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Isomerization of the constituents of ion/neutral complexes during the fragmentation of protonated dialkyl-substituted 1,3-diphenylpropanes

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Dedicated to Professor Tino Gäumann on the occasion of his 85th birthday.

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ABSTRACT

The fragmentation of gaseous ion/neutral complexes $[R^+\cdots C_6H_5CH_2CH_2CH_2C_6H_4–R']$ with (i) R = R′ = C_4H_9, (ii) R = C_4H_9 and R′ = CH_3 and (iii) R = C_6H_{11} and R′ = H has been studied by CI(CH_4)-MIKE spectrometry of the corresponding alkyl-substituted 1,3-diphenylpropanes. Different from all other isomers containing two *para*-alkyl substituents, the $[M+H]^+$ ion generated from the symmetrical ion [(4-*tert*-C_4H_9-C_6H_4)$CH_2CH_2CH_2$(C_6H_4-4-*tert*-C_4H_9) + H]$^+$ shows the characteristic fragmentation pattern of ion–neutral complexes containing a *meta*-alkyl-substituted 1,3-diphenylpropane. This indicates a proton-induced 1,2-shift of one or even both of the *tert*-C_4H_9 groups and requires the presence of the *meta*-(*tert*-C_4H_9)-substituted diphenylpropane as the neutral constituent of the eventually fragmenting I/N complex. As a consequence, it appears that the reactive complex $[C_4H_9^+\cdots C_6H_5CH_2CH_2CH_2(C_6H_4$-3-*tert*-$C_4H_9)]$ is formed prior to the generation of the expected "*para*-isomer", $[C_4H_9^+\cdots C_6H_5CH_2CH_2CH_2(C_6H_4$-4-*tert*-$C_4H_9)]$. Isobutyl analogues, such as [(4-*iso*-C_4H_9-C_6H_4)$CH_2CH_2CH_2$(C_6H_4-4-*iso*-C_4H_9) + H]$^+$, do not show evidence for the intermediacy of "isomerized" I/N complexes containing a *tert*-$C_4H_9^+$ ion. The fragmentation of ion–neutral complexes containing $C_6H_{11}^+$ ions, formed from the $[M+H]^+$ ions of (4-cyclohexyl)- and of 4-(1-methylcyclopentyl)-substituted 1,3-diphenylpropane, indicate that the $C_6H_{11}^+$ ions only partially retain their structural identity: while the secondary isomer, $(CH_2)_5 > CH^+$, predominantly transfers a proton in competition to hydride abstraction, indicating its stronger Bronsted acidity, the tertiary isomer, $(CH_2)_4 > C^+CH_3$, mainly reacts by hydride abstraction. In spite of the partial isomerization, deuterium labelling experiments corroborate the usual regioselectivity of the hydride abstraction from the benzylic methylene groups in both cases.

1. Introduction

For an organic chemist who is fascinated by the beauties of organic mass spectrometry, the *unimolecular* formation of ion/neutral complexes as reactive intermediates [1–9] during the fragmentation of synthetically designable precursor molecules is a long-lasting motif of research. And since the ionic and the neutral component of such I/N complexes behave, at least in part, physical in nature, physical chemists may keep being fascinated as well. While the physical basis of I/N complexes has been well established [10,11], the chemical diversity of mass spectrometric fragmentation reactions that necessarily require the intermediacy of I/N complexes is still growing [12,13]. More recent examples have not fallen short of the fascination on the phenomenon, the more so as understanding of the chemistry in the highly diluted gas phase of a mass spectrometer is often ignored. Therefore, as mentioned in previous reports in this series [14–23], the study of "designed" gaseous ions that are prone to form "tailored" gaseous ion/neutral complexes may have its justification even nowadays.

The "organic-synthesis" approach to study the reactivity of small carbenium ions solvated within I/N complexes α,ω-diphenylalkanes and related alkylbenzenes [7,8,14–21,24–27] as well as functionalized neutrals [23,28–31] has brought many detailed insights into the "intra-complex" chemistry (Scheme 1). In particular, tertiary cations such as *tert*-$C_4H_9^+$, released by protonolysis into complexes with α,ω-diphenylalkanes of different Bronsted basicity and hydride donor reactivity, react by proton transfer to the "large" neutral constituent, or/and by highly regioselective hydride abstraction from the benzylic positions of the propylene (or oligomethylene [15]) chain. It has become obvious that the ease of proton transfer reflects the basicity of the entire diphenylalkane molecule, rather than only of the benzene ring originally bearing the *tert*-butyl group. In turn, the competition between the two fragmentation channels of the $[M+H]^+$ ions also reflects the structure of the alkyl cation released into the complex. For example, the complex {2.2.2[bicyclooct-1-yl]$^+\cdots$1,3-diphenylpropane}, generated from protonolysis of the corresponding *para*-(2.2.2-bicyclooct-1-yl)-substituted 1,3-

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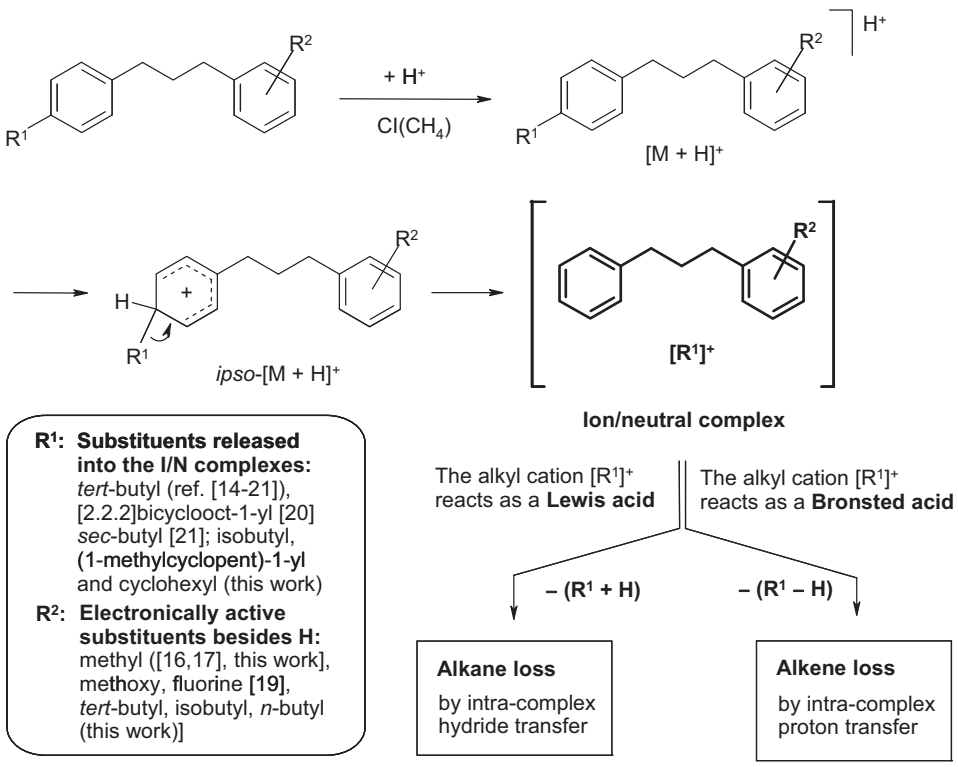


