Substituent Effects on the McLafferty Rearrangement of Methyl 4-Phenylbutyrates

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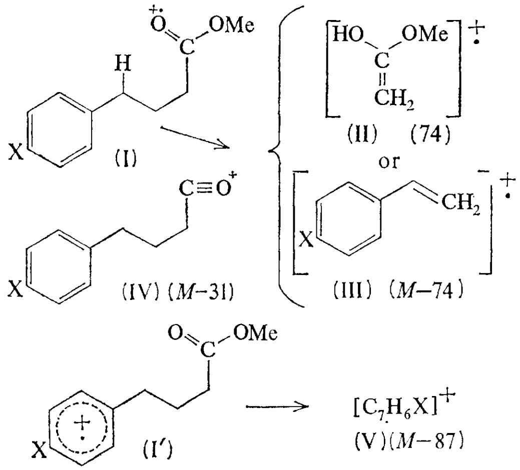
THE importance of substituent effects in determining the factors governing mass spectrometric rearrangements has been shown by some recent rearrangements of carbonates[1] and butyrophenones.[2] We now report that the McLafferty rearrangement of methyl 4-phenylbutyrates (I) does not obey the standard equation ($\log Z/Z_0 = \rho\sigma$)[3] for mass spectrometric reactions, but a modified form. Substituted methyl 4-phenylbutyrates (I) fragment at 15 ev to yield the four ions (II)–(V) as the only abundant ions (besides the molecular ion) in all cases examined, except when $X = NO_2$ or CN; similar fragmentations were recently reported for 5-phenylpentan-2-one.[4] The relative intensities of certain of these ions are shown in the Table.

The observed dramatic substituent effect on the intensity of ion (II) (column two) could be explained on the basis of a substituent effect on the energy of the transition state leading from (I) to (II). However, the substituent-effect observed for the formation of ion (IV) (column three) cannot be explained on this basis since the chain of three saturated carbon atoms between the reaction-site and the phenyl ring would minimize any interaction between the two. The most reasonable alternative explanation is that substituents alter the relative proportions of molecular ions existing as (I) [capable of decomposing to (II) or (III)] and (I′) [not capable of decomposing to (II) or (III)].



We conclude therefore that the observed effects on the rates of formation of ions (II) and (III) are due to a combination of at least two factors: (i) a substituent effect on the energy of the transition state leading to each ion, (ii) a substituent effect on the fraction of molecular ions capable of undergoing rearrangement. These two effects may be separated by using the fact that the molecular ions which decompose to ions (II) and (III) are of the same type as those which decompose to ion (IV). It may be shown that the quantities $Z_{(II)} = [74]^+/[M\text{-}31]^+$ and $Z_{(III)} = [M\text{-}74]^+/[M\text{-}31]^+$ are thus measures of the rates of formation of ions (II) and (III) from ion (I).

Electron-withdrawing substituents have little, if any, effect on the rate of the McLafferty rearrangement to ion (II). This result is best interpreted in terms of transfer of hydrogen as a hydrogen atom;[5] a similar lack of substituent-effect has been noted in other hydrogen-abstraction reactions.[6] The formation of ion (III), however, is retarded by electron-withdrawing substituents

TABLE

Relative intensities of ions (I)–(IV) *in the mass spectra of* p-X-$C_6H_4 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO_2Me$[a]

X	$Z = \frac{[74]^+}{[M]^+}$	$\frac{[M-31]^+}{[M]^+}$	$Z_{(II)} = \frac{[74]^+}{[M-31]^+}$	$Z_{(III)} = \frac{[M-74]^+}{[M-31]^+}$
NO_2	3·9	0·87	4·5	0·64
CN	3·0	0·79	3·8	0·78
Cl	2·7	0·65	4·2	2·8
F	1·5	0·35	4·2	2·9
H	1·1	0·29	3·7	3·2
Ph	0·13	0·16	0·8	8·0
MeO	0·02	0·15	0·13	14·3
NH_2	0·0006	0·008	0·08	6·8

[a] Measured on a Hitachi RMU-6D mass spectrometer.

and accelerated by most electron-donating substituents. This suggests that stabilization of ion (III) is an important driving-force in the rearrangement. The values of log $Z_{(III)}/Z_{(III)0}$ for all substituents except *p*-amino correlate reasonably well with Brown's σ^+ values[7] ($\rho = 0{\cdot}90$, correlation coefficient $= 0{\cdot}97$).

The reasons for the decrease in the values of $Z_{(II)}$ for electron-donating substituents and of $Z_{(III)}$ for the *p*-amino-substituent are under investigation.

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