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ION/MOLECULE COMPLEXES AS INTERMEDIATES DURING THE ELIMINATION OF ARENES FROM β-ARYLETHYL ARENIUM IONS

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ABSTRACT

β-Arylethyl arenium ions substituted by methyl and methoxy groups, respectively, have been generated by electron impact-induced dissociation from the correspondingly substituted 1-(β-arylethyl)-1,4-dihydrobenzoic acids. The mechanism of the arene elimination from these ions, which is the main reaction of metastable ions in the second field free region (2.FFR) has been elucidated by determination of substituent effects, by measurement of the appearance energies of relevant ions in the 2.FFR and by calculations of model systems. The substituent effect favouring elimination of the arene with the greater proton affinity is independent of the original position of the substituent at the β-arylethyl group or at the arenium moiety because of a fast hydrogen transfer between both aryl groups but depends on the position of the substituent relative to the ethylene chain. The appearance energies of the product ions of the arene eliminations are only compatible with the formation of α-arylethyl ions or their methyl tropylium isomers, indicating a rearrangement by a 1,2-hydrogen shift during the reaction. No isotope effect is observed in the reactions of appropriate deuterated derivatives and nor is any large kinetic energy release. It is shown by an estimation of the stabilisation energy of an ion/molecule complex formed by a β-arylethyl ion and an arene molecule that this loose complex is an intermediate of the arene elimination reaction, which explains the experimental details of this fragmentation.

INTRODUCTION

Alkyl-substituted benzenium ions formed by chemical ionisation of alkylated benzene fragment mainly via two reaction channels [1]: (i) elimination of an alkene and formation of a protonated benzene molecule and (ii) elimination of a neutral aromatic molecule and formation of an alkyl cation.

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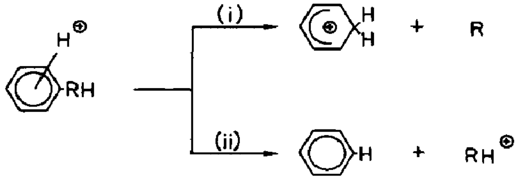
Scheme 1.



Prior to these fragmentations, hydrogen migrations occur between the alkyl groups and aryl groups of the ions [2] and a proton-bound complex between the alkene and the aromatic hydrocarbons has been proposed as a common intermediate of exchange reactions and fragmentations [3].

The elimination of benzene has also been observed [4] from protonated 1,2-diphenyl ethane, **1**, formed via an electron impact route from 1-(β-phenylethyl)-1,4-dihydrobenzoic acid **1a** (see Scheme 2) and from related ω-phenylalkyl benzenium ions [5]. A study of metastable ω-phenylalkyl benzenium ions fragmenting in the second field free region (2.FFR) of a VG ZAB-2F mass spectrometer revealed a fast interannular exchange between all hydrogen atoms at the aromatic nuclei before the benzene elimination, but no participation from hydrogen atoms at the aliphatic moieties of the ions.

Furthermore, elimination of an alkene [reaction (i) in Scheme 1] is not observed and elimination of benzene is by far the most important fragmentation reaction of these ω-phenylalkyl benzenium ions. In order to get more insight into the mechanism of this rather specific reaction of the σ complex **n** (Scheme 2), the influence of substituents R^1 and R^2 at the different positions of the phenyl groups on this reaction has been studied.

EXPERIMENTAL

All experiments were performed using a ZAB-2F double-focusing mass spectrometer [23]. Ions were produced by electron bombardment (maximum energy 70 eV). Fragmentations were observed in the field-free region located between the magnetic and electric sectors. Measurements of appearance energies of metastable peaks were carried out by the method described by Burgers and Holmes [16]. The methyl fragmentation from ionised diethyl ether was used as a reference reaction in the ion source and in the 2.FFR(AE 10.26 eV).

Compounds **1a**, **3a**, **5a**, **7a**, **8a**, **9a**, **11a**, and **12a** were synthesized from benzoic acid and suitably substituted phenylalkyl bromides by reductive alkylation in liquid ammonia [5(b),24]. Tolylethyl bromides were prepared from the appropriate alcohols [25] which were accessible by reduction of the corresponding tolylacetic acids with $LiAlH_4$ in THF. Methoxy-substituted

β-(methoxyphenyl)-ethanols were prepared from methoxy-substituted benzaldehydes, which reacts with hippuric acid to give azlactones [26]. Hydrolysis leads to a mixture of substituted pyruvic acids and benzoic acid and subsequent oxidation with H_2O_2 [10%) leads to methoxyphenylacetic acids. Reduction of the mixture with $LiAlH_4$ in THF, followed by careful chlorination only of the formed benzylalcohol with $SOCl_2$ in diethyl ether at room temperature, hydrolysis and distillation affords the necessary alcohols. Compounds **2a**, **4a**, **6a**, **10a**, **13a**, and **14a** were prepared from methyl- and methoxy-substituted benzoic acids, respectively, β-phenylethyl bromide and dideuterated β-phenylethyl bromide, respectively. β-Phenyl-α,α-d_2-ethanol was prepared by the reduction of methyl phenyl acetate with $LiAlD_4$ (84%, degree of deuteration > 95%, ^{1}H-NMR) and 2-phenyl-β,β-d_2-ethanol was synthesized by the reduction of d_3-phenylacetic acid (83%, degree of deuteration > 95%, ^{1}H-NMR).

Melting points are uncorrected. ^{1}H-NMR and MS spectra were recorded with a Varian EM 360 and a MAT 311A instrument, respectively. From the mass spectra, only characteristic peaks are represented.

2a: m.p. 149–151°C; NMR($CDCl_3$) $\delta = 7.18$(s, 5H), 5.4–6.1(m, 3H), 2.8(m, 2H), 2.6(m, 2H), 2.1–2.5(m, 2H), 1.7(s, 3H); MS *m/z* 242(5%), 197(5%), 138(8%), 119(19%), 105(100%), 93(15%), 91(53%).

3a: m.p. 90–92°C; NMR($CDCl_3$) $\delta = 7.1$(s, 4H), 5.9(s, 4H), 2.7(m, 2H), 2.25(s, 3H), 1.7–2.7(m, 4H); MS *m/z* 242(3%), 197(8%), 124(8%), 119(100%), 105(71%), 91(29%).

4a: m.p. 136–138°C; NMR($CDCl_3$) $\delta = 7.1$(s, 5H), 5.7(m, 2H), 5.4(m, 1H), 2.7(s, 2H), 1.7(s, 3H), 1.9–2.2(m, 2H), 2.3–2.5(m, 2H); MS *m/z* 242(3%), 197(12%), 138(6%), 119(37%), 105(100%), 93(20%), 91(63%).