Scheme 1. Formation of ion/neutral complexes as intermediates of the fragmentation of metastable protonated alkyl-substituted 1,3-diphenylalkanes. A selection of substituents (R^1), from which cationic constituent of the I/N complexes may be generated, and of substituents (R^2) which modify the reactivity of the neutral constituent, are mentioned.

diphenylpropane, exclusively undergoes the hydride transfer process, as expected for this tertiary carbocation, thus excluding the isomerization to the {2.2.2[bicyclooct-2-yl] ion within the I/N complex [20]. Again in turn, secondary carbocations, such as *sec*-$C_4H_9^+$ ions released from protonated *para*-(*sec*-butyl)-substituted 1,3-diphenylpropane and even *iso*-$C_3H_7^+$ ions released from protonated *para*-(isopropyl)-substituted 1,3-diphenylpropane, show far predominant proton transfer to the neutral constituent but also minor but significant hydride abstraction [21].

In this contribution, we demonstrate that the fragmentation behavior of the metastable $[M+H]^+$ ions of diphenylalkanes may reflect the isomerization of either the neutral constituent or the ionic partner of the intermediate I/N complexes. Thus, not only may the I/N complexes play a crucial role for the overall fragmentation, as it is well accepted in the literature [10,11]; the I/N complex may also act as a probe for a preceding structural rearrangement of the initial ionic structure [8]. These insights were obtained from CI(CH_4)-MIKE spectrometric measurements performed with the previously unknown hydrocarbons **1** and **6**–**12** depicted in Scheme 2.

2. Experimental

2.1. Mass spectrometry

All measurements were carried out on a double-focusing instrument, AutoSpec (Fisons, Manchester/UK) with a three-sector, EBE geometry. The compounds were introduced into the CI source via the heatable inlet rod. Methane was used as the reactant gas at a (nominal) pressure of $4 \times 10^{-5} \leq p \leq 1 \times 10^{-4}$ mbar. The electron energy was set at 70 eV, the trap current at 200 μA, the accelerating voltage at 8000 V, and the source temperature at ca. 170 °C. Fragmentation of the metastable ions in the third field-free region was registered by selecting the precursor ion by the magnetic field and scanning the field of the second electrostatic analyzer. The MIKE spectra are representative examples for several independent measurements and averaged from at least ten consecutive scans.

2.2. Synthesis

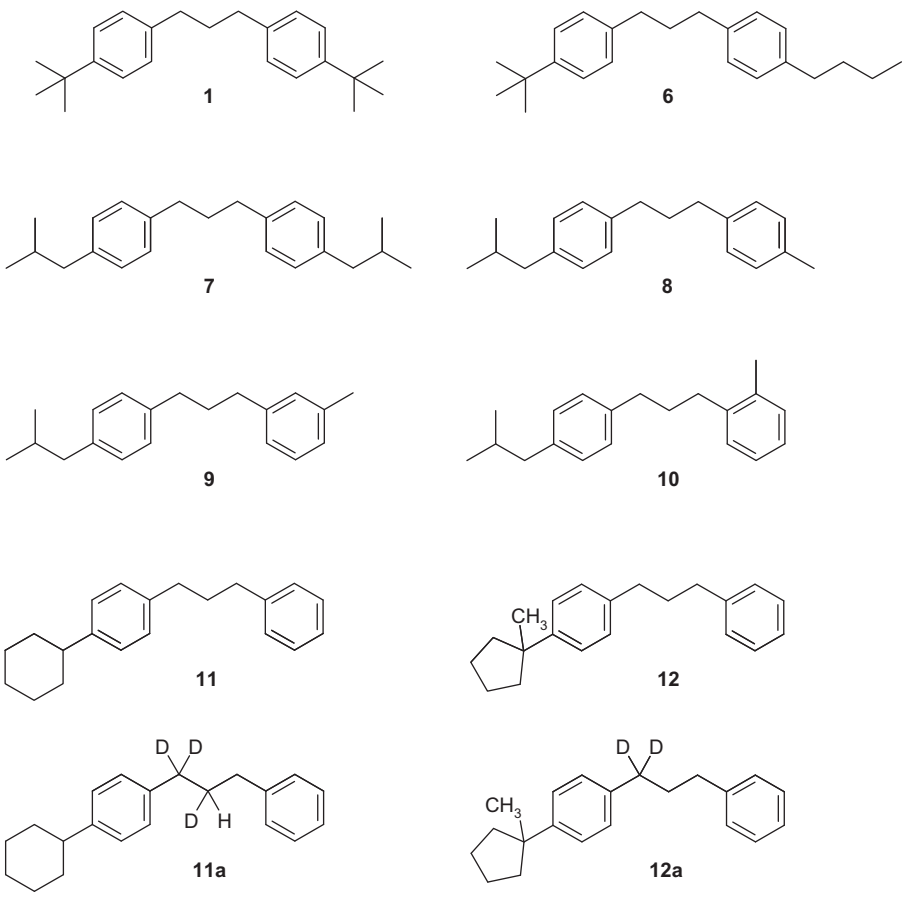
General: ^{1}H NMR spectra (300 MHz or 500 MHz, $CDCl_3$/TMS) were measured on a Bruker AM 300 instrument and a Bruker DRX 500 instrument, respectively. Mass spectra were obtained with a VG Autospec double-focusing instrument by electron ionization (EI, 70 eV). Deuterium contents were evaluated from the EI mass spectrometric data after correction for naturally occurring ^{13}C. IR spectra were recorded on a Nicolet-380 FT-IR spectrometer; solids were measured in KBr pellets and liquid as films. Melting points (uncorrected): Electrothermal melting point apparatus. Combustional analyses: Leco CHNS-932. All distillations were performed using a Büchi GKR 50 kugelrohr apparatus. TLC: Silica (Kieselgel 60) on aluminum foil with fluorescence indicator F_{254}, thickness 0.2 mm (Merck).

