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THE M-CH_3 FRAGMENTATION IN THE MASS SPECTRA OF SUBSTITUTED ETHYL AND t-BUTYLBENZENES

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The structure of the $C_7H_7^+$ ion formed by electron impact has been the focus of considerable interest which has generated evidence for benzyl ions in the mass spectra of fluoro n-alkylbenzenes (1), nitrobenzyl compounds (2), benzyl phenyl ethers (2,3,4), bibenzyls (5) and n-butylbenzenes (6). The use of substituents on the aromatic ring has been particularly helpful in determining possible structural reorganization. Thus, from his wide range electron energy technique, Brown (3,7) has presented strong evidence consistent with ring expansion in "the" [M-1] fragmentation of substituted toluenes when the substituents are CH_3, F, Cl, Br and CN (tropylium-like activated complexes), and retention of substituent orientation for OCH_3 (benzylic transition states). For the [M-CH_3] fragmentation of substituted ethylbenzenes, Brown has shown that for NH_2 and OCH_3 substituents benzyl ions obtain; whereas, for OH, CH_3, F, Cl, Br and CF_3 rearranged structures are visualized (7). We have investigated the [M-CH_3] fragmentation of substituted ethylbenzenes and t-butylbenzenes and wish to present appearance potential data which bear on the interpretation of ion structures involved.

The appearance potential differences method and assumptions[1] of Tait, Shannon and Harrison (8) were used to determine the structures of ions formed at threshold from substituted ethyl- and t-butylbenzenes. Briefly, this difference method utilizes energy cycles for meta- and para-$XC_6H_4CR_2CH_3$ (R = H, or R = CH_3) leading to the equation below in which the differences in appearance potentials for the $XC_7H_4R_2^+$ isomers is approximately equal to the difference in ionization potentials of the same isomeric benzyl radicals ($XC_7H_4R_2\cdot$). Thus, if the $XC_7H_4R_2^+$

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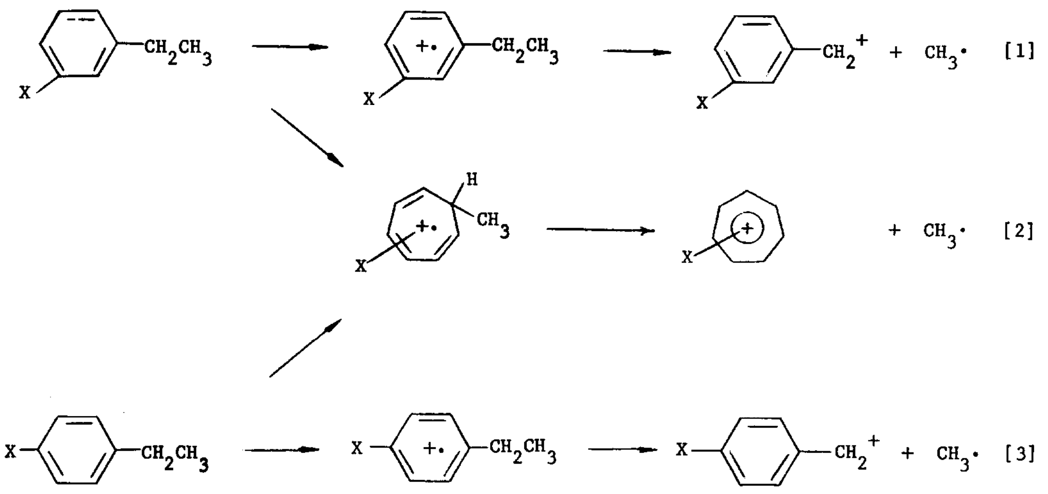
[1] These assumptions include, reasonably, that the homolytic bond dissociation energies (leading to benzyl radicals for the neutral m- and p-isomers are approximately equal, that the heats of formation of those neutral isomers are also equal, and that the excess energies of ionization are also equal.

ions formed at threshold have *benzyl* structures with ring orientation of the substituent maintained, the difference in appearance potentials between *meta* and *para* isomers is expected to

$$A\,(\underline{m}\text{-}XC_7H_4R_2^{\;+}) \;-\; A\,(\underline{p}\text{-}XC_7H_4R_2^{\;+}) \;\approx\; I\,(\underline{m}\text{-}XC_6H_4CR_2\cdot) \;-\; I\,(\underline{p}\text{-}XC_6H_4CR_2\cdot)$$

approximate the experimentally determined difference between the ionization potentials of the corresponding benzyl radicals (8,9). If the difference in appearance potentials is found to be zero and the predicted value is non-zero, we assume that rearrangement has occurred at threshold to structures (symmetrical tropylium) in which the original substituent orientation is no longer significant.