5a: m.p. 91–93°C; NMR($CDCl_3$) $\delta = 6.8$–7.2(m, 4H), 5.78(s, 4H), 2.65(m, 2H), 2.25(s, 3H), 1.7–2.8(m, 4H); MS *m/z* 242(2%), 197(4%), 124(3%), 119(40%), 105(100%), 91(50%).

6a: m.p. 110–114°C; NMR($CDCl_3$) $\delta = 7.2$(s, 5H), 5.85(s, 4H), 2.4(s, 3H), 1.7–2.8(m, 5H); MS *m/z* 242(2%), 197(2%), 138(11%), 119(31%), 105(100%), 93(13%), 91(62%).

7a: m.p. 107–108°C; NMR($CDCl_3$) $\delta = 7.0$(s, 4H), 5.8(s, 4H), 2.7(m, 2H), 2.3(s, 3H), 1.7–2.7(m, 4H); MS *m/z* 242(4%), 197(4%), 124(18%), 119(100%), 105(83%), 91(38%).

8a: m.p. 95–97°C; CMR($CDCl_3$) $\delta = 6.6$–7.2(m, 4H), 5.83(s, 4H), 3.73(s, 3H), 2.68(m, 2H), 1.7–2.7(m, 4H); MS *m/z* 258(9%), 213(5%), 135(100%), 121(24%), 105(66%), 91(45%).

9a: yellow oil; NMR($CDCl_3$) $\delta = 6.5$–7.5(m, 4H), 5.87(s, 4H), 3.7(s, 3H), 2.67(m, 2H), 1.8–2.7(m, 4H); MS *m/z* 158(10%), 213(10%), 135(64%), 121(54%), 105(96%), 91(100%).

10a: yellow oil; NMR($CDCl_3$) $\delta = 7.1$(s, 5H), 5.8(m, 2H), 4.7(m, 1H), 3.5(s, 3H), 2.7(m, 2H), 1.9–2.3(m, 2H), 2.4–2.7(m, 2H); MS *m/z* 258(16%), 213(55%), 153(33%), 135(28%), 109(100%), 105(82%), 91(54%).

11a: m.p. 104–105°C; NMR($CDCl_3$) $\delta = 6.6$–7.2(m, 4H), 5.82(s, 4H), 3.7(s, 3H), 2.66(m, 2H), 1.7–2.7(m, 4H); MS *m/z* 258(12%), 213(3%), 135(100%), 121(38%), 105(37%), 91(18%).

12a: m.p. 127–129°C; NMR($CDCl_3$) $\delta = 7.2$(s, 5H), 5.4–6.1(m, 3H), 2.8(m, 2H), 2.6(m, 2H), 1.5–2.3(m, 4H), 1.7(s, 3H); MS *m/z* 254(4%), 211(5%), 138(4%), 133(21%), 119(100%), 105(43%), 91(28%).

13a: m.p. 136–138°C; NMR($CDCl_3$) $\delta = 7.1$(s, 5H), 5.7(m, 2H), 5.4(m, 1H), 2.3–2.7(m, 4H), 1.7(s, 3H); MS *m/z* 244(4%), 199(15%), 138(19%), 121(28%), 107(100%), 93(28%), 91(62%).

14a: m.p. 137–138°C; NMR($CDCl_3$) $\delta = 7.1$(s, 5H), 5.7(m, 2H), 5.4(m, 1H), 2.7(m, 2H), 2.0(M, 2H), 1.7(s, 3H); MS *m/z* 244(4%), 199(16%), 139(7%), 121(28%), 107(100%), 93(20%), 91(26%).

RESULTS AND DISCUSSION

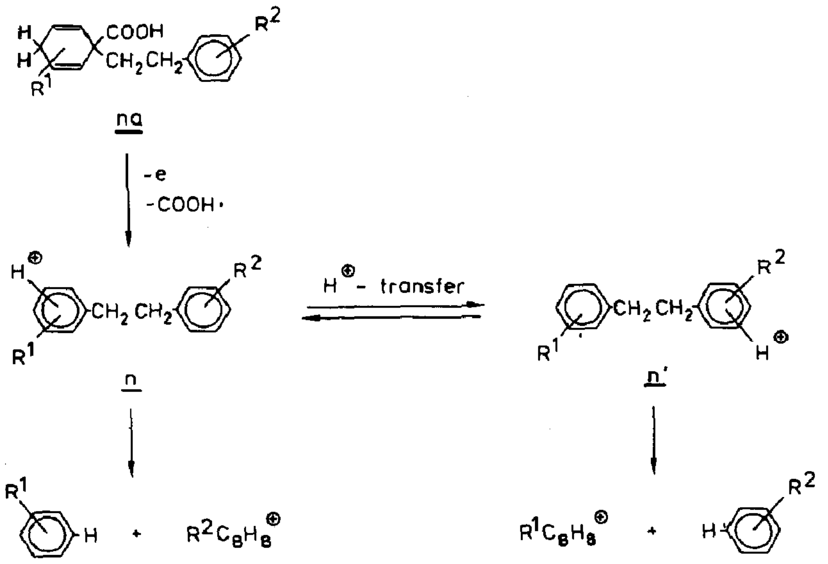
The substituted β-phenylethyl benzenium ions **2**–**14** have been generated in the ion source of a mass spectrometer by electron impact-induced fragmentation of the corresponding 1,4-dihydrobenzoic acids (Scheme 2). The interannular hydrogen exchange reaction in the asymmetrically substituted ions is still much faster than the fragmentation reaction, hence a benzene molecule and a substituted benzene molecule, respectively, can be eliminated from metastable ions **2**–**14** in the 2.FFR. The intensity ratio for both reactions is given in Table 1.

TABLE 1

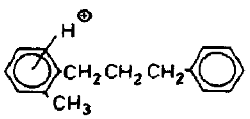
Preference factor for the elimination of toluene and anisole, respectively, from metastable β-arylalkylarenium ions **2**–**14** in the 2.FFR

Compound	[Arene]/[Benzene]
2	3.1
3	3.0
4	1.3
5	1.2
6	1.4
7	1.3
8	1.0
9	1.3
10	1.4
11	1.3
12	1.5
13	1.4
14	1.4

Scheme 2.



n	R^1	R^2	n	R^1	R^2
1	H	H	7	H	4-CH_3
2	2-CH_3	H	8	H	2-OCH_3
3	H	2-CH_3	9	H	3-OCH_3
4	3-CH_3	H	10	3-OCH_3	H
5	H	3-CH_3	11	H	4-OCH_3
6	4-CH_3	H			



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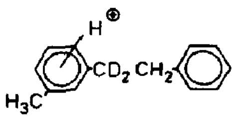

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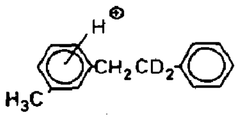

