylbenzenium ions

Scheme 4 shows a carbon atom interchange in the 1-isopropyl-4,4-dimethylbenzenium species, **ipDMB0**. Note that the reaction path presented in Scheme 4 does not scramble ring carbon atoms with alkyl group atoms. Instead, it shows a path that exchanges a carbon atom in the isopropyl group with a carbon atom in one of the two methyl groups. Species **ipDMB1** is only 6 kJ mol^{-1} above **ipDMB0**. The ring expansion is a two-step process and takes place via two transition states, as was found

also in the isopropylbenzenium case (Scheme 2). The first transition state barrier is $(131 - 6 =) 125 \text{ kJ mol}^{-1}$. After passing the transition state **ipDMB8TS**, **ipDMB5** is formed again but now only one of the carbon atoms in the *gem*-dimethyl group is marked by an asterisk. This species may contract and form an isopropyl group. The two carbon atoms marked with an 'x' in **ipDMB1** are exchanged after this reaction sequence. In analogy to Scheme 3, an exchange of ring and alkyl chain carbon atoms would take place if the methyl group migrated all around the ring. The highest energy in Scheme 4 is 142 kJ mol^{-1} .

Carbon atom scrambling in 1-ethyl-3,4,4,5-tetramethylbenzenium ions

Scheme 5 shows a scrambling reaction sequence for 1-ethyl-3,4,4,5-tetramethylbenzenium, **eTeMB0**. Note that this reaction path does not exchange any of the carbon atoms in the ethyl group, but instead it exchanges a ring and a methyl carbon atom. Species **eTeMB1** is 26 kJ mol^{-1} less stable than **eTeMB0**. The ring expansion of **eTeMB1** takes place in one elementary step, via **eTeMB2TS**, with a barrier of $(186 - 26 =) 160 \text{ kJ mol}^{-1}$. After the ring expansion to **eTeMB3**, a hydrogen atom may migrate along the ring until **eTeMB7** is formed. If a hydrogen atom from the CH_2 group in **eTeMB7** (marked # in the scheme) migrates to the ring carbon atom as shown



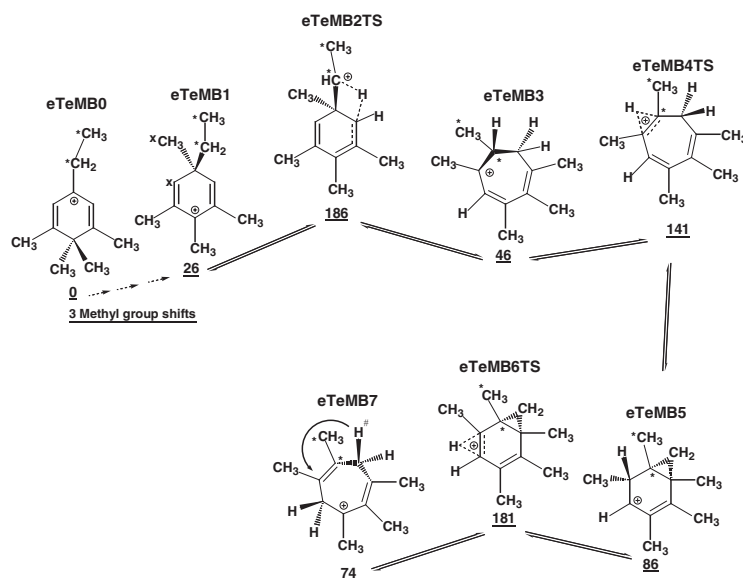
Scheme 4. Carbon atom scrambling in isopropyl-dimethylbenzenium ions. The energies (kJ mol^{-1}) are given below each structure, and are relative to **ipDMB0** (see text)

by the arrow, an enantiomer of **eTeMB3** is formed, **eTeMB3'**. This species may then contract and re-form **eTeMB1**, albeit with two carbon atoms interchanged, i.e. the two carbon atoms marked with an 'x' in **eTeMB1**.

