MASS SPECTRA OF DERIVATIVES OF N-ALKYL- AND N-ALKOXYALKYL-IDENEIMINE-2-CARBOXYLIC ACIDS

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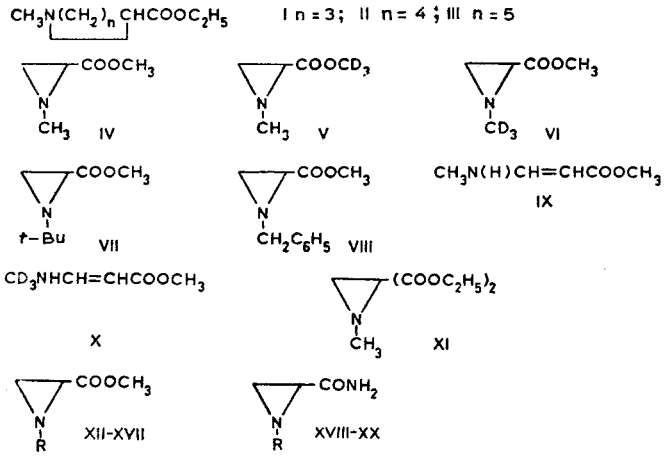
The fragmentation of compounds of the $RN(CH_2)_nCHCOX$ (n = 1-5) and $RNCH_2C(COX)_2$ type, where X = OAlk and NH_2 and R = H, D, OAlk, and Cl, under electron impact was studied. When n = 2-5, the chief fragmentation process is amine fragmentation, and the $(M - COX)^+$ ion peak is the principal peak in the spectra at 30 and 12 eV. The fragmentation of three-membered heterocycles differs radically. The dominant fragmentation for 1-alkylaziridine-2-carboxylic and -2,2-dicarboxylic esters is splitting out of a radical from the ester group. This process is absent when R = H, D, C, and OAlk. Fragmentation with splitting out of the elements of alcohol for the esters and of ammonia for the amines is characteristic in the case of derivatives of 1-alkoxyaziridine-2-carboxylic and -2,2-dicarboxylic acids.

The principal fragmentation path for esters of α-amino acids (including proline ethyl ester) under the influence of electron impact is splitting out of a carbalkoxyl radical to give an amine fragment, the peak of which is the maximum peak in the spectra [1]. In the case of N-methylproline the principal peak corresponds to the $(M - COOH)^{2+}$ fragment. In the spectra of amino acids $(CH_2)_nC(COOH)NH_2$ the intensity of the $(M - COOH)$ peak when n = 4-7 is about 50% of the total ionic current, whereas it amounts to only 16 and 4%, respectively, when n = 2, 3 [3]. This difference is due to the peculiarities of the fragmentation of small carbon rings [4-7].

We have previously shown that the principal fragmentation pathway for N-alkylazetidine-2-carboxylic esters is splitting out of an ester group to given an $(M - COOR)^+$ amine fragment, the peak of which is the maximum peak in the spectra at 30 and 12 eV [8].



