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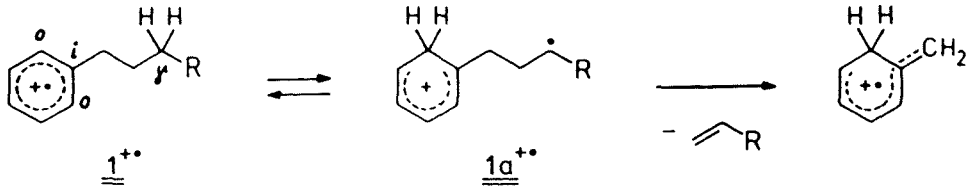
OMS Letter

Dear Sir:

Concerning the Fragmentation of *Ortho,Ortho*-Dimethyl Substituted Alkylbenzenes Induced by γ-H Migration

Two recent papers[1,2] describe the McLafferty reaction of *n*-alkylbenzenes[3] **1** without taking notice of the well-established existence of distonic ions $\mathbf{1a}^{+\cdot}$ [4] as crucial intermediates. From a PEPICO/RRKM investigation of *n*-butylbenzene, Baer *et al.*[1] invoked the formation of an intermediate species during the elimination of propene. Kingston *et al.*[2] reported on the occurrence of the McLafferty reaction of a number of ionized (*iso*-pentyl)-benzenes bearing two methyl groups in the *ortho* positions. The latter finding is highly remarkable because it contradicts a long-standing 'dogma',[2] according to which this fragmentation channel is sterically blocked by 2,6-dimethyl substitution.[5] The blocking effect provided a strong argument in favour of the migration of the γ-H atom to one of the *ortho* positions of the aromatic ring and the formation of $C_7H_8^{+\cdot}$ ions having the structure of 5-methylene-1,3-cyclohexadiene (*ortho*-isotoluene, Scheme 1), instead of toluene or cycloheptatriene ions.[3,5]

Scheme 1

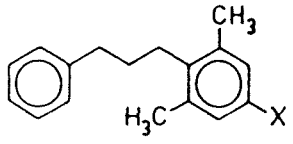


1 $^{+\cdot}$ 1a $^{+\cdot}$

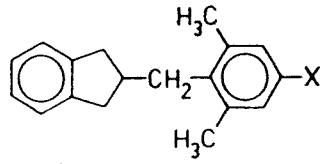
This letter is aimed to corroborate Kingston's[2] observations and to stress the role of the distonic ion isomers $\mathbf{1a}^{+\cdot}$. It is demonstrated that, under favourable conditions, the McLafferty reaction may even generate the base peak in the 70 eV mass spectrum of an *'ortho*-blocked' alkylbenzene. In addition, it will be shown that *the H migration to alkyl substituted ring positions is of greater general importance than recognized previously*. It will be recalled that the *local proton affinity* (PA) of the alkyl substituted ring positions is a governing factor of the fragmentation of alkylbenzenes.[6]

A conclusive proof for the γ → *ortho* H migration and the existence of transient $\mathbf{1a}^{+\cdot}$ type ions[4] is the particularly selective H exchange found in 1,3-diphenylpropane[7b] and 2-benzylindan ions,[8] the donor γ-C—H bonds of which are more reactive than in simple *n*- or *iso*-alkylbenzene ions. The ease of the H migration and hence of the formation of the distonic ion intermediate corresponding to $\mathbf{1a}^{+\cdot}$ is further enhanced by increasing the *local* PA (or hydrogen atom affinity, HA) of the acceptor positions by electron-donor substituents at the ring(s).[3,6-8]

In line with these arguments, the 70 eV mass spectra (Table 1) of 2,6-dimethyl and 2,4,6-trimethyl substituted 1,3-diphenylpropanes **2** and **3** and 2-benzylindans **4** and **5** exhibit significant peaks corresponding to the McLafferty reaction.



2 (X = H)
3 (X = CH_3)



4 (X = H)
5 (X = CH_3)

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Kingston *et al.*[2] observed that the McLafferty reaction is significantly suppressed only in those alkylbenzenes which bear a methyl group in the *para* position of the ring, in addition to the 2,6-dimethyl substitution. Thus, an apparent paradox emerged[2] in that a *para*-methyl group suppresses the McLafferty reaction whereas two *ortho*-methyl groups do not. In contrast, the two mesitylene derivatives presented here show remarkably high (**5**) and moderate (**3**) relative abundances of the corresponding ion (m/z 134) in the 70 eV spectrum. This effect is attributed to the particular labile γ-C—H bond in the dinuclear alkylbenzenes.[6] In the case of **5**, this factor is amplified by the (entropically) favourable steric features of the indan skeleton. The suppression of the McLafferty reaction by the *para*-methyl group in *n*- and *iso*-alkylbenzenes[2,5b] is attributed to the competing effect of the 'simple' benzylic cleavage, which is favoured by the presence of this additional substituent. Accordingly, the McLafferty peaks are less pronounced in the 70 eV spectra of **3** and **5** than in those of **2** and **4**, respectively. In the absence of the *para*-methyl group the McLafferty reaction gives rise to a notable peak (**2**) and to the base peak (**4**). In general, however, the occurrence of the McLafferty reaction in the 70 eV mass spectra of **2-5** is attributed to the particular stability of the corresponding γ-distonic[4] ions $\mathbf{2a}^{+\cdot}$-$\mathbf{5a}^{+\cdot}$ (Scheme 2).