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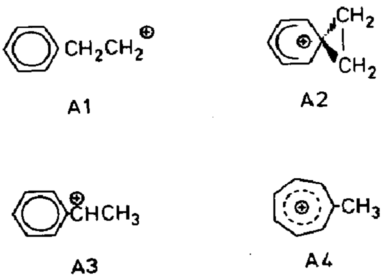
The data show, as a general trend, the preferred elimination of the aromatic molecule with the higher proton affinity (PA), regardless of whether the substituent is at the originally protonated phenyl group or not. The identical values within the limits of error for ions **2** and **3**, **4** and **5**, **6** and **7**, **9** and **10**, respectively, corroborate the equilibrium between these pairs of ions by a fast proton transfer. In addition to the effect of the PAs, a positional substituent effect is observed. In the series of methyl-substituted ions, the *ortho*-substituted ions **2** and **3** undergo preferred elimination of toluene over benzene by a factor of 3, whereas this factor is only 1.2–1.4 for the *meta*- and *para*-substituted isomers. In contrast to this, the *ortho*-substituted ions, **8**, of the methoxy-substituted series eliminate equal amounts of benzene and anisole, in spite of the much larger PA of anisole *, and the *meta*- and *para*-isomers **9/10** and **11** prefer the elimination of anisole, again only by a factor of 1.3–1.4. Finally, the special "*ortho-effect*" of the CH_3 substituent is absent for the decomposition of ions **12** containing a propylene instead of an ethylene chain, showing the "normal" preference factor of 1.5 for toluene elimination. Obviously, the positional substituent effect, at least of the CH_3 group, is a specific feature of the configuration of ions **2** and **3** and, clearly, an explanation of these substituent effects is not straightforward but must involve a special mechanism of the arene elimination from β-arylethyl benzenium ions.

The elimination of benzene from β-phenylethyl benzenium ions, **1**, gives rise to $C_8H_9^+$ ions. By extrapolation from the structure of **1** and for thermodynamic reasons, one can expect one or several of the structures shown in Scheme 3 for these ions. Other isomers of the $C_8H_9^+$ ions which are known to be stable species [7] are not very likely to arise from the fragmentation of **1**.

Scheme 3.



The heat of formation of the 1-phenylethyl ion **A3** has been derived from photoionization experiments to be 860 kJ mol^{-1} [8]. A calculation of the heat of formation of **A3** from PA(styrene) [9] gives 816 kJ mol^{-1}. It is assumed that the heat of formation of the methyl tropylium ion **A4** is almost identical [8].

The heat of formation of the bridged ethylene benzenium ions **A2** should be larger than that of **A3** and **A4**, but no experimental values are known.

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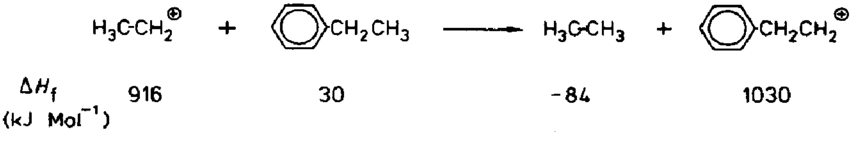
* PA(anisole) = 830 kJ mol^{-1} [6].

Hehre [10] has estimated a difference of 80–100 kJ mol^{-1} for the heats of formation of ions **A1** and **A2**. The heat of formation of **A1**, which is probably an unstable species [7], is also not known but can be estimated by the isodesmic reaction of Scheme 4. The result is $\Delta H_f(\mathbf{A1}) \approx 1030$ kJ mol^{-1}

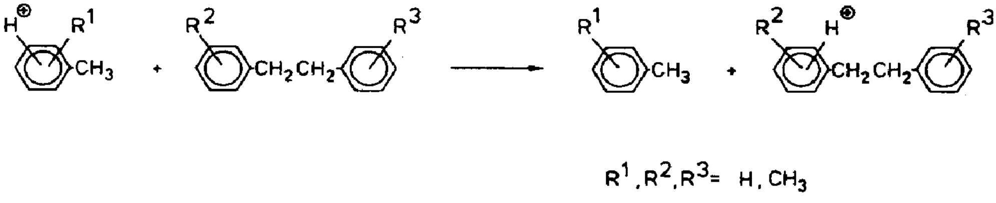
Scheme 4.



and hence $\Delta H_f(\mathbf{A2}) \approx 950$ kJ mol^{-1} *. As expected, the thermodynamic stability of ions $C_8H_9^+$ decreases in the order **A4** ≈ **A3** > **A2** > **A1**.

A prerequisite of arene elimination from ion **1** and its substituted derivatives **2–14** is the migration of a hydrogen atom to the site of bond cleavage. Hence, an *ipso*-protonated 1,2-diarylethane is either an intermediate or a transition state of the arene elimination. The heat of formation of the *ipso*-protonated ions **i** and **i′** and those of the ions **o**, **o′**, **m**, **m′**, and **p**, **p′** carrying the proton at the *ortho, meta* and *para* position, respectively, to the ethylene chain, depends on the type and the position of the substituent (see Figs. 1–3). In the case of the methyl-substituted ions **2–7**, the heats of formation of the isomeric species have been estimated from the calculated heats of formation of the different protonated toluenes and xylenes [6,12,13] by the aid of the isodesmic reaction of Scheme 5.

Scheme 5.



The resulting values for the heats of formation of the isomeric ions **2–7** are presented in Table 2 together with other thermochemical data necessary to construct the schematic energy profiles of the arene elimination reaction shown in Figs. 1–3. As expected, the *ipso*-protonated intermediates **i** and **i′** represent higher energy states than the isomeric protonated forms. However, if the direction of the fragmentation of ions **2–7** were to depend on the

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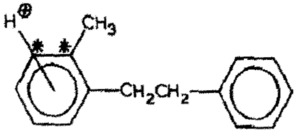
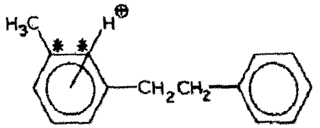
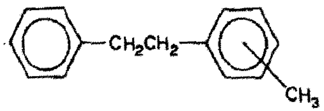
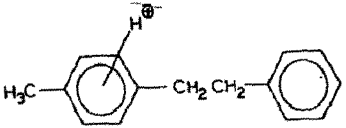
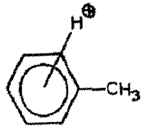
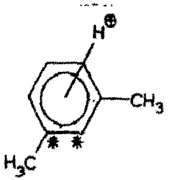
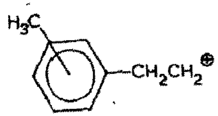
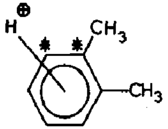
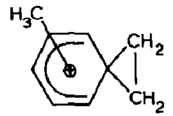
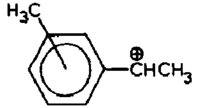
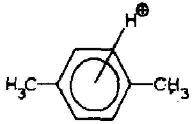
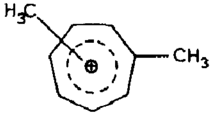
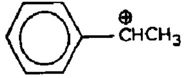
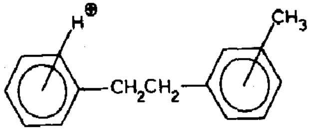
* An energy difference of only about 26 kJ mol^{-1} between ions **A2** and **A3** has been calculated by some authors (see ref. 11).