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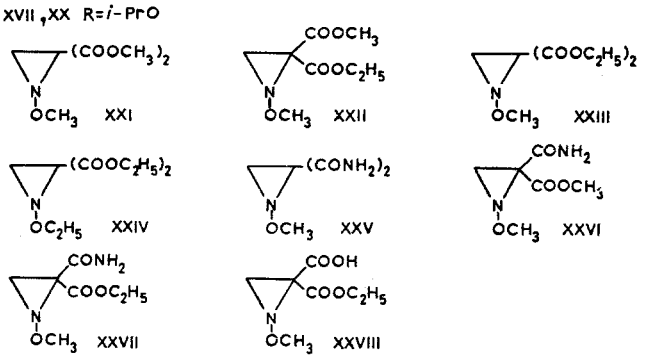
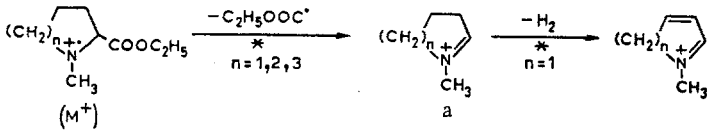
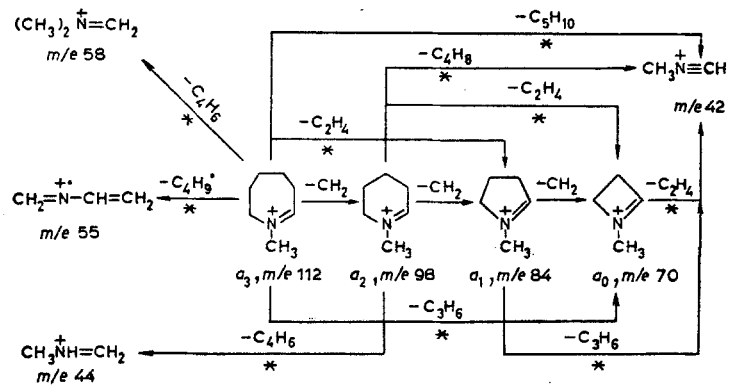
XII R=H; XIII R=D; XIV R=Cl; XV, XVIII R=CH_3O; XVI, XIX R=C_2H_5O; XVII, XX R=*i*-PrO



In the present research we have studied the character of the fragmentation as a function of the side of the nitrogen-containing ring in the case of esters and amides of amino acids.* As in the case of N-alkylazetidine-2-carboxylic acid esters [8], the principal peak in the spectra of five-, six-, and seven-membered analogs I-III (Fig. 1) at 30 and 12 eV is the $(M - COOR)^+$ amine fragment (fragment a):



for which a single scheme of the principal fragmentation processes is observed distinctly when n = 0, 1, 2, and 3:



The characteristic (for nitrogen-containing heterocycles) detachment of H_2 from fragment a [4] is observed for I-III, but it is weakly expressed (Fig. 1).

The fragmentation of the analogous derivatives of three-membered heterocycles is completely different and depends substantially on the character of the substituent attached to the nitrogen atom.

In the case of IV the principal process is rearrangement fragmentation with unusual splitting out of an alkyl radical from the ester group to give an ion with m/e 100 (Fig. 2).† This process is completely absent in the case of higher analogs (from four- to seven-membered esters of N-alkylalkyleneimine-2-carboxylic acids). The splitting out of a radical exclusive-

*The low-resolution mass spectra were studied with an MKh-1303 spectrometer with a cylinder inlet system at ionizing voltages of 30 and 12 eV and a cathode emission current of 0.75 μA. The high-resolution mass spectra were recorded with a JSM-01SG-2 spectrometer with an automatic system for information processing.

†We have briefly examined this case in [9].