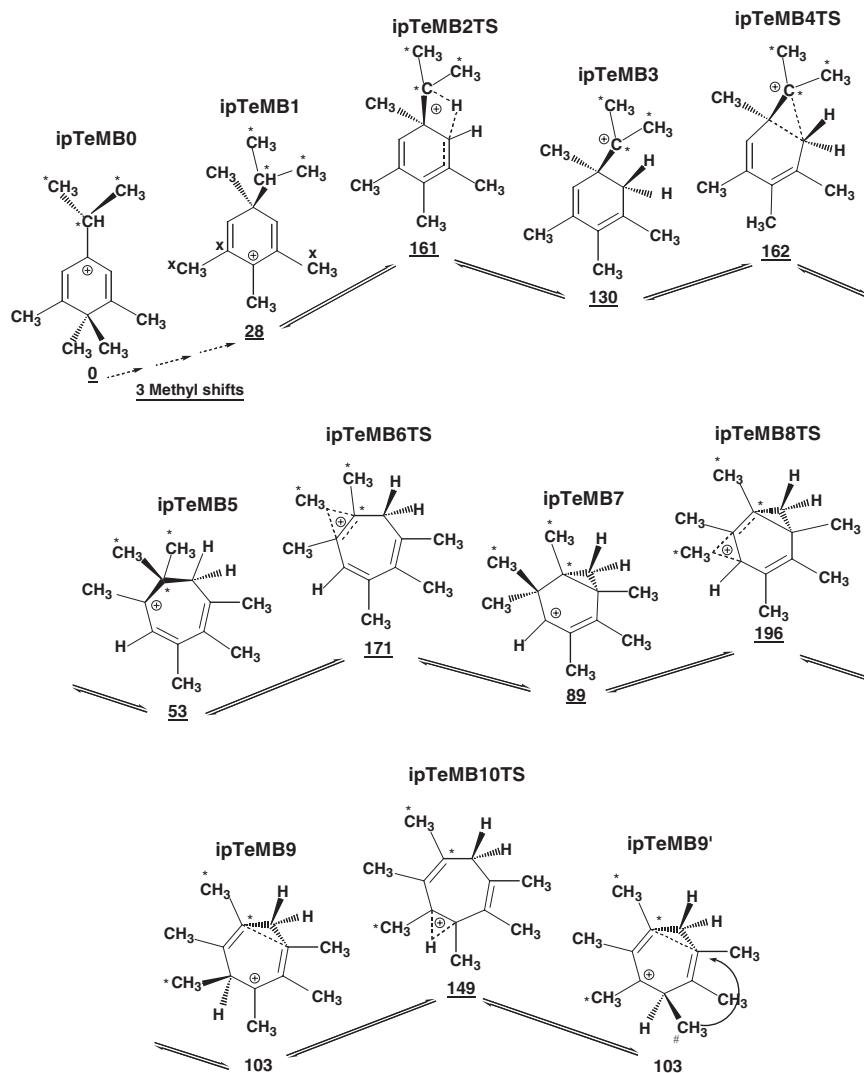
Carbon atom scrambling in 1-isopropyl-3,4,4,5-tetramethylbenzenium ions

Scheme 6 shows a path for scrambling carbon atoms in 1-isopropyl-3,4,4,5-tetramethylbenzenium ion, **ipTeMB0**. The

ring expansion from **ipTeMB1**, as expected, takes place via two transition states. The barrier from **ipTeMB1** to **ipTeMB2TS** is $(161 - 28) = 133 \text{ kJ mol}^{-1}$. After another transition state **ipTeMB4TS**, a seven-membered ring (**ipTeMB5**) is formed. The reaction may progress further with two more methyl shifts until **ipTeMB9** is formed. A hydrogen shift in **ipTeMB9** (via transition state **ipTeMB10TS**) brings about the formation of the enantiomer of **ipTeMB9**, **ipTeMB9'**. The methyl and hydrogen shifts that led to **ipTeMB9** may now proceed backwards from **ipTeMB9'**, but this time the migrating methyl



