THE M-43 FRAGMENTATION IN THE MASS SPECTRA OF SUBSTITUTED

N-BUTYLBENZENES

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The intervention of tropylium ions in the electron impact induced fragmentations of aroma-

tic compounds has been recognized in a number of instances, of which alkylbenzenes and their

derivatives have provided the majority of examples (1). We wish to report some preliminary re-

sults which have bearing on the structures of the ions involved in butylbenzene fragmentation.

Substituted n-butylbenzenes decompose, upon electron impact, by two major routes: 1) loss

of 42 amu (a) via McLafferty rearrangement (1,2), and 2) loss of 43 amu (b) which is interpreted

diagrammatically as benzylic cleavage.[1]

M

(a) → M-42

(b) → M-43

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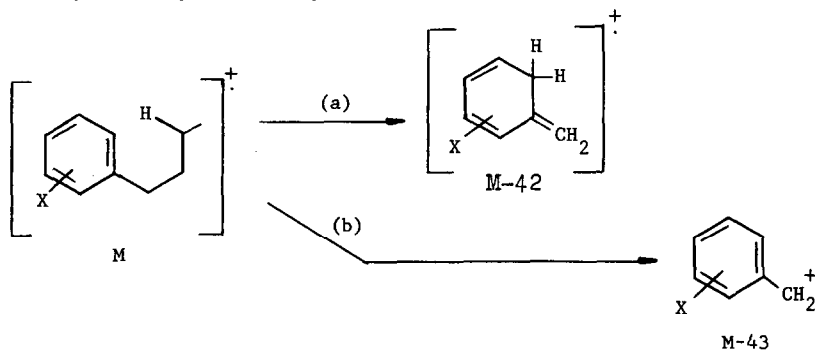
[1]The benzylic cleavage product (M-43) might also arise from M-42, but for this process no
more than 10% of the $C_7H_7^+$ ion are derived from $C_7H_7D^+$ in the mass spectrum of n-butylben-
zene-3-d.   See F. W. McLafferty, p. 337 in reference 1b.

TABLE I

Substituent effects on the abundance of M-43 ions from

$$[X\ C_6H_4CH_2CH_2CH_2CH_3]^{\stackrel{+}{\cdot}} \qquad Z = [X\ C_7H_6]^+/[X\ C_6H_4CH_2CH_2CH_2CH_3]^{\stackrel{+}{\cdot}}$$

X	Z/Z_o 12 eV para	meta	Z/Z_o 70 eV para	meta
H	1.00		1.00	
NH_2	2.70	0.01	1.20	0.27
OH	2.52	0.05	1.08	0.33
OCH_3	1.92	0.03	1.08	0.21
F	0.77[b]	0.06	1.08	0.43
I	0.77	0.33	0.33	0.16[a]
CH_3	1.08	0.16	0.97	0.56
$COOCH_3$	0.11	0.12	0.35[a]	0.43[a]
COOH	0.12	0.15	0.43[a]	0.56[a]
CN	0.03	0.03	0.43[a]	0.31[a]
NO_2	0.02	0.05	0.07[a]	0.15[a]

[a] Peaks at m/e 43 are observed in the mass spectrum.

[b] The value at 14 eV is 1.77.

However, in light of previous evidence for symmetrical (tropylium) structures at the appearance potential threshold of $XC_7H_6^+$ from labelled toluene and substituted toluene deriva- tives (1), similar species might be involved in the M-43 decomposition of butylbenzenes. Fur- thermore, if complete substituent orientation in the ring is lost at the appearance potential threshold, the substituent effects on the fragmentations (3) should be identical for meta and para isomers with the same substituent.[2]

[2] For methylethylbenzene, the mechanism proposed for tropylium ion formation by electron impact involves complete loss of positional identity of the methyl substituent (F. Meyer and A. G. Harrison, J. Am. Chem. Soc., 86, 4757 (1964)). However, for the formation of of tropylium ions, there are, in principle, routes which do not involve complete loss of positional identity. In such instances, a relatively small substituent effect on C-C cleavage should be anticipated.