TABLE 2

Heats of formation, ΔH_f, and thermochemical data used for the construction of the energy profiles (Figs. 1–3)

Molecule/ion		ΔH_f (kJ mol^{-1})	Molecule/ion		ΔH_f (kJ mol^{-1})
Benzene		83^{a}		*o*	858*/845^{d}
Toluene		50^{a}		*m*	845*/829^{d}
o-Xylene		19^{a}		*p*	829^{d}
m-Xylene		17^{a}		*i*	858^{d}
p-Xylene		18^{a}			
				*o*	823*/810^{d}
	*o*	109^{b}		*m*	902*/882^{d}
	m	105^{b}		*p*	810^{d}
	p	105^{b}		*i*	902^{d}
				*o*	830^{d}
	*o*	792^{c}		*m*	830^{d}
	m	824^{c}		*p*	843^{d}
	p	780^{c}		*i*	843^{d}
	i	845^{c}			
	*o*	735*/722^{c}		*o, m, p*	917^{e}
	m	814*/794^{c}			
	p	722^{c}			
	i	814^{c}			

	o m p i	768*/755^{c} 755*/739^{c} 739^{c} 768^{c}		o m p	< 917^{e} 917^{e} < 917^{e}
				o, m, p	784^{b}
	o m p i	743^{c} 743^{c} 756^{c} 756^{c}			784^{g}
					817^{b}
	o m p i	880^{d} 911^{d} 867^{d} 933^{d}			

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[a] R.C. Weast (Ed.), Handbook of Chemistry and Physics, CRC Press, Cleveland, OH, 54th edn., 1973–1974.

[b] Estimated by the group equivalent method; values from ref. 27.

[c] Estimated from relative energy values calculated by Heidrich [12] and from PAs [6].

[d] Estimated by isodesmic substitution (Scheme 5).

[e] Estimated by isodesmic substitution.

[f] Estimated by isodesmic substitution from ΔH_f(**A1**) (Scheme 3).

[g] Ref. 8.

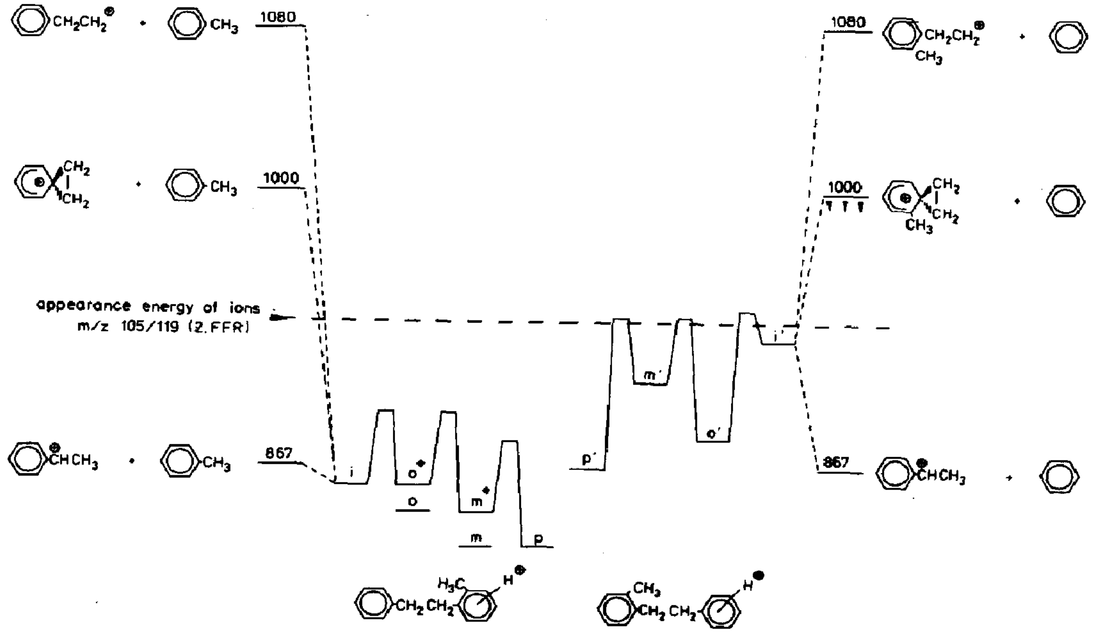


Fig. 1. Schematic reaction energy profile for the arene elimination of *o*-methyl-substituted *β*-phenylethyl benzenium ions **2/3**.

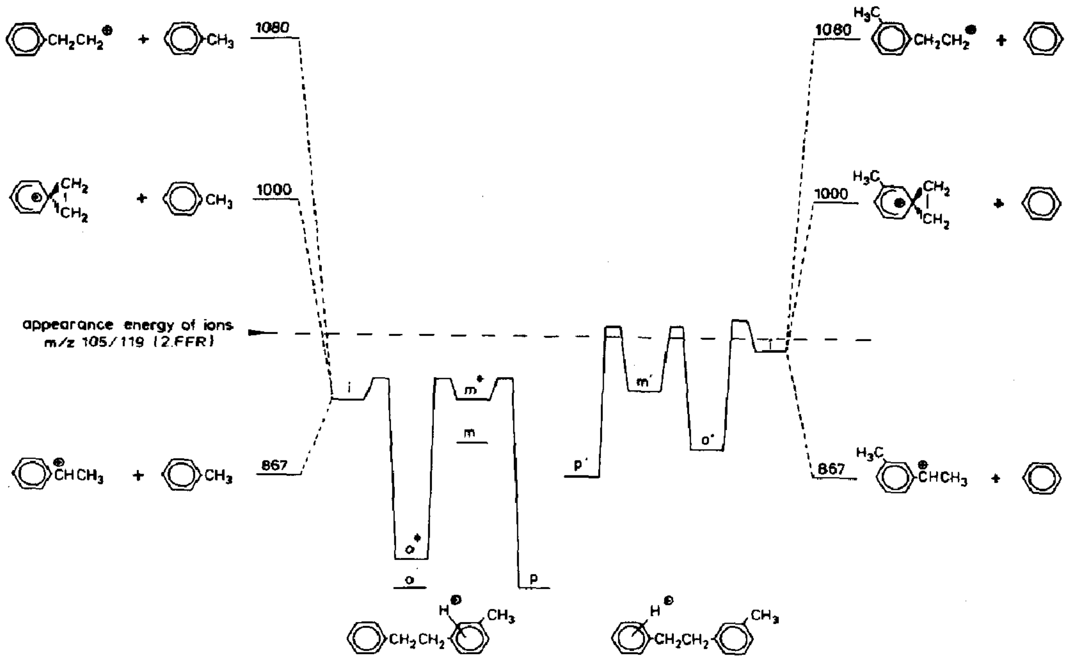


Fig. 2. Schematic reaction energy profile for the arene elimination of *m*-methyl-substituted *β*-phenylethyl benzenium ions **4/5**.