Scheme 5. Carbon atom scrambling in ethyltetramethylbenzenium ions. The energies (kJ mol^{-1}) are given below each structure, and are relative to **eTeMB0** (see text)



Scheme 6. Carbon atom scrambling in isopropyltetramethylbenzenium ions. The energies (kJ mol^{-1}) are given below each structure, and are relative to **ipTeMB0** (see text)

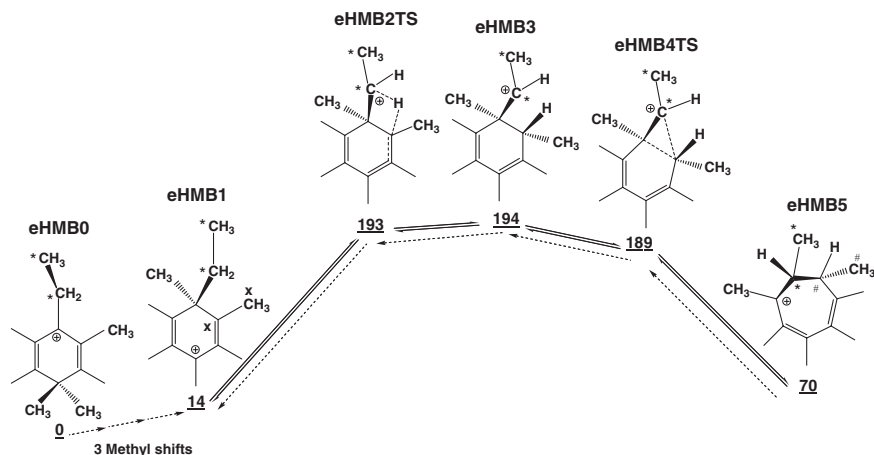
group is the one marked #. Eventually the enantiomer of **ipTeMB5** is formed. It may contract and re-form **ipTeMB1**, but there will be an interchange between some of the atoms. This sequence of reactions will exchange the three carbon atoms marked with an 'x' in **ipTeMB1** with those marked with asterisks. Thus, none of the 'new' isopropyl group carbon atoms were previously in the isopropyl group in **ipTeMB1**. The highest energy in Scheme 6 (196 kJ mol^{-1}) is found for **ipTeMB8TS**.

Carbon atom scrambling in 1-ethyl-2,3,4,4,5,6-hexamethylbenzenium ions

Scheme 7 shows a scrambling reaction sequence for the 1-ethyl-2,3,4,4,5,6-hexamethylbenzenium cation, **eHMB0**. Geometry optimizations resulted in a formally stable state **eHMB3**, but, because the two transition states

eHMB2TS and **eHMB4TS** were found to have slightly lower energies, **eHMB3** may well be considered as part of the transition state. The potential energy surface (PES) is evidently very flat in this region. With the available computational accuracy, we cannot resolve this question; the energy differences involved are, however, small enough to be of no practical consequence.

The reaction series presented in Scheme 7 shows carbon atom exchange with relatively few steps. The seven-membered ring, **eHMB5**, has two adjacent $-\text{CH}-\text{C}(\text{CH}_3)-$ groups. If there is a conformational change in **eHMB5**, analogous to the conformational changes **eB5** \rightarrow **eB7** in Scheme 1 and **eDMB3** \rightarrow **eDMB7** in Scheme 3, it may take an equivalent reverse reaction path, but this time two other carbon atoms (marked # in **eHMB5**) become the new ethyl group. The two carbon atoms marked with asterisks in **eHMB1** are interchanged with those marked with an 'x' in the same species. The



Scheme 7. Carbon atom scrambling in ethylhexamethylbenzenium ions. The energies (kJ mol^{-1}) are given below each structure, and are relative to **eHMB0** (see text)

initial barrier is $(193 - 14 =) 179 \text{ kJ mol}^{-1}$. Other reaction sequences departing from **eHMB5** might also take place but they have not have been explored.

