Methoxy-group Migrations in the Mass Spectra of Aliphatic Dimethyl Esters

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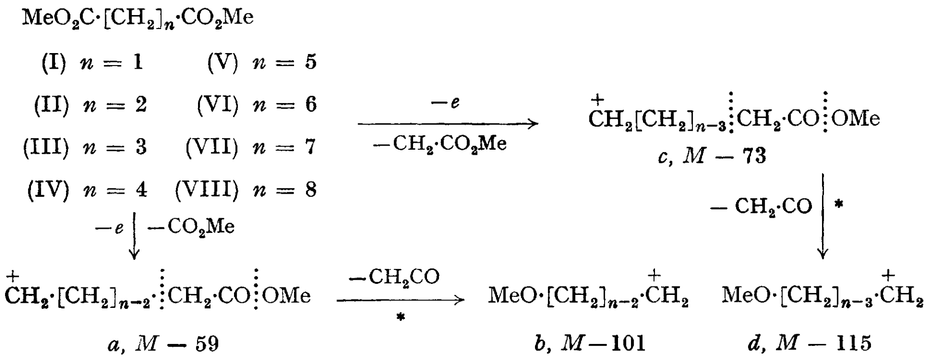
ALTHOUGH reactions involving the migration of groups other than hydrogen upon electron impact are the exception rather than the rule in monofunctional aliphatic compounds, there is increasing evidence that bifunctional molecules frequently rearrange in this way (for representative examples see methoxy- and hydroxy-cyclohexanones,[1] cyclohexanediols,[2] and bromo-esters[3]).

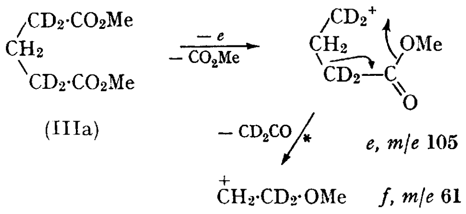
Since alkoxy-group migrations to carbonium-ion centres generated upon electron impact have been demonstrated,[3] it seemed possible that simple aliphatic dimethyl esters might undergo analogous rearrangements. Although the mass spectra of such simple dimethyl esters have been previously reported[4,5] and discussed,[5,6] such rearrangements would have escaped detection since a high-resolution spectrometer was not employed. The mass spectra of the simplest dimethyl esters (I—VIII) have now been determined using a double-focusing AEI MS9 mass spectrometer and methoxy-group migration shown to be a common occurrence in these cases. The methoxy-group migrations generate ions which, *a priori*, would appear characteristic of saturated aliphatic ethers and could therefore lead to confusion in the structure elucidation of natural products by mass spectrometry.

Two generally important reactions involving methoxy-group migrations occur. First, $M-CO_2Me$ ions decompose by loss of keten as indicated by the sequence $a \rightarrow b$. Second, $M-CH_2 \cdot CO_2Me$ ions also decompose by loss of keten (see $c \rightarrow d$). Both these rearrangement reactions are of course precluded when $n = 1$.

These reactions are defined by a combination of



high-resolution measurements, deuterium labelling, and metastable peaks. For example, the $M-CO_2Me$ (m/e 101) ion from dimethyl glutarate (III) undergoes the transition m/e 101 → m/e 59 as established by the presence of an appropriate metastable peak. Since the m/e 59 base peak is a doublet [$C_2H_3O_2$ (55%) and C_3H_7O (45%)], expulsion of C_3H_6 or C_2H_2O from m/e 101 can be entertained. The spectrum of dimethyl 2,2,4,4-[$^2H_4$]glutarate (IIIa) contains a metastable peak for the transition m/e 105 (e) to m/e 61 (f, or possibly an isomeric structure) by loss of [$^2H_2$]keten, thus establishing the sequence of steps which produces the $C_3H_7O^+$ rearrangement ion from dimethyl glutarate (III) itself.



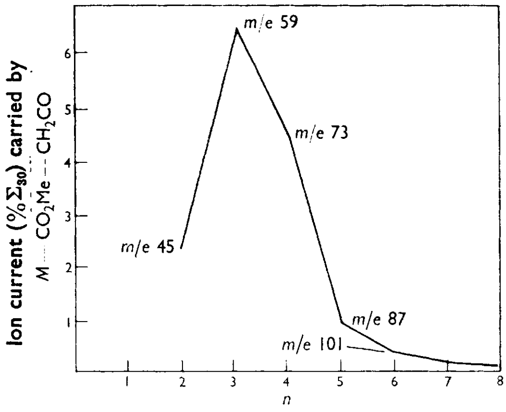


FIGURE 1

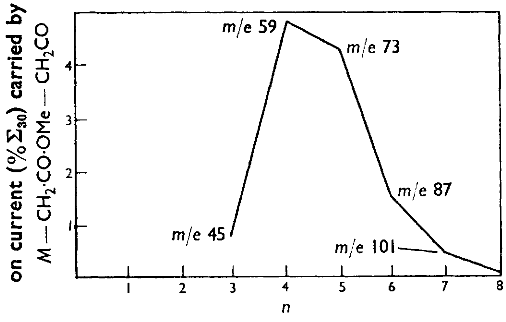
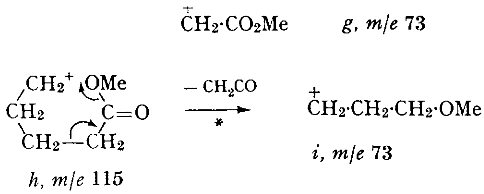


FIGURE 2



Figures 1 and 2 show how the abundances (in terms of percentage total ion current, Σ_{30}) of the rearrangement ions formed from the $M-CO_2Me$ and $M-CH_2{\cdot}CO_2Me$ species by further loss of keten vary with chain-length. It is evident that the transitions m/e 101 → 59 and m/e 115 → 73 (*via* loss of keten) give rise to the most prevalent rearrangement ions and these formally require 5- (*e.g.*, $e \rightarrow f$) and 6-membered transition states for the methoxy-group migration. The reactions rapidly become less prevalent with increasing chain-length. It is emphasised that since a carbonium ion adjacent to a carbonyl group is unfavourable,[7] the m/e 73 ions from dimethyl adipate ($n = 4$) and dimethyl pimelate ($n = 5$) (48% and 25% of the base peak intensities, respectively) are not associated to any significant extent with *g*, but correspond completely to $C_4H_9O^+$ which is generated by keten elimination from *m/e* 115, probably as depicted by the sequence *h* → *i*.

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