Table 1. Selected Peaks in the 70 eV Mass Spectra of 1-(2,6-Dimethylphenyl)-3-phenylpropane (2), 1-(2,4,6-Trimethylphenyl)-3-phenylpropane (3), 2-(2,6-Dimethylbenzyl)-indan (4), and 2-(2,4,6-Trimethylbenzyl)-indan (5). [a]

2	$M^{+\cdot}$: m/z 224 (50.3 %B), 133 (38.8), <u>120</u> (48.8), 119 (100), 118* (48.4), 117 (17.0), 105 (40.4), 92 (11.1), 91 (35.4).
3	$M^{+\cdot}$: m/z 238 (62.2 %B), 147 (28.3), <u>134</u> (36.9), 133 (100), 120† (38.3), 119 (20.3), 118* (52.9), 105 (21.8), 92 (6.9), 91 (31.5).
4	$M^{+\cdot}$: m/z 236 (48.0 %B), 130* (48.2), <u>120</u> (100), 119 (62.3), 118 (11.8), 117 (79.0), 116 (30.0), 115 (36.1), 105 (36.9), 91 (28.4).
5	$M^{+\cdot}$: m/z 250 (50.0 %B), <u>134</u> (64.7), 133 (100), 130* (88.2), 120† (8.3), 119 (27.4), 118 (8.7), 117 (34.3), 116 (19.4), 115 (25.2), 105 (12.9), 91 (19.6).

[a] Underlined m/z values correspond to the major McLafferty reaction of each compound (γ → ortho H rearrangement); starred (*) and daggered (†) values indicate peaks corresponding to processes which are induced by γ → ipso H rearrangement (see Scheme 2). The relative abundances are not corrected for naturally occurring ^{13}C contributions.

Table 2. MIKE Spectra of the Molecular Ions $2^{+\cdot}$ - $5^{+\cdot}$ [a]

2	m/z 133 (5.3 %Σ), <u>120</u> (9.5), 118* (85.3).
3	m/z 223 (0.7 %Σ), 147 (6.0), <u>134</u> (3.5), 133 (1.8), 130 (1.5) 120† (19.0), 118* (67.6).
4	m/z 130* (77.7 %Σ), <u>120</u> (14.1), 117 (1.5), 116 (6.8).
5	m/z <u>134</u> (5.2 %Σ), 130* (93.2), 121 (0.7), 120† (0.3), 116 (0.6).

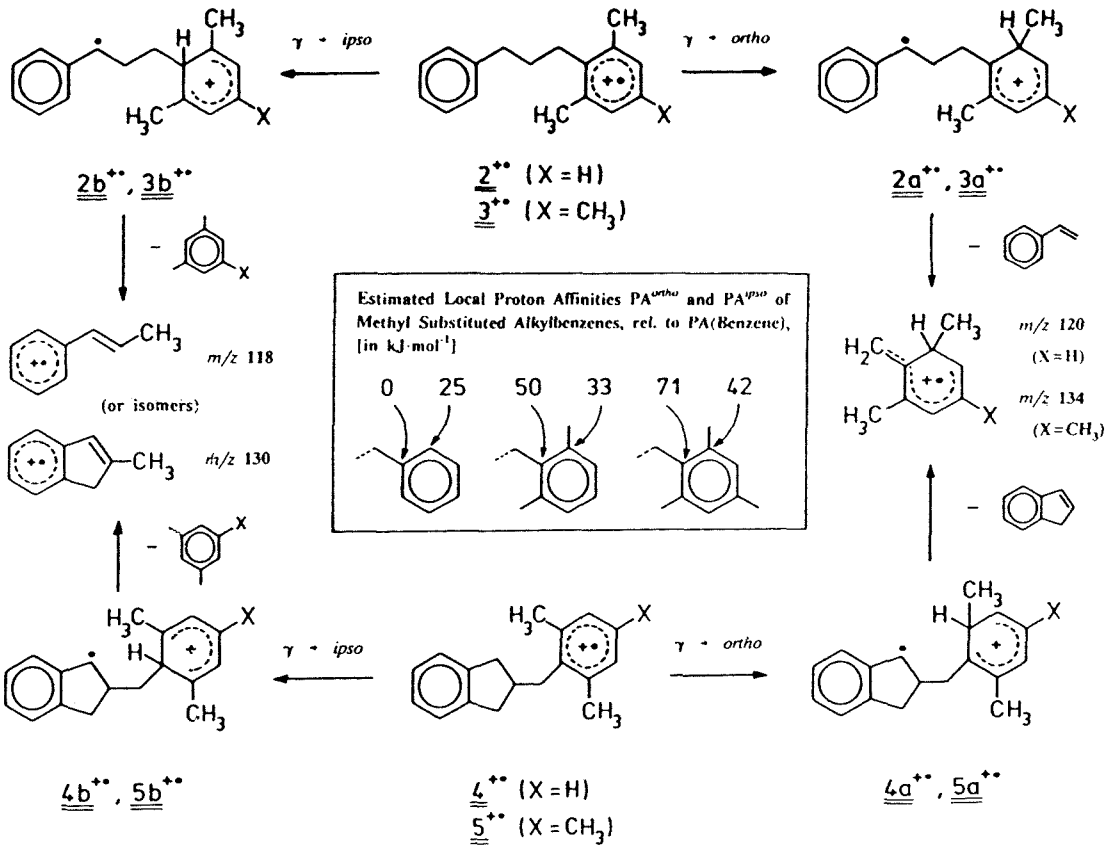
[a] See footnote to Table 1.