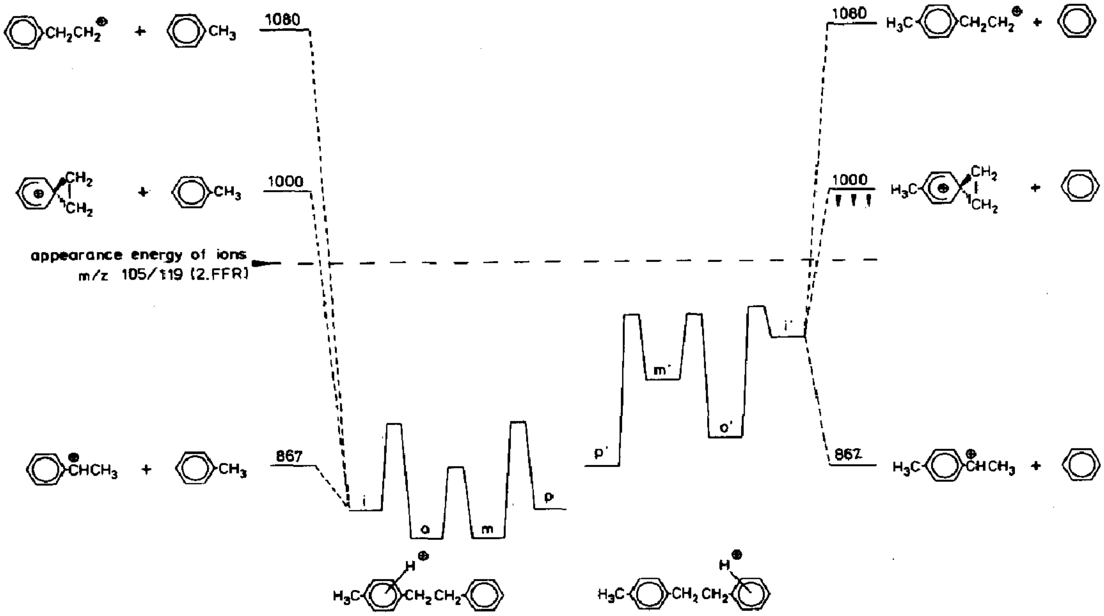


Fig. 3. Schematic reaction energy profile for the arene elimination of *p*-methyl-substituted *β*-phenylethyl benzenium ions **6**/**7**.

relative energy of **i** and **i′** in each case, the *ortho*-substituted ions **2** and **3** and the *para*-substituted ions **6** and **7** should strongly prefer the elimination of toluene and, in **4** and **5**, one should observe only a slightly preferred elimination of toluene compared with the benzene elimination. In the series of methoxy-substituted ions **8**–**11**, this positional substituent effect should be even stronger because of the stronger effect of the methoxy substituent on the site of protonation [14]. This order of substituent effects is not observed experimentally (see Table 1).

It is not very likely that the expected substituent effect is masked by the activation energies necessary for the hydrogen migrations. The activation energies of the *intra-annular* hydrogen shifts have been estimated [15] and are included in the energy profiles (Figs. 1–3). The activation energy of an *interannular* hydrogen transfer is not known but is probably smaller than for the intra-annular migration [5]. Finally, a randomization of all hydrogen atoms at the aromatic moieties of ions **2**–**14** *prior to* elimination of the arene has been observed [5]. Consequently, the rate and the direction of the arene elimination from these ions must depend on a transition state *after* the formation of the *ipso*-protonated ions **i** and **i′**.

The appearance energies (AE) of the product ions $C_8H_9^+$ and $C_9H_{11}^+$ of the arene elimination from the methyl-substituted ions **2**–**7** have been determined for the fragmentation within the ion source and within the 2.FFR of a VG ZAB-2F mass spectrometer [16] (Table 3). Although the measurement error is quite large, the AEs reveal some interesting details of the fragmentation. For fragmentation in the ion source, the AEs of ions $C_9H_{11}^+$, *m/z* 119, are larger than those of the ions $C_8H_9^+$, *m/z* 105, for the dihydrobenzoic acids leading to **2**, **4** and **6**, whereas the reverse is true for the dihydrobenzoic acids leading to **3** and **7**. Inspection of the structures of the dihydrobenzoic acids shows that, in the former case, only the ions $C_8H_9^+$ and, in the latter case, only the ions $C_9H_{11}^+$ can be formed by direct bond cleavages in the molecular ions of the dihydrobenzoic acids. To be sure that both $C_8H_9^+$ *and* $C_9H_{11}^+$ arise only from the β-arylethyl arenium ions **2**–**7**, the AEs must be measured from metastable ions. Identical AEs are obtained within the limits of error for ions $C_8H_9^+$ and $C_9H_{11}^+$ arising from the same precursor ion with slightly increasing values in the order *ortho-* < *meta-* < *para*-methyl substitution.

By comparing the experimental AEs with the thermochemical thresholds in Figs. 1–3 calculated for the formation of ions **A1**–**A4** (Scheme 3) and their CH_3-substituted analogues from **2**–**7**, the primary β-phenylethyl ion **A1** and the bridged ethylenebenzenium ion **A2** as well as their homologues can be clearly excluded as the product ions of the arene elimination reaction. The AE values rather correspond to the more stable α-phenylethyl ion **A3** or to the methyl tropylium ion **A4** and their CH_3-substituted analogues. It is important to note that, for the formation of both product ions **A3** and **A4** *the arene elimination has to be accompanied by a rearrangement of the incipient carbenium ion*. A rearrangement of the β-phenylethyl benzenium ions **2**–**7** prior to the fragmentation can be excluded because this would result in scrambling of the hydrogen atoms at the aliphatic groups *and* at the aromatic rings, which is not observed.