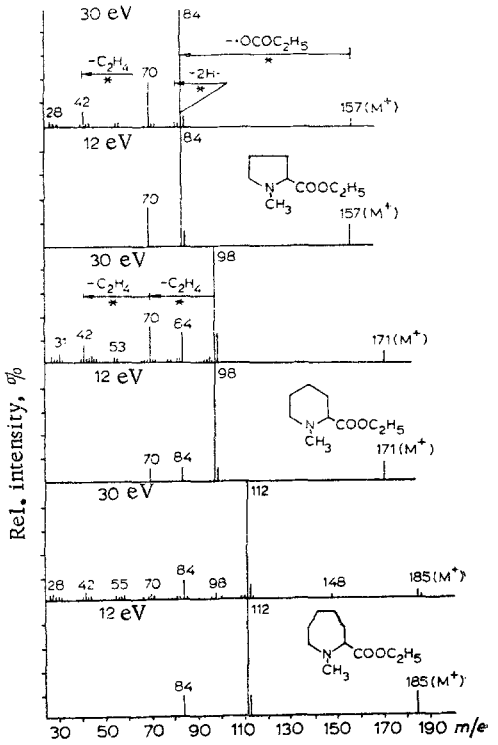


Fig. 1

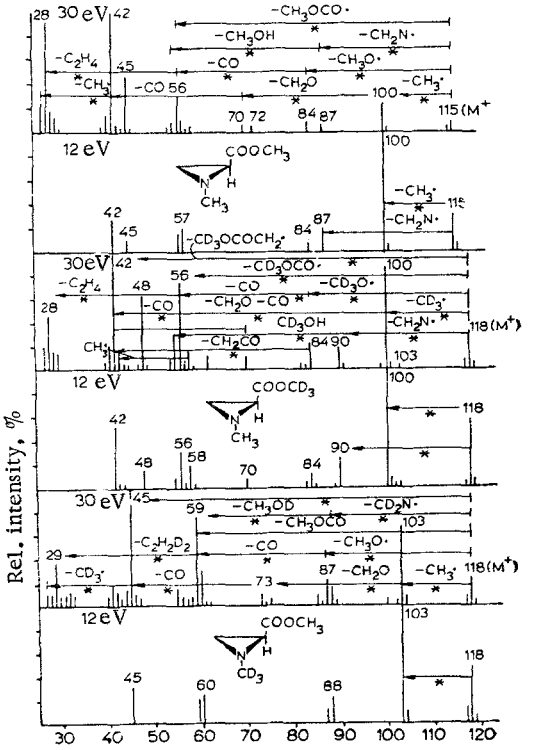


Fig. 2

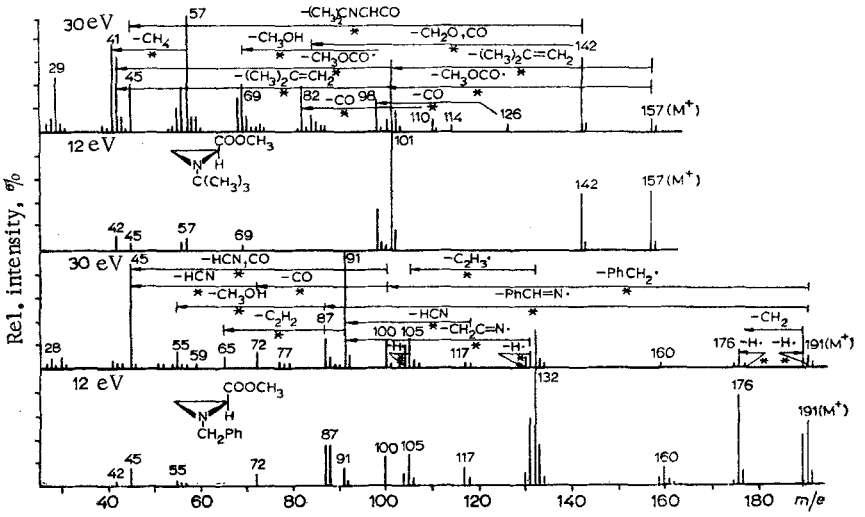
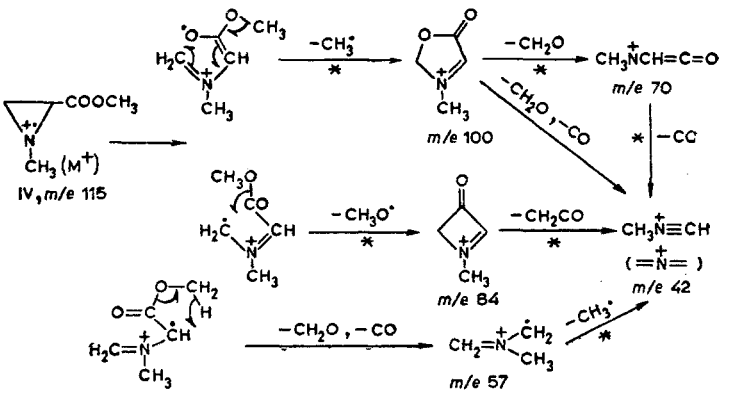