The data of Table I implicate benzyl ions at the threshold and therefore pathways [1] and [3] for the loss of CH_3 from the substituted ethylbenzenes when X = NH_2, OCH_3, and CN.[2] However, when X = CH_3 and OH, the near zero A(meta) - A(para) values suggest rearranged structures (pathway [2]), which were also proposed in earlier work (7,8). In addition, our data suggest that the fluorine substituent belongs with NH_2, OCH_3 and CN, which is not completely in discord with the suggestion of Brown (7) who determined that rearranged structures were involved *to some extent* for the fluoro substituent. It is quite possible that a mixed mechanism (some benzyl,



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[2] An apparent anomaly exists for the NH_2 substituent: the large A(meta) - A(para) value exceeds the *calculated* value and is also at variance with Harrison's value of 0.2 ± 0.2 eV (cited in a footnote as a private communication in reference 7, p 1323). However, our calculated value is derived from a σ not a σ^+ correlation. Since the former correlation fits p-OCH_3 somewhat poorly (reference 9) with a resultant *lower* A(meta) - A(para) value, the *calculated* value for NH_2 might be viewed as low. In spite of this, we can offer no explanation for discrepancy between our experimental value and Harrison. It should be noted, however, that our value is consistent with Brown's (reference 7) wide range kinetic energy data for NH_2, *viz.* a non-zero value is anticipated.

some tropylium) is involved here.

We felt that rearrangement to tropylium structures from substituted *t*-butylbenzenes would be less likely to occur than from ethylbenzenes inasmuch as greater structural reorganization is required in the former. However, as yet, there are no data available for the ionization potentials of the substituted cumyl radicals; therefore, the appearance potential differences can be compared roughly only to the benzyl radical difference data (8,9). It is important to note that for all substituents, non-zero values are found for A(meta) - A(para), except NO_2 for which interpolated benzyl radical data predict a near zero value (see Table I).[3] In fact, in most examples, the observed difference in appearance potentials is closely approximated by the ionization potential differences for the benzyl radicals. The data of Table I suggest

TABLE I

Appearance Potentials Differences[a] for $XC_7H_6^+$ and $XC_9H_{10}^+$ Ions from *meta* and *para* Substituted $XC_6H_4CH_2CH_3$ and $XC_6H_4C(CH_3)_3$

X	A(meta) - A(para), ± 0.1 eV $XC_6H_4CH_2CH_3$	A(meta) - A(para), ± 0.1 eV $XC_6H_4C(CH_3)_3$	I(meta) - I(para)[b] $XC_6H_4CH_2\cdot$
NH_2	1.10[c]	0.72	0.65
OCH_3	0.81	0.92	1.00
OH	-0.03	0.49	0.64
F	0.27	0.19	0.41 (0.40)[e]
CH_3	0.08	0.43	0.30 (0.19)[e]
CN	0.42	0.82[c]	-0.18 (0.22)[e]
NO_2	[d]	0.07	-0.08

[a] Measurements were determined by the method of Warren using an unsubstituted alkylbenzene as internal reference and are an average of several determinations. J. M. Warren, *Nature*, **165**, 810 (1950).

[b] Values are determined from σ or σ^+ correlations (see reference 9). The experimentally determined values are given in parentheses.

[c] The error in these measurements is ± 0.2 eV.

[d] The [M-15] ion intensities were too weak to obtain reproducible data.

[e] Values in parentheses are the experimentally determined differences (see reference 9).

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[3] The approximately zero value for A(meta) - A(para) also allows for the possibility of rearranged (tropylium) ion parent ions in the [$M-CH_3$] fragmentation. However, in another system, nitrobenzyl phenyl ethers, evidence is marshalled for benzyl and not rearranged ions. See R. H. Shapiro and J. W. Serum, *Org. Mass Spectrom.*, **2**, 533 (1969).

non-rearranged benzyl (cumyl) ions for all the substituted t-butylbenzenes, and this finding is in agreement with wide range electron measurements (10). However, if the molecular ions do undergo rearrangement to substituted trimethylcycloheptatrienes, the appearance potential difference may be non-zero unless facile methyl and substituent scrambling occurs, viz., the meta and para isomers may rearrange to structurally different trimethylcycloheptatriene molecular ions and thus lead to non-zero values for A(meta) - A (para).

Studies on the [M-CH_3] fragmentation of an intermediate series, substituted isopropylbenzenes, are in progress and will be reported in the full paper on this work.

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