Compounds: Details of the syntheses (Scheme 3) and physical and spectroscopic properties of the compounds are collected as Supplementary data.

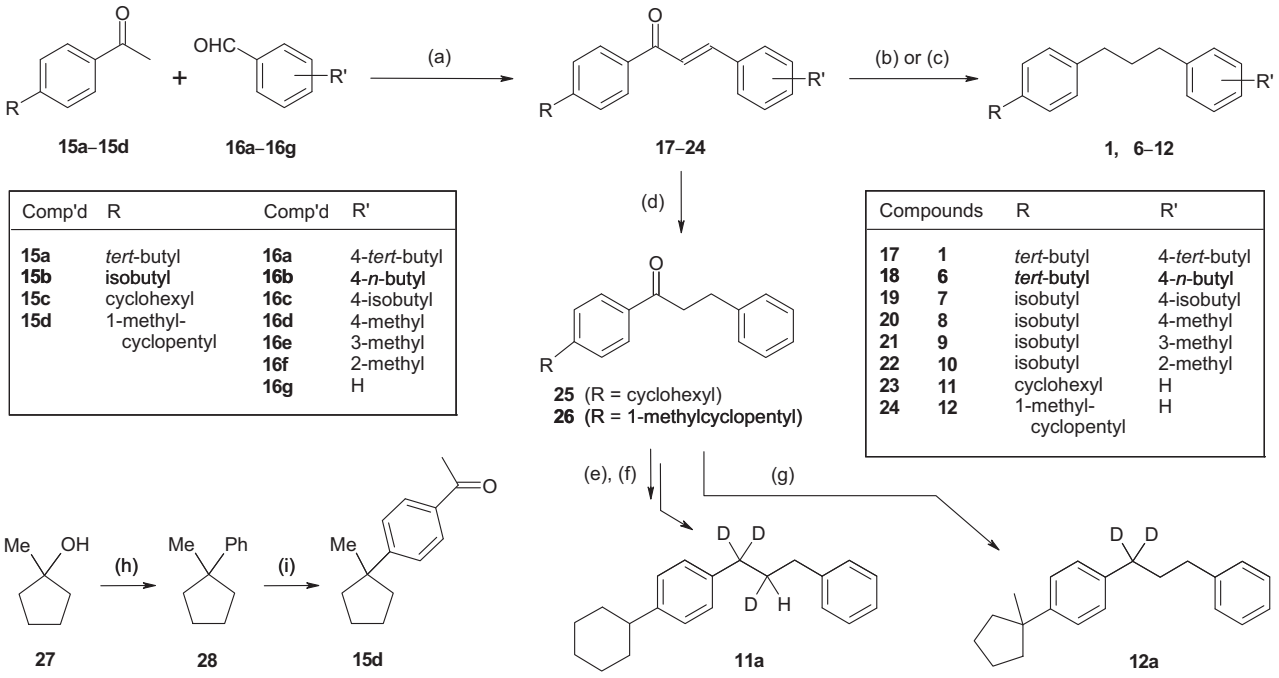
3. Results and discussion

3.1. Proton-induced 1,2-tert-butyl shift

A single experimental result provided the initiative for this study. When 1,3-bis-(4-*tert*-butylphenyl)propane **1** was subjected to chemical ionization with methane as the reactant gas in a double-focusing sector-field mass spectrometer, the metastable ions $[\mathbf{1}+H]^+$ were found to eliminate isobutene through the preponderant fragmentation channel (*m*/*z* 253, 72%) and isobutane though the minor one only (*m*/*z* 251, 28%). This is shown in the



Scheme 2. Alkyl-substituted 1,3-diphenylpropanes synthesized and studied in this work.



Comp'd	R	Comp'd	R'
15a	*tert*-butyl	**16a**	4-*tert*-butyl
15b	**isobutyl**	**16b**	**4-*n*-butyl**
15c	cyclohexyl	**16c**	4-isobutyl
15d	1-methyl-cyclopentyl	**16d**	4-methyl
		16e	3-methyl
		16f	2-methyl
		16g	H

Compounds		R	R'
17	**1**	*tert*-butyl	4-*tert*-butyl
18	**6**	***tert*-butyl**	**4-*n*-butyl**
19	**7**	isobutyl	4-isobutyl
20	**8**	isobutyl	4-methyl
21	**9**	isobutyl	3-methyl
22	**10**	isobutyl	2-methyl
23	**11**	cyclohexyl	H
24	**12**	1-methyl-cyclopentyl	H

Scheme 3. Syntheses of compounds hydrocarbons **1**, **6**–**12** and the isogtopomers **11a** and **12a**. (a) KOH, MeOH/H_2O; (b) H_2, Pd/C, HOAc, 5 bar, 25 °C (see Supplementary data); (c) H_2, Pd/$BaSO_4$, EtOH, 5 bar, 25 °C (see Supplementary data); (d) H_2, PtO_2, EtOAc, 25 °C; (e) $LiAlD_4/AlCl_3$, Et_2O, 0 → 36 °C, 24 h (see Supplementary data); (f) D_2, $RhCl(PPh_3)_3$, benzene, 25 °C; (g) $LiAlD_4/AlCl_3$, Et_2O, 0 → 36 °C, 70 h; (h) benzene, $AlCl_3$, 25 → 80 °C; (i) AcCl, $AlCl_3$, 1,2-dichloroethane, 0 → 25 °C.

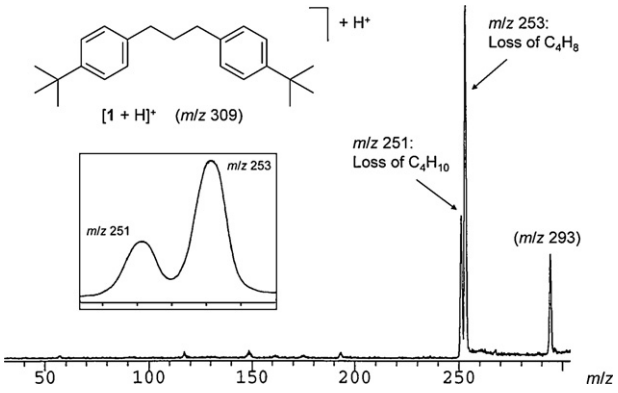


Fig. 1. MIKE spectrum of protonated 1,3-di-(4-*tert*-butylphenyl)propane, [**1**+H]$^+$, generated by CI(CH_4). The peak at *m*/*z* 293 is due to the methyl loss from the isobaric ions [$^{13}C_1$]-**1**$^{+\bullet}$.