A mechanism accounting for this argument is a 1,2-hydride shift in the *ipso*-protonated form **i** of the β-phenylethyl benzenium ions concomitant

TABLE 3

Appearance energies, AE[a], of $CH_3C_8H_8^+$ ions and $C_8H_9^+$ ions measured in the ion source and in the 2.FFR

Precursor[b]	AE[$CH_3C_8H_9^+$]		AE[$C_8H_9^+$]	
	Ion source	2.FFR	Ion source	2.FFR
2	11.0	9.4	10.3	9.4
4	11.1	9.7	10.0	9.7
6	10.7	10.0	10.1	10.0
3	10.4	9.7	10.8	9.7
7	10.1	10.1	11.1	10.1

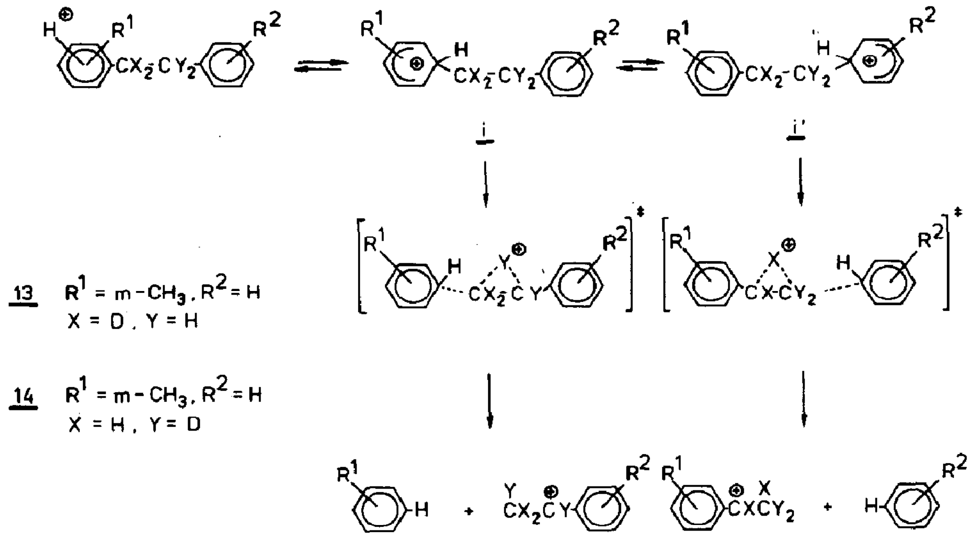
[a] In eV; ion source ±0.01 eV, 2.FFR ± 0.3 eV.

[b] Formed from the corresponding dihydrobenzoic acid in the ion source.

with the elimination of the arene molecule (Scheme 6). Such "hidden hydrogen rearrangements" are well documented and may be detected by unexpected deuterium isotope effects [17].

In the case of the deuterated ions **13** and **14** (Table 1 and Scheme 6), an isotope effect on the 1,2-hydride shift should influence the elimination of benzene and toluene in opposite directions. Hence, the preference factor for toluene elimination from **13** and **14** should be different and should also differ from that found for the undeuterated ion **4**. However, the preference factor is the same for all three ions, indicating the absence of an isotope effect and excluding the mechanism of Scheme 6 as the rate-determining step of the elimination reaction.

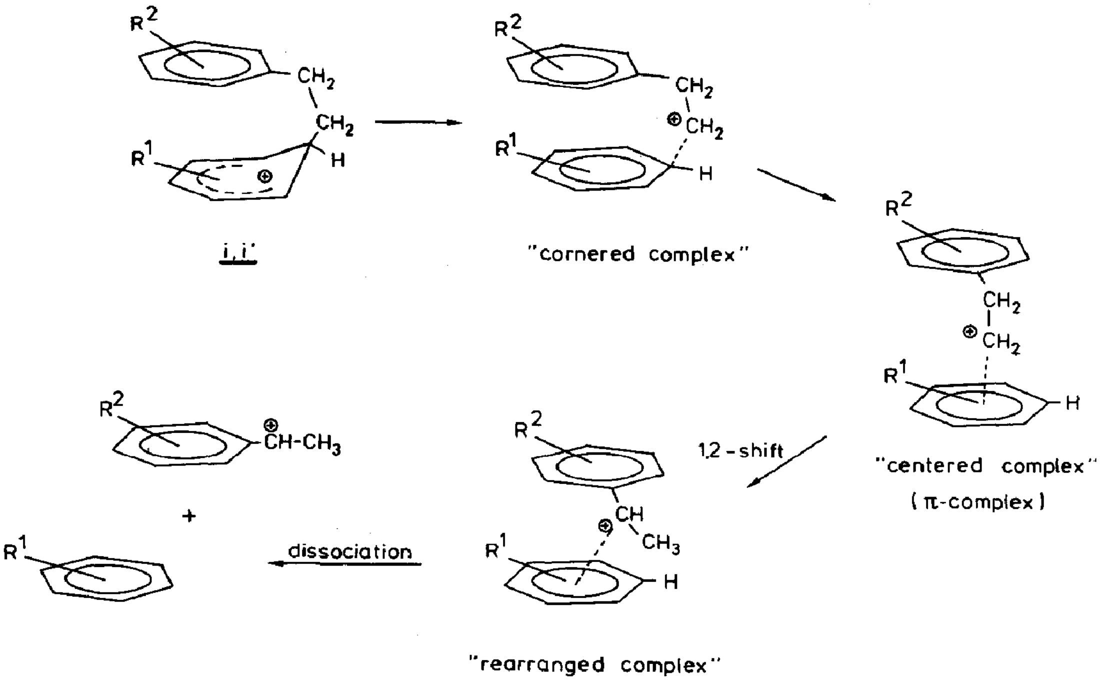
Scheme 6.



It follows from these results that the rate- and energy-determining transition state of the overall fragmentation reaction has to be passed *prior* to the rearrangement of the β-arylethyl moieties of the reactand ions **1**–**7** to the α-arylethyl or tropylium type fragment ions **A3** or **A4**, respectively. However, in spite of this situation, the MIKE spectra of all β-arylethyl benzenium ions studied here show Gaussian-shaped peaks, the kinetic energy released being in the range of $\langle T \rangle = 35$–45 meV. Hence, the elimination of the arene in the final step of the reaction occurs from a rather loose complex without considerable transfer of its excess energy into the translation of the dissociation products.

From the experimental details, a mechanism of the arene elimination from the β-arylethyl benzenium ions emerges (Scheme 7) by which the *ipso*-protonated form **i**/**i'** of these ions dissociates into an ion/molecule complex

Scheme 7.



consisting of a β-arylethyl ion and an arene molecule during the rate-determining reaction step. This ion/molecule complex can be visualized either as a π-complex or as β-arylethyl ion being stabilized by a solvating arene molecule. In this loose complex, the ion and the arene molecule are held together by attractive ion–dipole interactions, leaving the ion free for the rearrangement to the more stable α-arylethyl ion.

The rearrangement of incipient alkyl cations during mass spectrometric fragmentations has been suggested before [18]. The following discussion will show, for the present case, that a mechanism involving an ion/molecule complex does indeed take into account the experimental results concerning the energetics and the substituent effects.

The stabilisation energy of an ion/molecule complex can be estimated by the average-dipole-orientation theory (ADO theory) of Su and Bowers [19a]. According to the equations given in Scheme 8, it depends on the charge, z, of the ion, the dipole momentum, μ_D, and the polarisability, α, of the molecule and the distance, R, between ion and molecule.

