Migrations to Carbonium-ion Centres Generated upon Electron Impact

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THE occurrence in mass spectra of ions formed by the migration of groups other than hydrogen has received a great deal of attention during the last few years.[1] We report the occurrence of a novel type of migration which frequently leads to very abundant ions associated with combinations of carbon and oxygen atoms not present in the original molecule.

In general, the migration occurs to a carbonium-ion centre which has been generated by electron impact. For example, the base peak in the spectrum (Figure 1) of β-bromo-β-phenylpropionic acid (I) is found at *m/e* 107 ($C_7H_7O^+$),[2] which is shown by an appropriate metastable peak to arise from the $M-$Br ion [(a), *m/e* 149] by the loss of keten. The hydroxyl migration which must occur in this process is depicted by [(a) → (b)], but a less likely 1,5-migration [(c) → (d)] cannot be ruled out on the evidence at present available. Ring expansion of the ions [(a), (b), (c), and (d)] to the corresponding tropylium ions[3] is of course not excluded. The spectrum of the methyl ester of (I) shows a completely analogous rearrangement giving

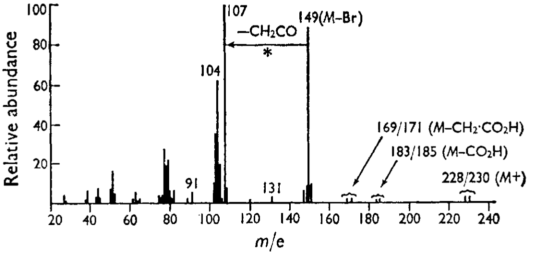
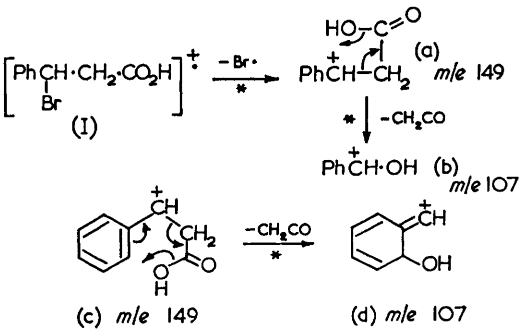
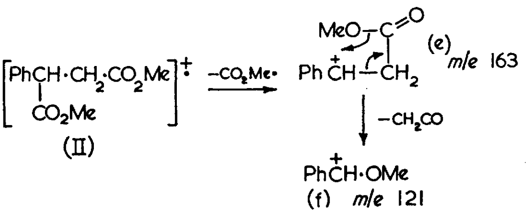


FIGURE 1



rise to the ion $C_8H_9O^+$ (*m/e* 121, 12% of base peak).

To indicate the general scope of this kind of reaction, the mass spectrum of dimethyl phenylsuccinate (II) may be cited. In this case the base peak corresponds to a methoxytropylium ion, or substituted benzyl cation (f), which is formed by the elimination of keten from the $M-CO_2Me$ species at *m/e* 163 (e).



The case for rearrangement of groups to carbonium-ion centres is supported by the observation of hydroxyl and alkoxyl migrations in compounds in which the carbonium ion may be generated immediately adjacent to an acid or ester function, respectively. Thus the $M-Br$ ion from α-bromophenylacetic acid (III) decomposes by loss of carbon monoxide as indicated in Figure 2. The necessary hydroxyl migration may be depicted as (g → b).

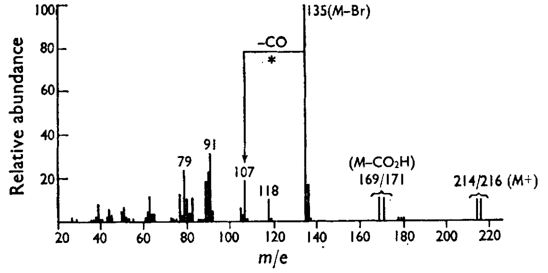
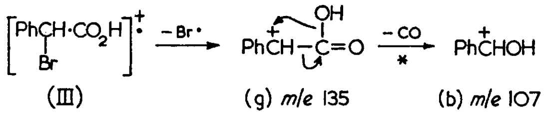
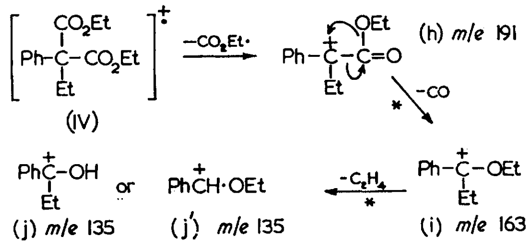


FIGURE 2



Again this type of reaction is quite general, and the previous observation[4] that the base peak in the spectrum of diethyl phenylethylmalonate (IV) is due to a $C_9H_{11}O^+$ ion is now brought within the scope of a general reaction [see (IV) → (h) → (i) → (j) or (j′)].



Other examples of the formation of major fragment ions which can be rationalized in terms of alkoxyl, hydroxyl, or phenyl migrations to carbonium-ion centres *via* 3-, 4-, and 5-ring transition states have been observed and will be reported in a full Paper.

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[1] For the summary of such reactions see P. Brown and C. Djerassi, *Angew. Chem.*, in the press.

[2] The compositions of all ions discussed in this paper have been established by exact mass measurements.

[3] For appropriate references to tropylium-ion formation, see H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions", ed. F. W. McLafferty, Academic Press, New York, 1963, ch. 10.

[4] J. H. Bowie, D. H. Williams, S.-O. Lawesson, and G. Schroll, *J. Org. Chem.*, 1966, **31**, 1792.