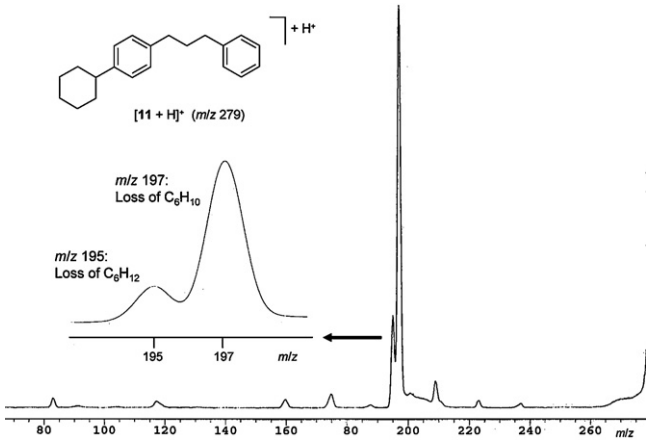


Fig. 2. MIKE spectrum of protonated 1-(4-cyclohexylphenyl)-3-phenylpropane, [**11**+H]$^+$, generated by CI(CH_4). The minor peaks at *m*/*z* 117, 160 and 175 are due to the fragmentation of the isobaric ions [$^{13}C_1$]-**11**$^{+\bullet}$. The latter ions also contribute in minor amounts (ca. 4%) to the peak at *m*/*z* 197.

mass-analyzed ion kinetic energy (MIKE) spectrum (Fig. 1). The direct release of $C_4H_9^+$ ions was minute only. The branching ratio $[M+H-C_4H_{10}]^+$:$[M+H-C_4H_8]^+$ = 0.39 was far different from what should be the expected value for an I/N complex consisting of a *tert*-$C_4H_9^+$ ion and a *para*-alkyl-substituted 1,3-diphenylpropane. The reasons are given in the following.

In an early study the role of ion/neutral complexes as reactive intermediates in the fragmentation of protonated *tert*-butylbenzenes bearing an ω-phenylalkyl group, we found that the MIKE spectra of the three isomeric protonated 1-*para*-*tert*-butylphenyl)-3-tolylpropanes reflect the different gas-phase basicities of the neutral 1-phenyl-3-tolylpropane constituent of the I/N complexes (Scheme 4) [16,17]. Whereas the *para*-tolyl isomer, [**2**+H]$^+$, undergoes exclusive elimination of isobutane by hydride abstraction from both of the benzylic methylene groups, the *meta*-tolyl isomer, [**3**+H]$^+$, exhibits predominant loss of isobutene by proton transfer from the *tert*-$C_4H_9^+$ ion to the neutral hydrocarbon. The *ortho*-tolyl isomer, [**4**+H]$^+$, represents an intermediate case with predominant hydride abstraction and minor proton transfer. Clearly, this reflects the well-known order gas-phase basicity of underlying dimethylbenzenes: GB(*para*-xylene) < GB(*ortho*-xylene) < GB(*meta*-xylene) [32–37]. When the *ortho*-methyl substituent was introduced – by synthesis design (vide supra) – at the same benzene ring as the *tert*-butyl group, cf. [**5**+H]$^+$, the fragmentation was found to be the same as with its "ring isomer" [**4**+H]$^+$. This and other findings revealed that the basicity of the whole 1,3-diarylalkane neutral, rather than that of the aromatic ring originally bearing the *tert*-butyl group, governs the propensity of the I/N complex to transfer a proton. In addition, the electronic influence of the methyl (or other) electron-releasing substituents on the hydride abstraction channel amplify the overall effect [17,19].

On the basis of these arguments, the predominant isobutene loss from metastable ions [**1**+H]$^+$ points to ("hidden") formation of the isomerized I/N complex **IN(*m*-^{t}Bu)**, rather than the putative complex **IN(*p*-^{t}Bu)**, as the reactive intermediate from which the loss proper of the C_4H_8 and C_4H_{10} fragments occurs (Scheme 5). The *meta*-*tert*-butyl substituent in **IN(*m*-^{t}Bu)** should increase the basicity of the 1,3-diphenylpropane constituent with the complex to a similar extent as does the *meta*-methyl group in the complex formed upon fragmentation of ions [**3**+H]$^+$. In the same time, the hydride donor ability of the 3-CH_2 group should be decreased as compared to the *para*-*tert*-butyl isomer. It appears that the release of the *tert*-$C_4H_9^+$ ion from the two (equivalent) *para*-protonated tautomers of ions $[\mathbf{1}+H]_p^+$ into the complex **IN(*p*-^{t}Bu)** requires more energy than the 1,2-C shift leading to the protonated *meta*,*para*-di-*tert*-butyl isomer $[\mathbf{13}+H]_m^+$. In fact, the formation of tautomeric ions [**13**+H]$^+$ from ions [**1**+H]$^+$ should be exothermic, as should be the subsequent isomerization of ions [**13**+H]$^+$ to the even more stable tautomers of the protonated *meta*,*meta*-di-*tert*-butyl isomer [**14**+H]$^+$, such as $[\mathbf{14}+H]_m^+$. In particular, owing to the presence of a *meta*-dialkylbenzene unit, both ions $[\mathbf{13}+H]_p^+$ and $[\mathbf{14}+H]_m^+$ should be more stable than the isomeric ion $[\mathbf{13}+H]_m^+$. Thus, the formation of the reactive complex **IN(*m*-^{t}Bu)** and its fragments should be favourable due to the intermediacy of relatively stable *meta*-dialkylbenzenium ions.

To account for the increased size of the C_4-residue, when comparing the fragmentation of the twofold *para*-alkyl-substituted ions [**1**+H]$^+$ and [**2**+H]$^+$, we also synthesized the isomer **6** containing an *n*-butyl substituent in the *para* position. As expected, the metastable ions [**6**+H]$^+$ suffer far predominant loss of isobutene, whereas isobutene loss is of minor importance only (Table 1). It is obvious that the *n*-butyl group is retained in the *para*-position of the "remote" benzene ring, probably giving rise to a small increase of the overall gas-phase basicity of the neutral constituent of the I/N complex, as may be inferred from the proton affinity (PA) and gas-phase basicity scale of the simple alkylbenzene homologues [34,35]. In this particular case, it is noted that GB(*n*-butylbenzene) exceeds GB(toluene) by ca. 8 kJ mol^{-1} [34,35].