Carbon atom scrambling in 1-isopropyl-2,3,4,4,5,6-hexamethylbenzenium ions

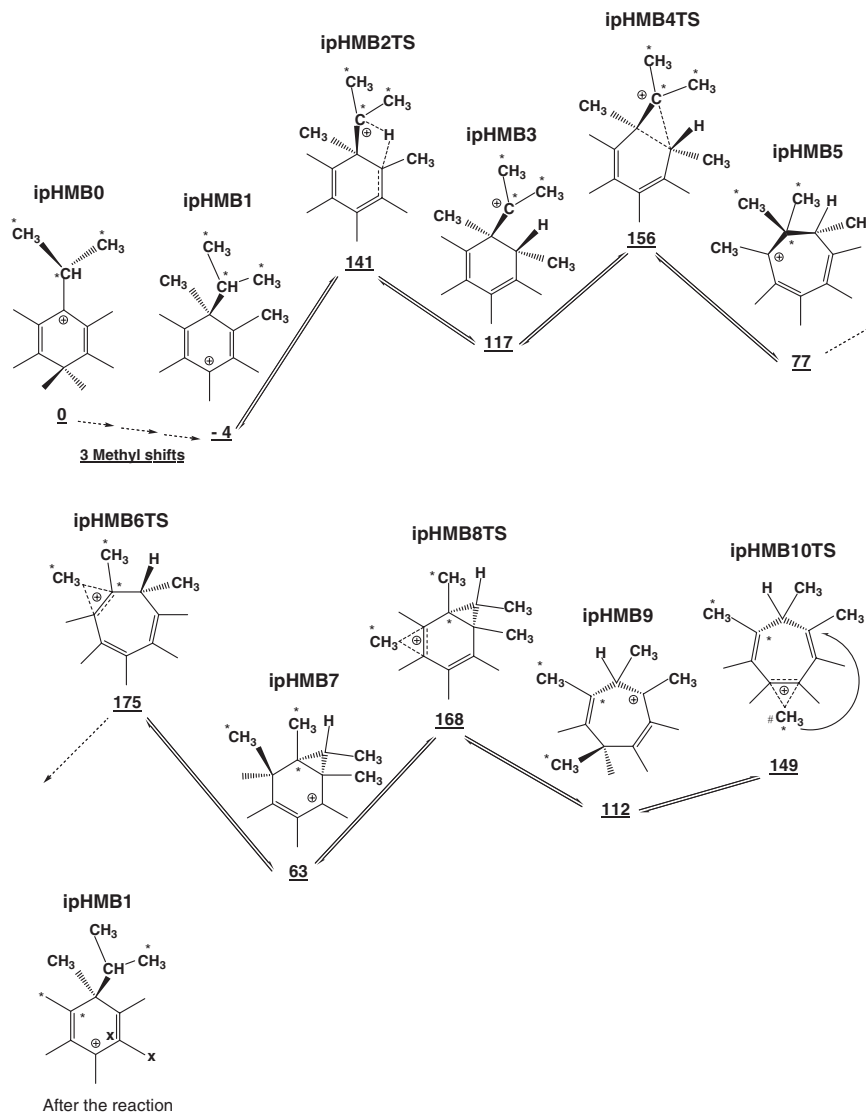
Scheme 8 shows a carbon atom scrambling reaction for the 1-isopropyl-2,3,4,4,5,6-hexamethylbenzenium cation, **ipHMB0**. The ring expansion starts from **ipHMB1**, which is actually 4 kJ mol^{-1} more stable than **ipHMB0**. Species **ipHMB1** is the only one studied here with a proton or a methyl group in the *ipso*-position to an alkyl chain that is more stable than the chosen initial structure. The ring expansion to a seven-membered ring, **ipHMB5**, also takes place here in two elementary steps. The first barrier is $[141 - (-4) =] 145 \text{ kJ mol}^{-1}$. If the methyl group migrates one step further via **ipHMB6TS**, a bicyclic species (**ipHMB7**) is formed. The same methyl group may then migrate further along the ring as shown in the scheme. After the methyl group has shifted all the way around the ring, the enantiomer of species **ipHMB5** is formed. This enantiomer may then contract and reform an isopropyl group. The resulting species after the scrambling reactions is shown in a separate structured drawing at the bottom of Scheme 8. In this structure the two carbon atoms marked with an 'x' are included in the new isopropyl group, and the two former carbon atoms in the alkyl chain have become a methyl group and part of the benzenium ring.