In addition to the McLafferty reaction, elimination of the methyl substituted arene moiety is a prominent fragmentation channel (Table 1). For the *metastable* ions $\mathbf{2}^{+\cdot}$-$\mathbf{5}^{+\cdot}$, this reaction is the major fragmentation pathway (Table 2), whereas the McLafferty reaction is a minor process. We propose that the arene elimination is initiated by γ → *ipso* (1,4) H migration to form the δ-distonic[4] ions $\mathbf{2b}^{+\cdot}$-$\mathbf{5b}^{+\cdot}$, followed by further hydrogen (or skeletal) rearrangement(s) to give a stable fragment ion (m/z 118 and m/z 130, respectively). The mechanisms of the two competing elimination reactions are depicted in Scheme 2.

It is evident that both of these major fragmentation reactions of ions $\mathbf{2}^{+\cdot}$-$\mathbf{5}^{+\cdot}$ involve an initial H migration to an alkyl substituted ring position, either to an *ortho* or to the *ipso* position of the methylarene ring. The relative rates of the two elimination channels correlate directly with the local PA values of the *ortho* and *ipso* positions

and, hence, with the relative stability of the γ- and δ-distonic ions **2a**$^{+\cdot}$-**5a**$^{+\cdot}$ and **2b**$^{+\cdot}$-**5b**$^{+\cdot}$, respectively. Local PA values [relative to PA(benzene)], estimated from the data published by Hehre *et al.*[9], are given in the insert of Scheme 2. For unsubstituted benzyl groups, the McLafferty reaction is favoured both in the 70 eV and in the MIKE spectra,[7,8] because of the greater PA (≃ 6 kcal·mol^{-1}) of the 'unblocked' *ortho* positions. 2,6-Dimethyl substitution in **2** and **4** leads to further, slight increase of PA^{ortho}, but enhances PA^{ipso} by ≃ 12 kcal·mol^{-1}. 2,4,6-Trimethyl substitution in **3** and **5** further increases the PA of the two proton acceptor sites, in particular of the *ipso* position. Similar directory effects of the local proton affinities at alkyl substituted arenes were found previously, especially with 2-benzylindans[8,10] and 2-benzyl-1-indanols.[11]

Scheme 2



Compounds **2-5** were synthesized in conventional manner[7,8,12;2] and checked by ^{1}H-NMR spectrometry for isomeric identity and purity. The 70 eV mass spectra and MIKE spectra were measured by using a Finnigan MAT 311 A and a Vacuum Generators ZAB-2F instrument (cooled direct inlet systems, source temperature ≃ 200 °C). More detailed investigations on the role of distonic ions in the fragmentation of alkylbenzenes will be reported from this laboratory.

Yours

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6 As argued previously (loc. cit. 7a), the stability of $\mathbf{1a}^{+\cdot}$ relative to $\mathbf{1}^{+\cdot}$ is given by $\Delta H_f(\mathbf{1a}^{+\cdot}) - \Delta H_f(\mathbf{1}^{+\cdot}) = D(\gamma\text{-C—H}) + IE(H^{\cdot}) - PA^{ortho}(\text{Arene}) - IE(\text{Arene})$.
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