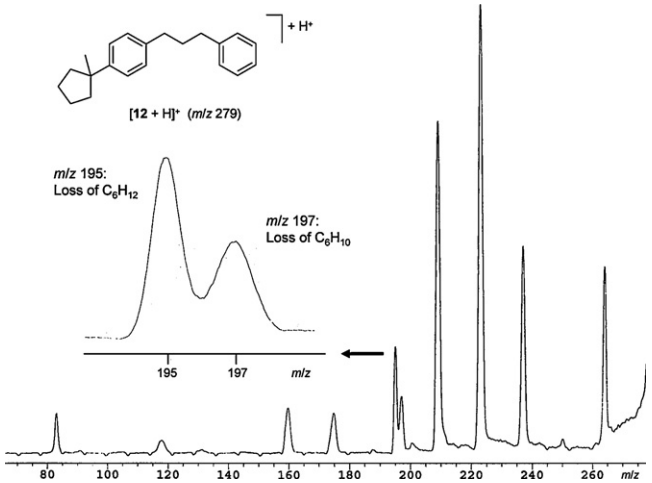
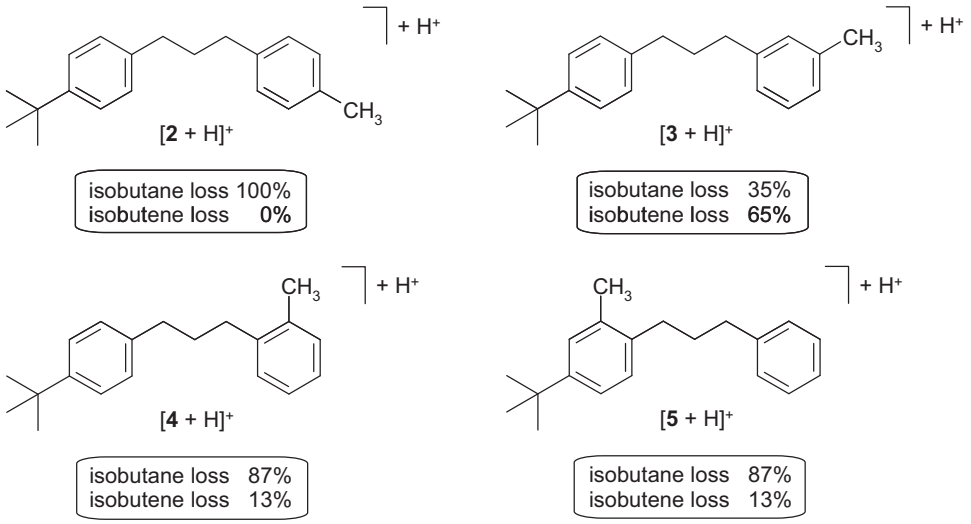


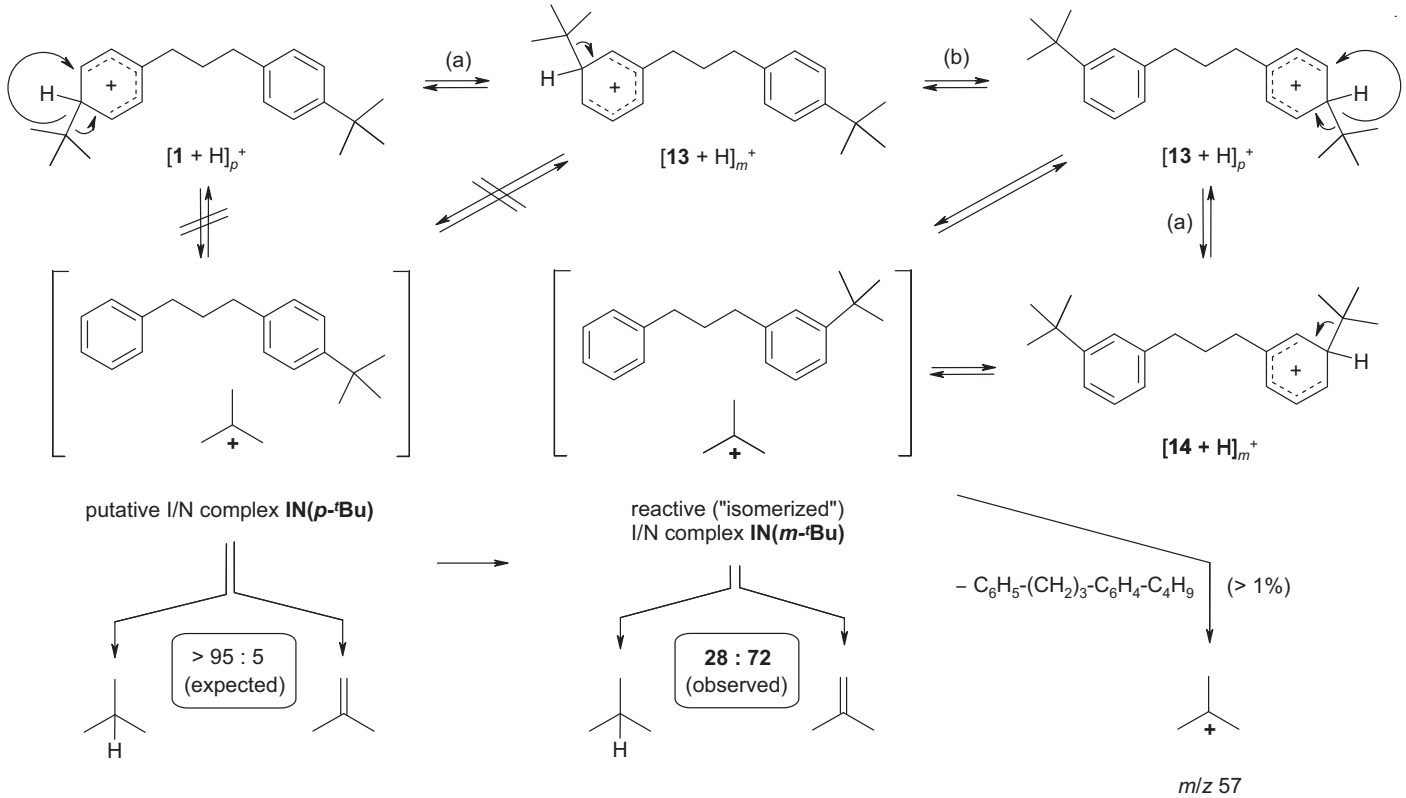
Fig. 3. MIKE spectrum of protonated 1-[1-methylcyclopentyl)phenyl]-3-phenylpropane, [**12**+H]$^+$, generated by CI(CH_4). The peaks at *m*/*z* 117, 160, 175 and 264 are due to the fragmentation of the isobaric ions [$^{13}C_1$]-**12**$^{+\bullet}$. The latter ions also contribute (ca. 20%) to the peak at *m*/*z* 197.