In addition to the scrambling reactions shown in Scheme 8, **ipHMB3** may be transformed into **ipHMB12** via **ipHMB11TS** as shown in Scheme 9. The barrier for this methyl shift is only $(142 - 117 =) 25 \text{ kJ mol}^{-1}$, which is 16 kJ mol^{-1} lower than **ipHMB4TS**. The energy of **ipHMB12** is only 5 kJ mol^{-1} above **ipHMB0**.

DISCUSSION

A clear distinction between the ring expansions, depending on the alkyl group on the benzenium ring, is borne out by the results presented above. In Schemes 1, 3, 5 and 7 the ring expansion takes place in a benzenium ion with an ethyl group. In all these cases the ring expansion is essentially a one-step process, although the calculations suggest that in some cases there may be a very shallow minimum corresponding to a substituted ethyl carbocation, $\text{CH}_3\text{CH}^+-\text{X}$. In the cases where the expansion takes place in a benzenium ion with an isopropyl group, the expansion is a two-step process with an intermediate displaying a formally positive charge on the isopropyl group. We have previously studied ring expansion in dimethylbenzenium ions²³ and in that case the ring expansion was clearly a one-step process. The barriers for ring expansion decline when we go from methyl- to ethyl-, and further to isopropyl groups on the benzenium ring. Typical transition state energies, in the same order, are $240, 180$ and 160 kJ mol^{-1} , a series that is in good accord with what might be expected when going from formally primary, via secondary to tertiary alkyl ions.

The question whether the observed scrambling of carbon atoms in the MTH reaction is a direct result of alkene formation via intramolecular reactions of methylbenzenium species has been raised.¹⁷ Further investigations into the origin of the observed carbon atom scrambling are therefore in place. Earlier, we presented two studies on unimolecular reactions of methylbenzenium ions,^{23,24} and these studies are also relevant to the present discussion. They described reactions for alkene formation from methylbenzenium cations and it was found that carbon atom scrambling is an inherent part of some of these reactions. The reactions presented here take place in ethyl- or isopropylbenzenium ions, as



Scheme 8. Carbon atom scrambling in isopropylhexamethylbenzenium ions. The energies (kJ mol^{-1}) are given below each structure, and are relative to **ipHMB0** (see text)

opposed to the pure methylbenzenium ions described previously.

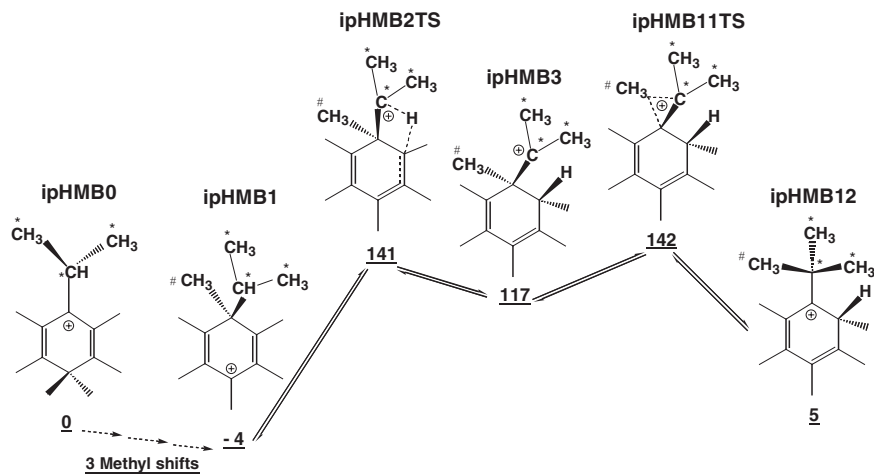
The reactions that are considered in Schemes 1–9 are all isomerizations. Fragmentations are neglected but it is, however, clear that in an experimental situation there might be fragmentation: the ethyl or isopropyl group might be split off. If fragmentation reactions are much faster than isomerization reactions, isomerization as investigated here may be unimportant.

