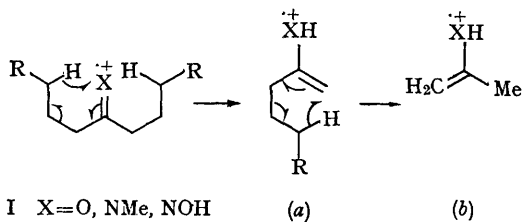


Suppression of McLafferty Rearrangements in the Mass-spectrometric Fragmentation of Even-electron Systems

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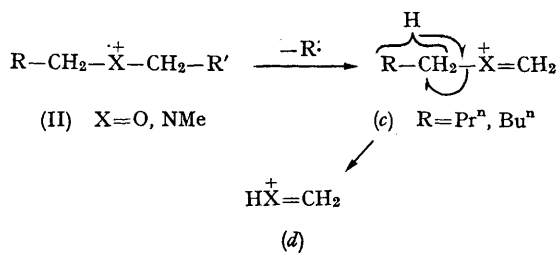
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THE most widely studied hydrogen rearrangement in mass spectrometry is the McLafferty rearrangement of carbonyl compounds.¹ Specific rearrangement of a γ -hydrogen (I) \rightarrow (a) has been demonstrated by deuterium labelling² and this process can occur twice (a) \rightarrow (b) in suitably substituted ketones. An identical site-specific single and double McLafferty rearrangement has been demonstrated recently in the corresponding Schiff bases³ (I, X = NMe) and oximes⁴ (I, X = NOH).



On the other hand, isotope labelling experiments⁵ have shown that the hydrogen rearrangement (c) \rightarrow (d) of the α -fission products (c) of appropriately substituted ethers or amines (II) occurs

from every carbon atom of the alkyl chain and that no significant McLafferty rearrangement is encountered.



The question has been raised⁵ whether this difference in behaviour may not be due to the fact that an odd-electron (ion-radical) species (I) is involved in the McLafferty rearrangement in contrast to the even-electron fragment (c) of dialkyl ethers (II, X = O) and amines (II, X = NMe). We should now like to report some experiments, which suggest that this difference in the electron-deficient species does indeed play an important role.

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One of the most important electron-impact induced cleavage reactions of α -amino-acid esters⁶ is loss of the alkoxycarbonyl group [process (f) in (III)]. The resulting fragment (f) from a dialkyl- α -amino-acid ester may be considered to be the even-electron counterpart of an azomethine ion

abundance of the "McLafferty ions" (a) and (b) in the corresponding Schiff bases³ (I, R = Me or H; X = NMe) indicate that the intermediacy of odd- (I) as against even- (f) electron ions is of great importance in determining the prevalence of McLafferty rearrangements in mass spectrometry.

TABLE

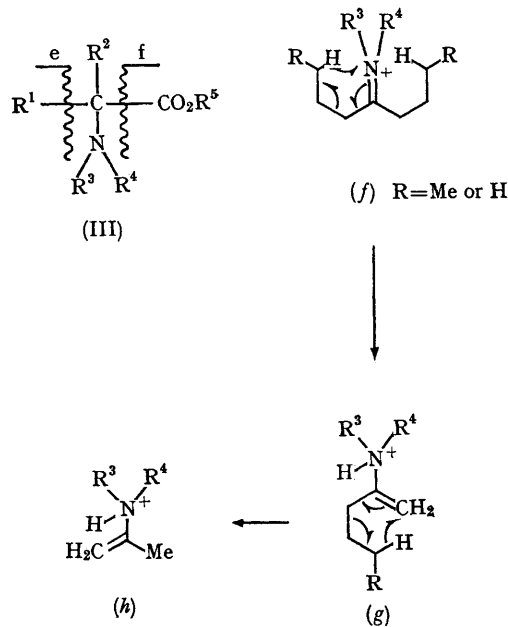
Percent total ionization (Σ_{26}^M) of selected ions in mass spectra of mono- and di-alkyl- α -amino-acid methyl and ethyl esters

Compound (III)	(e) (M - R ¹)	(f) (M - CO ₂ R ⁵)	McLafferty (g) single	Rearrangement (h) (double)
Pr ⁿ CH(NH ₂)CO ₂ Me	2.5	22	<2	—
Pr ⁿ CH(NH ₂)CO ₂ Et	0.5	28	<1.5	—
Bu ⁿ CH(NH ₂)CO ₂ Me	3	21	3	—
Bu ⁿ CH(NH ₂)CO ₂ Et	1.5	28	3	—
γ -[² H ₂]Bu ⁿ CH(NH ₂)CO ₂ Et	2	28	<3	—
Pr ⁿ ₂ C(NH ₂)CO ₂ Et	9	19	0.5	0
Pr ⁿ ₂ C(NHMe)CO ₂ Et	5	30	0.3	0.6
Pr ⁿ ₂ C(NMe ₂)CO ₂ Et	4	34	1	1
Bu ⁿ ₂ C(NH ₂)CO ₂ Me	11	26	<0.1	<0.1
Bu ⁿ ₂ C(NHMe)CO ₂ Me	11	28	0.3	0.5
Bu ⁿ ₂ C(NMe ₂)CO ₂ Me	5	23	0.1	0.1

radical (I, X = NMe), in which the single and double McLafferty rearrangement are known³ to be prevalent. The previously unknown dialkyl (III, R¹ = R² = Prⁿ or Buⁿ) α -amino-acid esters were prepared by Strecker synthesis from dipropyl or dibutyl ketone and, where required (III, R³ = Me or H, R⁴ = Me), were further methylated with methyl iodide and potassium carbonate. Mass spectra of these substances were secured at 70 ev with an Atlas CH-4 (70° heated inlet, 170° ion-source temp.) or CEC 21-103C (250° heated inlet, 250° ion-source temp.) mass spectrometer. The results with these two instruments were essentially identical and are summarized in the Table for the ions (e), (f), (g), and (h) in terms of percent total ionization.

High-resolution mass measurements (AEI MS-9 double focusing mass spectrometer) demonstrated that the "McLafferty ions" (g) and (h) did have the anticipated composition to the extent of 75–85% and the peak shift in the deuterated species showed that all of the transferred hydrogen did originate from the γ -position.

The extremely low intensities of ions (g) and (h) in the dialkyl- α -amino-acid ester spectra (Table) when compared with the 10–100 times greater



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² H. Budzikiewicz, C. Fenselau, and C. Djerassi, *Tetrahedron*, in the press, and references cited therein.

³ M. Fischer and C. Djerassi, *Chem. Ber.*, in the press.

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⁶ K. Biermann, J. Seibl, and F. Gapp, *J. Amer. Chem. Soc.*, 1961, **83**, 3795; C.-O. Andersson, R. Rhyage, S. Stållberg-Stenhagen, and E. Stenhagen, *Arkiv Kemi*, 1961, **19**, 405.