There exist two different orientations of the arene molecule in the complex relative to the ion. In the first arrangement, the ion sits above the plane of the arene molecule ("centered complex") while in the second, the ion is at an edge or a corner of the molecule ("cornered complex", Scheme 7). In the case of the centered complex, the stabilisation energy is determined by the

Scheme 8.

Stabilisation energy $V = -\frac{\alpha z^2}{2R^{4-}} - \left(\mu_D \frac{z}{R^2}\right) \overline{\cos \delta(R)}$ (1)

$$\cos \delta(R) = \frac{1}{3} \frac{kT}{A} \left[-2 + \epsilon + 2\epsilon \frac{e^{-\epsilon}}{(1 - e^{-\epsilon})} \right]$$

where $\epsilon = A/kT$, $A = \mu_D(z/R^2)$, k is the Boltzmann constant and T is the temperature.

Mean polarisability for centered complex

$$\bar{\alpha} = \frac{4}{N} \left[\sum_i \tau_i \right]^2 \quad (2)$$

Local polarisability for cornered complex

$$\alpha_{loc} = \frac{4}{N} \left[\sum_i d^{(n_i - 1)} \tau_i \right]^2 \quad (3)$$

mean polarisability, $\bar{\alpha}$, of the arene molecule calculated from the partial atom polarisabilities, τ_i, and the number, N, of electrons in the molecule [Eq. (2), Scheme 8] [20]. Since the distances of the C atoms of the arene molecule from the centre of the positive charge are different in the cornered complex, the stabilisation energy is determined by the *local* polarisability, α_{loc}, which can be calculated from Eq. (3) (Scheme 8) taking into account the number, n, of bonds between the interaction site of the charge and the different atoms and an empirical factor $d = 0.75$ [21]. $\bar{\alpha}$ and α_{loc} calculated from Eqs. (2) and (3) are given in Table 4. The stabilisation energies calculated for positional isomers of ion/molecule complexes between a β-arylethyl cation with the positive charge localized at the α-C atom and toluene by using $\bar{\alpha}$ and α_{loc} are shown in Fig. 4 as a function of the distance,

TABLE 4

Mean polarisabilities, $\bar{\alpha}$, and local polarisabilities, α_{loc}, of ion/molecule complexes of benzene, toluene and anisole [calculated by Eq. (2) and (3) in Scheme 8)

Precursor ion	Neutral	$\bar{\alpha} \times 10^{25}$ (cm^3)	$\alpha_{loc} \times 10^{25}$ (cm^3)
1	Benzene	104.0	43.13
2, **3**	Toluene	122.5	47.15
4, **5**	Toluene	122.5	44.29
6, **7**	Toluene	122.5	42.20
8	Anisole	128.8	45.49
9, **10**	Anisole	128.8	41.67
11	Anisole	128.8	38.91

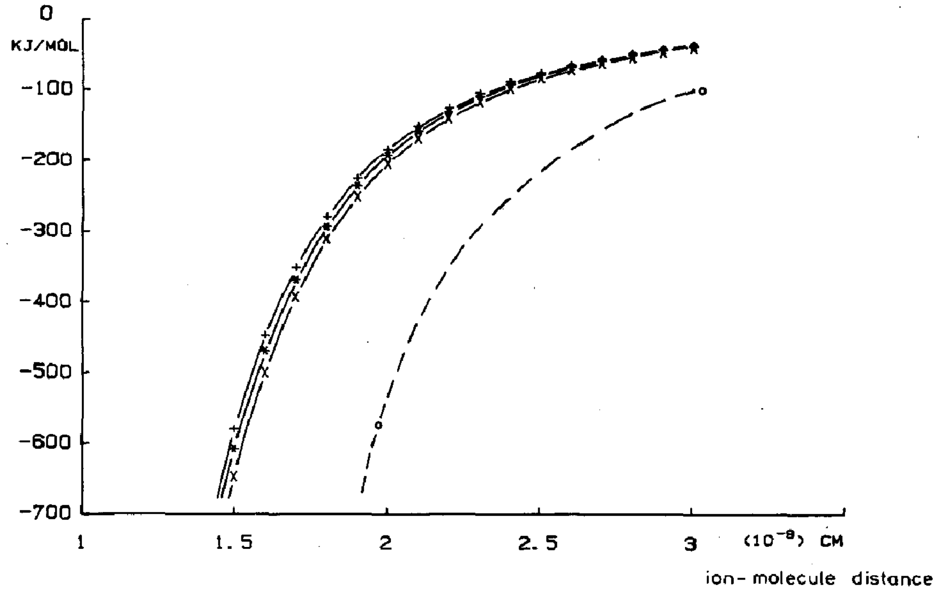


Fig. 4. Stabilisation energies of the cornered complex (solid lines) and the centered complex (broken lines), respectively, of β-phenylethyl ions and toluene. ×, *Ortho*-CH_3; *, *meta*-CH_3; +, *para*-CH_3; O, CH_3.

R, between ion and molecule. Of course, the attractive forces in the ion/molecule complex are counterbalanced by repulsion at short distances, but even at distances of ca. 2.5×10^{-8} cm, where repulsion is small, the stabilisation energy of the complex is quite large. Because $\alpha_{loc} < \bar{\alpha}$, the centered complex is more stable than the cornered. However, as the complex formation occurs by dissociation of an *ipso*-protonated β-arylethyl benzenium ion, i, the cornered complex is a better model of the early states of the dissociation, i.e. the transition state of the process, while the centered complex corresponds to the final state of the ion/molecule complex. The reaction is completed by a rearrangement of the β-arylethyl ion to the α-arylethyl ion via a 1,2-hydrogen shift within the centered complex and dissociation into the fragments. Since rearrangement and dissociation occurs from a loosely bound complex, no large kinetic energy release can be expected in spite of the excess energy gained by the rearrangements. A semiquantitative reaction energy profile of the complete reaction sequence is shown in Fig. 5 starting with the *ipso*-protonated form, i, of the β-arylethyl benzenium ion and including the cornered complex, the centered complex and the rearranged centered complex.