The fragmentation may proceed along two different paths. The products formed when the ethylbenzenium ion loses its ethyl group may be: the ethyl cation plus benzene or ethene plus the benzenium ion. The same dichotomy applies to the other alkylbenzenium ions. Data are available in the literature for evaluating the energies needed for dealkylation of the ethylbenzenium ion (**eB0**) and the isopropylbenzenium ion (**ipB0**). Based on the

NIST Chemistry Webbook,³⁵ the following reaction energies (kJ mol^{-1}) are obtained: **eB0**, 143 (ethene + benzenium ion) and 213 (ethyl cation + benzene), **ipB0**, 141 (propene + benzenium ion) and 139 (propyl cation + benzene).

The highest energy in Scheme 1 is 205 kJ mol^{-1} (**eB10TS**), which signifies that if **eB0** has enough energy to isomerize then it also has enough energy to fragment into ethene plus a benzenium ion. The energy needed for fragmentation into an ethyl cation and benzene is higher than 205 kJ mol^{-1} , so this reaction path may not be available. From Scheme 2 it is seen that the highest energy there is 186 kJ mol^{-1} (**ipB10TS**), so if **ipB0** has sufficient energy to isomerize it may also split off the alkyl chain, making both reaction paths available.

There is a lack of data needed for carrying out similar comparisons for the other alkylbenzenium ions. It is,



Scheme 9. *tert*-Butyl group formation from isopropylhexamethylbenzenium ions via **ipHMB3**. The energies (kJ mol^{-1}) are given below each structure, and are relative to **ipHMB0** (see text)

however, clear that the proton affinities of alkylbenzenes increase markedly with an increasing number of methyl groups. Because of this, the only fragmentation path that needs to be considered for the remaining alkylbenzenium ions is the fragmentation leading to ethene or propene plus an arenium ion. In the case of the isopropylidimethylbenzenium ion (**ipDMB0**) in Scheme 4, fragmentation (to propene and xylenium ion) and isomerization appear to have very similar energy requirements.

Breaking the bond to the alkyl group in **eB1**, **ipB1**, **eDMB1**, etc. is not likely to require significantly more energy than the reaction energy, but the reaction path where ethene or propene is formed along with an arenium ion implies the migration of a methyl hydrogen atom and therefore a barrier that is higher than the reaction energy may be expected. The magnitude of the barrier is not known, but in an earlier work we calculated the transition state energy for ethene elimination from the ethylbenzenium ion to be 116 kJ mol^{-1} higher than the summed energies of the products.²³ This corresponds to a barrier for formation of ethene plus a benzenium ion from **eB0** that is well above 200 kJ mol^{-1} . A corresponding transition state energy for elimination of propene from **ipB0** has not been calculated. This transition energy may be somewhat lower than in the above case, but the calculated barrier for propene elimination from **ipB0** is still likely to be about 200 kJ mol^{-1} .

The situation is, however, not very clear. Audier and co-workers studied the fragmentation of isopropylbenzenium, -toluenium and -xylenium ions in the mass spectrometer.³⁶ They found that the fragmentation of the above ions in the same order gave 13%, 2% and 1% propyl cations and benzene, the rest being propene and benzenium ions. These results suggest that the hydrogen migration that takes place when an alkene is formed may proceed without any notable activation energy. The decreasing formation of propyl cations and a neutral arene (observed when going from isopropylbenzenium

to -toluenium and further to -xylenium ions) is in agreement with the increasing proton affinity in the series benzene, toluene and xylene.