Scheme 4. Loss of isobutane vs. loss of isobutene from the metastable protonated 1-(4-*tert*-butylphenyl)-3-tolylpropanes, [**2**+H]$^+$, [**3**+H]$^+$ and [**4**+H]$^+$, and the "reversed" *ortho*-methyl isomer, [**5**+H]+ (from Ref. [16]).

3.2. Protonated isobutyl isomers

Incipient isobutyl cations formed upon protonolysis of isobutylarenes in the gas phase can easily isomerize to *tert*-butyl and even *sec*-butyl cations [25,26]. Therefore, we envisioned the possibility that the suspected rearrangement would become evident through the elimination of isobutane along with, or even instead of, the loss of isobutene from the [M+H]$^+$ ions of isobutyl-substituted 1,3-diphenylpropanes. In a previous study [21], we found that not only tertiary but also secondary alkyl cations, such as *sec*-$C_4H_9^+$ and *sec*-$C_3H_7^+$, undergo hydride abstraction from the 1,3-diphenylalkane neutral. Whereas the loss of *n*-alkyl groups as the corresponding alkanes can be excluded (as assumed for the case of [**6**+H]$^+$, for example), β-branched primary alkyl groups could undergo 1,2-hydride shifts under the protonolysis conditions of CI(CH_4)-MIKE spectrometry applied here. The typical loss of isobutane from metastable protonated bis-1,3-(4-isobutylphenyl)propane, [**7**+H]$^+$, would be a reliable probe for the presence of *tert*-$C_4H_9^+$ as the ionic component of an I/N-complex intermediate. Besides the diisobutyl isomer **7** of the di-*tert*-butyl compound **1**, we studied the three isobutyl- and methyl-substituted hydrocarbons **8**, **9** and **10** as the respective isomers of **2**, **3** and **4**.



Scheme 5. Isomerization of ions [**1**+H]$^+$ via the *para*-protonated tautomer, [**1**+H]$_p^+$, to the *meta*,*para*- and *meta*,*meta*-isomers [**13**+H]$^+$ and [**14**+H]$_m^+$, respectively, from which the reactive "isomerized" ion/neutral complex **IN(*m*-^{t}Bu)** is formed.

Table 1
Relative abundances[a] of the fragment ions generated by hydride abstraction (alkane loss) and by proton transfer (alkene loss) from the metastable $[M+H]^+$ ions of diphenylpropanes **1**–**4** and **6**–**12** (MIKE spectra).

$[M+H]^+$ m/z	Substituents R and R′ in the $[M+H]^+$ ions	Alkane loss m/z (%)[c]	Alkene loss m/z (%)[c]	Other fragment ions, m/z (%)	
[**1**+H]$^+$ 309	4-*tert*-C_4H_9, 4′-*tert*-C_4H_9	28	72.	$C_4H_9^+$	≈0.5[d]
[**2**+H]$^+$[b] 267	4-*tert*-C_4H_9, 4′-CH_3	>99.5	<0.5	$C_4H_9^+$	≈0.5[d]
[**3**+H]$^+$[b] 267	4-*tert*-C_4H_9, 3′-CH_3	35	65	$C_4H_9^+$	≈0.5[d]
[**4**+H]$^+$[b] 267	4-*tert*-C_4H_9, 2′-CH_3	87	13	$C_4H_9^+$	≈0.5[d]
[**6**+H]$^+$ 309	4-*tert*-C_4H_9, 4′-*n*-C_4H_9	92	8	$C_4H_9^+$	≤0.5[d]
[**7**+H]$^+$ 309	4-*iso*-C_4H_9, 4′-*iso*-C_4H_9	2.5	97.5	$C_4H_9^+$	3.5[e]
[**8**+H]$^+$ 267	4-*iso*-C_4H_9, 4′-CH_3	2.5	97.5	$C_4H_9^+$	8.0[e]
[**9**+H]$^+$ 267	4-*iso*-C_4H_9, 3′-CH_3	1.5	98.5	$C_4H_9^+$	8.0[e]
[**10**+H]$^+$ 267	4-*iso*-C_4H_9, 2′-CH_3	1.5	98.5	$C_4H_9^+$	8.0[e]
[**11**+H]$^+$ 279	4-*cyclo*-C_6H_{11}, H	20	80	$C_6H_{11}^+$	2.0[d]
[**12**+H]$^+$ 279	4-(1-CH_3-*cyclo*-C_5H_8), H	72	28	$C_6H_{11}^+$	35[d,f]

[a] Data as obtained after correction for the fragmentation of naturally occurring ions $[^{13}C_1]$-$M^{+\bullet}$.
[b] Data taken from Ref. [16].
[c] Data given as % of the sum of alkane and alkene losses.
[d] Abundances given as relative to the sum of alkane and alkene losses.
[e] Relative abundances given as relative to those of alkane loss only.
[f] The predominating fragment ions are due to the losses of C_3H_6, C_4H_8 and C_5H_{10} (see Fig. 3).