The transition state highest in energy along this reaction coordinate corresponds to the cornered ion/arene complex. The stabilisation energy of this complex at a certain distance between β-phenylethyl ion and toluene (or β-tolylethyl ion and benzene) increases with α_{loc} (Table 4) in the series

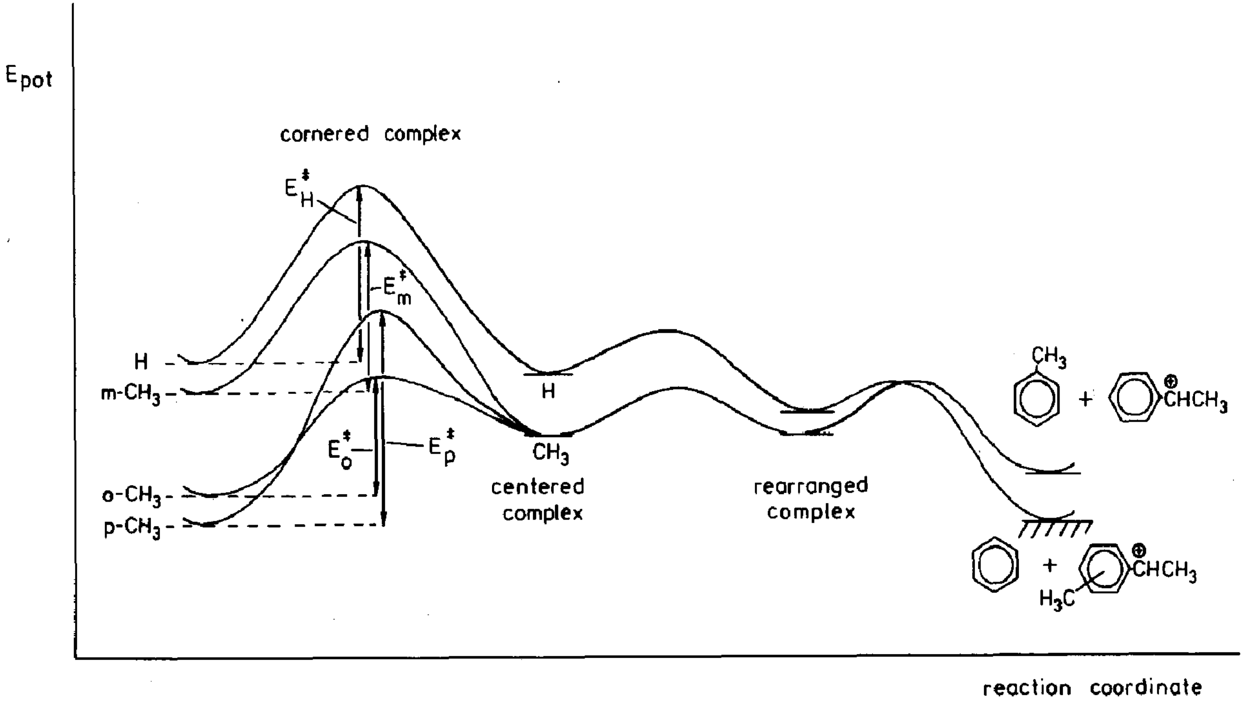
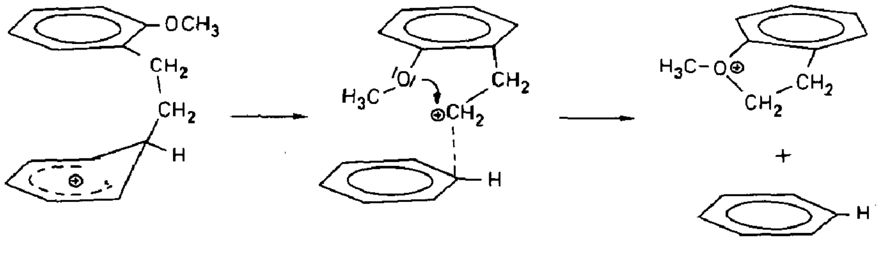


Fig. 5. Reaction energy profile for the arene elimination from *ipso*-protonated forms i of methyl-substituted β-phenylethyl benzenium ions.

toluene (*p*-orientation) < benzene < toluene (*m*-orientation) < toluene (*o*-orientation). However, the isomeric *ipso*-protonated β-phenylethyl toluenium ions giving rise to the cornered complex [β-phenylethyl ion/toluene] have heats of formation increasing in the series *para* < *ortho* < *meta* derivatives. Consequently, the increased stability of the *ipso*-protonated *p*-(β-phenylethyl)-toluenium ion **i** of **6** is counterbalanced by a lesser stabilisation energy in the cornered complex of the transition state, whereas in the *ortho* compound, both effects are in the same direction. The transition state for toluene elimination from *o*-(β-phenylethyl)-toluenium ions **2** and **3** will be lower in energy than that from the *para* and *meta* isomers **6**/**7** and **4**/**5**, respectively. The two *ipso*-protonated forms **i** and **i′** of each ion leading to the elimination of benzene and toluene, respectively, are in equilibrium with each other and, according to the Curtin–Hammett principle [22], the competition between elimination of benzene and toluene is only determined by the relative energies of the corresponding transition states. The mechanism depicted in Fig. 5 predicts that, relative to the benzene elimination, the *ortho*-substituted ions **2** and **3** will exhibit a strong preference of the toluene elimination while the *para*-substituted ions **6** and **7** will behave similarly to the *meta* compounds **4** and **5**, all these ions preferring the toluene elimination to a smaller, but nearly identical, extent. This substituent effect has been observed experimentally (Table 1).

The control of the arene elimination by the stability of the ion/arene complex and the local polarisability means that substituent effects on this reaction may show an unusual order because the interaction between the developing positive charge of the carbenium ion and the substituted arene molecule in the complex can be quite different from that known from solution. An example is the elimination of benzene and anisole from the *ortho*-methoxy-substituted ion **8** with a ratio of 1.0, although one would expect a similar preference for anisole elimination as in the case of the methyl-substituted ions. However, an *ortho*-methoxy substituent with its lone pair electrons interacts with a developing positive charge of a β-anisylethyl ion, as shown in Scheme 9, lowering the transition state for the elimination

Scheme 9.



[**8**-COOH]$^{\oplus}$

of benzene to a similar amount as the transition state for anisole elimination, which is stabilized by the enhanced local polarisability in a cornered complex with an *ortho*-methoxy group.

CONCLUSIONS

The substituent effect of CH_3 and OCH_3 groups on the arene elimination from metastable β-arylethyl arenium ions is independent of the original position of the substituent at the β-aryl group and at the arenium moiety, respectively, because of a fast interannular proton transfer between both aromatic groups. The PA of the aryl groups has only a rather small effect favouring the elimination of toluene and anisole, respectively, over the elimination of benzene by a factor of 1.3–1.5. *Ortho*-CH_3 and *ortho*-OCH_3 substituents exhibit special effects. These substituent effects exclude the *ipso*-protonated forms of the ions as the transition states of the elimination reaction.

Measurements of the AEs of the product ions in the 2.FFR are only compatible with α-arylethyl ions or isomeric tropylium ions as the product ions, indicating a rearrangement within the incipient α-arylethyl ion *prior to* dissociation. The absence of isotope effects on the arene elimination in appropriately labelled ions proves that the 1,2-hydride shift occurs *after* the β-arylethyl ion is more or less completely formed.

This apparent contradiction is explained by a mechanism involving the formation of an ion/molecule complex comprising a β-arylethyl ion and an arene molecule during the rate-determining step of the elimination. The application of the ADO theory formalism for calculation of the stabilities of these complexes shows that the energy gain is large enough to account for the experimentally determined reaction energies and for the observed order of substituted effects.

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