It has been suggested that the alkene elimination may take place via formation of an ion-neutral complex^{36,37} by breaking of the bond between the benzene ring and the isopropyl group. The pair supposedly form a rather stable complex. The complex may split up and form benzene and an isopropyl cation. Alternatively, a proton may be transferred from the isopropyl cation moiety to benzene, resulting in propene and a benzenium ion complex that may subsequently split up.

We have not investigated this type of reaction. Density Functional Theory (DFT) methods such as B3LYP are not able to give a good description of the long-distance interactions that are decisive for complex stabilities,^{38,39} and according to our experience with related problems it is very difficult to find stationary points for transition states; re-formation of the bond usually takes place. Berthomieu *et al.*³⁶ avoided this problem in their theoretical treatment by not allowing structural changes in the two moieties and thus not allowing the formation of new bonds. Such a procedure may, however, make the outcome of the computations somewhat unrealistic. Further investigations on this issue by use of high-level theoretical methods would be of interest.

The transition state barriers for ring expansions in the present work are generally lower compared with the barriers found for the methylbenzenium cations. Introducing higher alkyl chains, while keeping the number of methyl groups on the ring unchanged, reduces the barriers for ring expansions via a 1,3-hydrogen shift. This may be interpreted in terms of carbocation stabilities. The transition state structures for the ring expansions of methylbenzenes have primary carbocation character, whereas ring expansions from ethyl- or isopropyl groups have secondary and tertiary carbocation character, respectively.

Bjørgen *et al.*¹¹ reported an estimate of the activation energy for the incorporation of ¹³C-labeled methyl carbon atoms into benzenium rings of 105 kJ mol⁻¹. The estimate was pointed out to be on the low side because exchange of ¹³C atoms with other ¹³C atoms was unobservable. The ring expansion barriers found in the present work are all between 120 and 179 kJ mol⁻¹, and thus in fair accordance with experimental observations.

Previously we have investigated alkene addition/elimination from ethyl- or (iso)propylmethylbenzenes in the presence of a zeolite acidic site, the latter being modeled by a small cluster.⁴⁰ In the present work, the scrambling reactions start from *ipso*-protonated (or methylated) ethyl- or isopropylbenzenium species, as shown in Fig. 3. These species have structures that make it possible to eliminate alkenes via the zeolite-assisted pathway. One might therefore speculate that a benzenium species might undergo a number of scrambling reactions before an alkene is split off. On the other hand, many scrambling transition states are so high in energy that a splitting off of the alkene might be the preferred reaction.

Finally, we note that some of the reactions studied here may actually lead to the formation of an alkyl chain with a number of carbon atoms that is different from that of the original species.

CONCLUSION

Various intramolecular reaction paths for scrambling of carbon atoms in benzenium ions with ethyl- or isopropyl groups have been studied with DFT. All the studied reactions proceed through an initial ring expansion to a seven-membered ring. The ring expansion takes place in a species with a proton or a methyl group in *ipso*-position to the alkyl chain. This ensures that the relatively facile 1,3-hydrogen shift from the α -carbon atom in the alkyl chain onto the benzenium ring takes place.

The scrambling reactions studied here start from the same species as those that may give rise to alkene formation via the zeolite-assisted mechanism that we presented earlier.⁴⁰ Alkene formation may also take place directly from this species if the bond between the alkyl group and the ring breaks. *Carbon atom scrambling and alkene formation in the MTH reaction take place via the same intermediates.*

The scrambling reaction barriers found in the present work are generally lower compared with the intramolecular reactions leading to alkene formation from (gas-phase) methylbenzenium ions. Consequently, whether alkenes are formed via intramolecular rearrangements of methylbenzenium ions that lead to higher alkyl chains or through side-chain methylations, scrambling between ring- and alkyl carbon atoms may take place. The extent to which scrambling takes place before the bond that forms the connection between the ring and the alkyl

group is broken cannot be quantified yet. The present work therefore does not allow a clear discrimination between the 'paring' mechanism and the side-chain methylation pathway.

Supplementary material

Cartesian coordinates, absolute energies (Hartree), zero-point energy corrections and transition state imaginary frequencies for the species that are discussed here are available in Wiley Interscience.

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