The results are straightforward. In all cases, the metastable $[M+H]^+$ ions, generated under the same conditions as in the previous measurements, undergo almost exclusive loss of C_4H_8 (presumably isobutene, Table 1). Only about 2% of the fragmentation occurs through elimination of isobutane. Hence, there is no hint to a regiospecific effect of the methyl groups on the basicity of the 1-phenyl-3-tolylpropane neutral in the putative I/N complex (Scheme 1), if formed at all. Rather, it can be assumed that, in analogy to the fragmentation of simple long-lived alkylbenzenium ions [25,26], the protonolysis of isobutyl-substituted 1,3-diphenylpropanes like **7**–**10** occurs via a considerable activation barrier, with the proton being transferred to the benzene ring originally bearing the isobutyl group. Nevertheless, a minor fraction of the $[M+H]^+$ ions does form $C_4H_9^+$ cations which, however, appear as free (probably tertiary) butyl cations (m/z 57, Table 1). In the case of ions [**7**+H]$^+$, a ratio $\{C_4H_9^+\}:\{[M+H-C_4H_{10}]^+\} \approx 1.3$ was found, and for the methyl-substituted isomers [**8**+H]$^+$, [**9**+H]$^+$ and [**10**+H]$^+$, free $C_4H_9^+$ was generated in even larger relative abundances, $\{C_4H_9^+\}:\{[M+H-C_4H_{10}]^+\} = 4–5$. By contrast, the release of free $C_4H_9^+$ ions is negligible in the case of the *tert*-butyl analogues (Table 1 and Scheme 5). Therefore, it appears that any I/N complexes formed after the proton-induced (isobutyl → *tert*-butyl) rearrangement are too-highly activated and short-lived to undergo the intra-complex hydride abstraction; instead, they directly release the *tert*-$C_4H_9^+$ ions.

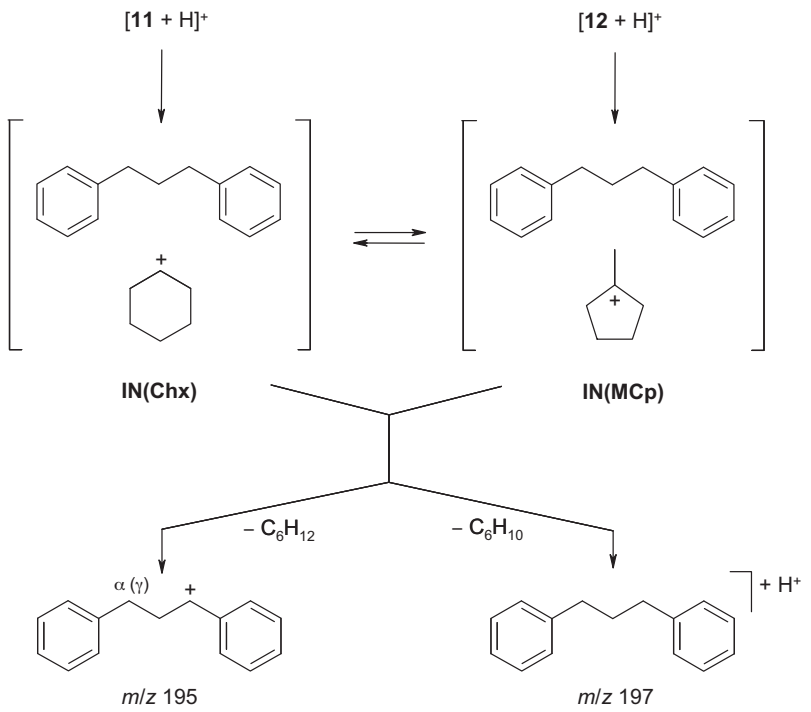
3.3. Intra-complex $C_6H_{11}^+$ ions from cyclohexyl and methylcyclopentyl derivatives

A previous study within this series indicated that more complex carbenium ions released by protonolysis into an I/N complex with 1,3-diphenylpropane may, at least in part, undergo skeletal rearrangement prior fragmentation by alkane and/or alkene loss. In particular, the [2.2.2]bicyclooct-1-yl group was found to lose its symmetrical bicyclic framework under the CI(CH_4) conditions, although intra-complex bicyclo[2.2.2]octyl ions, $CH(CH_2CH_2)_3C^+$, released by protonolysis, react exclusively by hydride abstraction, as expected for such tertiary, bridgehead cations [20]. On the other hand, as mentioned above, secondary alkyl cations, such as *sec*-$C_4H_9^+$ and *sec*-$C_3H_7^+$, react almost exclusively by proton transfer but with a minor contribution of the regioselective hydride abstraction from the 1,3-diphenylpropane constituent of the I/N complexes [21].

Gaseous cyclohexyl cations are known to undergo skeletal rearrangement to the (thermochemically more stable) 1-methylcyclopentyl cations [38–44]. Therefore, we synthesized the diphenylpropanes **11** and **12** bearing a cyclohexyl or a *tert*-methylcyclopentyl group, respectively, in one of the *para*-positions. Parts of the synthesis of these hydrocarbons as well as of their deuterium-labelled analogues **11a** and **12a** were not straightforward (see Supplementary data).

The MIKE spectrum of ions [**11**+H]$^+$ (Fig. 2) was found to be dominated by the loss of C_6H_{10} (most probably cyclohexene) but it also exhibited the elimination of C_6H_{12} (cyclohexane) as well as the formation of free $C_6H_{11}^+$ ions (m/z 83, ca. 2% only). By contrast, the MIKE spectrum of the isomeric ions [**12**+H]$^+$ (Fig. 3) was much more complex: these metastable ions eliminate several small neutrals, viz. C_3H_6, C_4H_8 and C_5H_{10}, in large relative abundances, showing that, in fact, protonolysis gives rise to deep-seated skeletal rearrangements of the alicyclic residue. Interestingly, however, minor fractions of $[M+H-C_6H_{10}]^+$ (m/z 197) and $[M+H-C_6H_{12}]^+$ (m/z 195) ions are also formed, with the latter ones predominating. This points to the expected losses of methylcyclopentene (or methylenecyclopentane) and methylcyclopentane by proton transfer and hydride abstraction, respectively. In addition, free $C_6H_{11}^+$ ions (m/z 83) are formed in noticeable amounts. Thus, in both cases, the cycloalkyl cations do not react as specific as expected for secondary (cyclohexyl) and tertiary (methylcyclopentyl) carbocations. Rather, the putative *cyclo*-$C_6H_{11}^+$ ions appear to undergo ring contraction to CH_3-*cyclo*-$C_5H_8^+$ ions, as indicated by the loss of C_6H_{12}. In turn, the latter carbenium ions, which should be released into the I/N complex with 1,3-diphenylpropane at least as easily as *tert*-$C_4H_9^+$, seemingly isomerize to secondary $C_6H_{11}^+$ structures, the *cyclo*-$C_6H_{11}^+$ ions being only one of the possible isomers. On the whole, the situation is considerably more complicated than with the $[M+H]^+$ containing (acyclic) alkyl groups and the propensity of cyclo- or bicycloalkyl cations to undergo skeletal rearrangement is confirmed. Nevertheless, the fact that hydride abstraction does occur to a minor extent with [**11**+H]$^+$ ions and to a (relatively) large extent with [**12**+H]$^+$ ions clearly reflects the participation of tertiary $C_6H_{11}^+$ ions, possibly in an incomplete equilibrium within the I/N complexes with the 1,3-diphenylpropane neutral (Scheme 6).