Our data (Table I) show significant differences in the Z/Z_o ratios between <u>meta</u> and <u>para</u> isomers of the same electron-donating substituent (-X). This difference, coupled with a similar difference in the behavior of their ratios in changing from 70 to 12 eV ionizing voltage, suggests that such isomers produce M-43 ions of differing appearance potentials (4) and structures at the threshold (5,6). Accordingly, -X substituents in the <u>para</u> and/or <u>meta</u> position would have their positional identity maintained, and the corresponding parent ions which lose 43 amu would have a benzyl and not a tropylium structure.[4]

Compounds bearing electron withdrawing substituents (+X) show a different behavior. For NO_2, CN, COOH, $COOCH_3$ derivatives in the <u>meta-para</u> pairs, differences in the rates of loss of 43 amu are minor, and the trend in changing from 70 to 12 eV is to decrease the Z/Z_o ratios. This trend, as well as the low value of the ratio, is found in almost all <u>meta</u> isomers. Since both <u>meta</u> and <u>para</u> isomers of +X substituted <u>n</u>-butylbenzenes show very similar Z/Z_o values, as would be expected in a loss of positional influence of the substituent, it might be concluded that those ions have undergone a structural rearrangement leading to loss of substituent orientation in the ring. However, inasmuch as the differences in ionization potentials of the derived benzyl radicals appear to be not nearly as pronounced with +X as with -X substituents,[4,5] both isomers may possess benzylic structures and show nearly identical Z/Z_o ratios.

The data indicate that both electron withdrawing and donating groups in the <u>meta</u> position cause a decrease in the rates of fragmentation relative to <u>n</u>-butylbenzene; whereas, an increase of the rate is observed only in the case of electron donating groups in the <u>para</u> position. Furthermore, it may be shown that there is a general lack of correlation with the Hammett equation (7) in the effect of substituents on the abundance of the M-43 ions. Plots

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[4]Unrearranged ions appear to dominate the M-CH_3 fragmentation in substituted anisoles (J.M.S. Tait, T. W. Shannon, and A. G. Harrison, <u>J. Am. Chem. Soc.</u>, <u>84</u>, 4 (1962)). However, these authors have also shown that rearranged ions are prevalent in several substituted toluenes, ethyl benzenes and benzyl halides, with the notable exception of methoxy and methyl mercaptobenzyl chlorides. See also F. Meyer and A. G. Harrison, <u>Can. J. Chem.</u>, <u>42</u>, 1762 (1964).

[5]The difference in ionization potentials between <u>m</u> and p-cyanobenzyl radicals is 0.22 ± 0.2 eV. If it is assumed that the C-Br bond dissociation energy differences found in substituted benzyl bromides apply also to the corresponding C-C dissociation in alkylbenzenes, the dissociation energy difference between <u>m</u> and p-cyanobutylbenzene would be about 0.03 eV. See M. Swarc, C. H. Leight, and A. H. Sehon, <u>J. Chem. Phys.</u>, <u>19</u>, 657 (1951).

of log Z/Z_o vs σ or σ^+ are reminiscent of those obtained with substituted benzophenones (8),

and the lack of correlation could be similarly attributable, in part, to further decomposi-

tion of M-43 ions, as well as to possible loss of substituent orientation in the ring for

the molecular fragment ions in some instances. Only a partial improvement in the relationship

is observed at low ionizing voltages.

<div align="center">References</div>

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    Compounds, Holden-Day, Inc., San Francisco, Calif. (1967) pp 73-85 and references
    cited therein; (b) H. M. Grubb and S. Meyerson in Mass Spectrometry of Organic Ions,
    F. W. McLafferty, ed., Academic Press, New York, N.Y. (1963) Chapter 10.

2. R. Nicoletti and D. A. Lightner, J. Am. Chem. Soc., 90, 2997 (1968).

3. For a review of substituent effects in mass spectrometry, see: M. M. Bursey, Org.
    Mass Spectrom., 1, 31 (1968).

4. Determinations of appearance potentials in progress.

5. If the neutral fragments (C_3H_7) from each pair of isomers are formed in the same
    energy state (D. P. Stevenson, Disc. Faraday Soc., no. 10, 35 (1951)) and if the
    homolytic bond dissociation energies in the un-ionized molecules are independent
    of the position of the substituent (T. L. Cottrell, The Strengths of Chemical
    Bonds, 2nd Ed., Buttersworth, London (1958)), the observed behavior correlates
    directly with the different ionization potentials of the meta and para benzyl
    radicals (A. G. Harrison, P. Kebarle, and F. P. Lossing, J. Am. Chem. Soc., 83,
    777 (1961)).

6. For a consideration of fragment ions above the appearance potential threshold,
    see: P. Brown, J. Am. Chem. Soc., 90, 2694 (1968).

7. L. P. Hammett, Physical Organic Chemistry, McGraw-Hill Book Co., Inc., New York,
    N.Y. (1940), Chapter 7.

8. M. M. Bursey and F. W. McLafferty, J. Am. Chem. Soc., 89, 1 (1967).