In this view, it is interesting to note that the deuterium labelling experiments again confirm the common behavior of the hydride-abstracting ions in the I/N complexes [$R^+\cdots$diphenylalkane], found already in many previous cases: the MIKE spectrum of the methylcyclopentyl-substituted isotopomer [**12a**+H]$^+$ bearing an α,α-dideuterated methylene group exhibits the typical ratio of H^- and D^- abstraction, viz. [**12a**+H–C_6H_{12}]:[**12a**+H–$C_6H_{11}D$] = 1.7 (±0.1) (Fig. 4b). Although the respective complementary labelling has not been performed here, it can be safely assumed that the methylcyclopentyl ions



Scheme 6. Isomerizing ion/neutral complexes **IN(Chx)** and **IN(MCp)** generated from the protonated precursors **11** and **12**. In both cases, the hydride abstraction occurs from both the α-CH_2 and the γ-CH_2 groups of the diphenylpropane neutral.

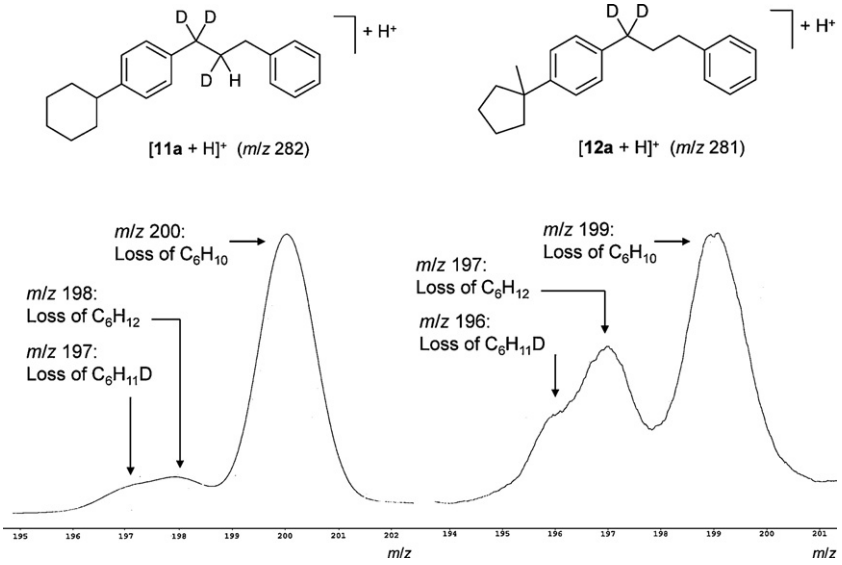


Fig. 4. Partial MIKE spectra of protonated isotopomers [**11a**+H]+ (a) and [**12a**+H]+ (b). To minor extents, the peaks at *m*/*z* 200 and at *m*/*z* 199, respectively, indicating the loss of C_6H_{10} (H^+ transfer channel), are due to the fragmentation of the corresponding isobaric ions [$^{13}C_1$]-**11a**$^{+\bullet}$ and [$^{13}C_1$]-**12a**$^{+\bullet}$ (see text).

within the I/N complex [$C_6H_{11}^+ \cdots C_6H_5C^{\alpha}H_2CH_2C^{\gamma}H_2C_6H_5$] react with the usual and characteristic regioselectivity, $k_\gamma/k_\alpha = 1$, at both of the benzylic methylene groups, and with the typical kinetic isotope effect observed for these hydrocarbon ions, $k_H/k_D \approx 1.6$ [14–21]. This holds true even for the $C_6H_{11}^+$ ions undergoing the hydride abstraction in the I/N complex formed from ions [**11**+H]+. Although the fractions of cycloalkane loss are really minor here, the MIKE spectrum of the corresponding protonated (α,α,β-trideuterated) isotopomer, [**11a**+H]+, reflects about the same ratio: [**11a**+H–C_6H_{12}]:[**11a**+H–$C_6H_{11}D$] = 1.6 (±0.15) (Fig. 4a). Thus, it is very likely that, in fact, *tert*-methylcyclopentyl ions are formed upon gas-phase protonolysis of the cyclohexyl derivative **11** (Scheme 6). These results demonstrate that, at least in favourable cases, the characteristic fragmentation behavior of the intermediate I/N complexes can also reflect the isomerization of the ionic constituent of an intermediate I/N complex.

4. Conclusion

Long-lived, metastable [M+H]+ ions of 1,3-diphenylpropanes bearing branched alkyl groups (R, R′) at one or both of the aromatic rings eliminate these groups mostly as alkenes (by proton transfer) and alkanes (by hydride transfer). These processes involve the ion/neutral complexes [$R^+ \cdots C_6H_5CH_2CH_2CH_2C_6H_4$–R′] as reactive intermediates. In some of the examples presented in this work, the proton-induced isomerization of the constituents of these I/N com-

plexes is reflected by the relative rates of the alkene and alkane losses. Thus, the 1,2-shift of a *tert*-butyl group from the *para*- to a *meta*-position of the protonated benzene ring gives rise to a characteristic increase of the alkene loss due to the increase of the gas-phase basicity of the neutral component of the I/N complex, together with a decreased alkane loss. Isobutyl-substituted isomers behave different from the *tert*-butyl-substituted $[M+H]^+$ ions; they do not form I/N complexes containing *tert*-$C_4H_9^+$ ions which would reflect the basicity of the neutral constituent. Rather, isomerization to the more acidic *sec*-$C_4H_9^+$ ions should occur. The competing losses of cycloalkene(s) and cycloalkane(s) from the metastable $[M+H]^+$ ions of cyclohexyl- and (methylcyclopentyl)-substituted 1,3-diphenylpropanes reflects the at least partial isomerization of the ionic constituents of the corresponding I/N complexes, $[(CH_2)_5{>}CH^+\cdots C_6H_5CH_2CH_2CH_2C_6H_5]$ and $[(CH_2)_4{>}C^+CH_3\cdots C_6H_5CH_2CH_2CH_2C_6H_5]$. Thus, in suitably tailored cases, the fragmentation of organic ions via reactive ion/neutral complexes can reflect the structure–reactivity relation of the ionic and/or the neutral constituents of these intermediates.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ijms.2010.10.007.

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