Fig. 3

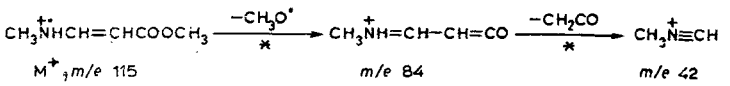
ly from the ester group was proved by means of deuterium labeling [$COOCD_3$ (V) and $N-CD_3$ (VI)] (Fig. 2). The rearrangement character of the fragmentation follows from the maximum intensities of the peaks with m/e 100 and 103 in the low-voltage mass spectra of IV-VI and is confirmed by the appearance of the corresponding metastable peak with a broad flat apex, which attests to the energic advantageousness of the process.

The fragmentation scheme shown below can be conceived of for IV on the basis of the deuterium labels and the metastable transitions. The structure of the ion with m/e 100 is confirmed by the subsequent fragmentation with one- and two-step splitting out of CH_2O and CO.

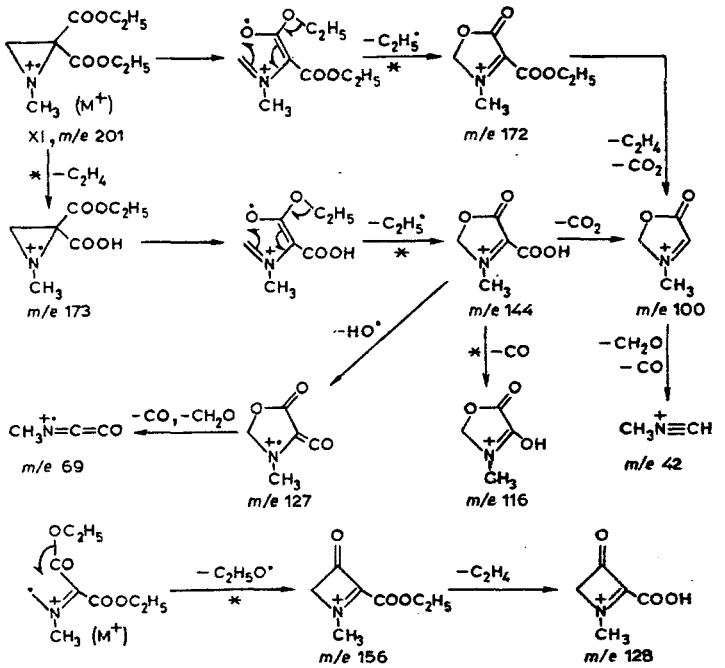
An intense (M-15) ion peak is also observed in the spectra of the methyl esters (VII and VIII) of N-tert-butyl- and N-benzylaziridine-2-carboxylic acids (Fig. 3).



The possibility of fragmentation of IV from the isomerized form of the molecular ion (MeNHCH-CHCOOMe) was excluded by a study of the spectrum of IX and d_3-analog X (Fig. 4), since the chief fragmentation pathway for these compounds is splitting out of MeO$^{\cdot}$:



Detachment of an alkyl radical from the ester group to give an ion with m/e 172 is also the dominant fragmentation process for diester XI (Fig. 5):



The rearrangement detachment of an alkyl radical from the ester group that is characteristic for N-alkylaziridine-2-carboxylic acid esters is not observed at all in the case of nitrogen-unsubstituted analog XII, 1-chloroaziridine XIV (Fig. 6), and 1-alkoxy derivatives XV-XVII and XXI-XXVI (Figs. 7, 9, and 10). In this case other fragmentation processes, which can be represented from the open form of the molecular ion (see below), become the chief processes. These examples show that functional derivatives and homologs, including the first representatives of the series, must be investigated for the accurate prediction of the scheme of fragmentation, under electron impact, of a given class of compounds.

The rearrangement fragmentation (given below) with the participation of an ester group and the substituent attached to the nitrogen atom, which was confirmed by means of deuterium-labeled XIII, is observed for XII (Fig. 6).

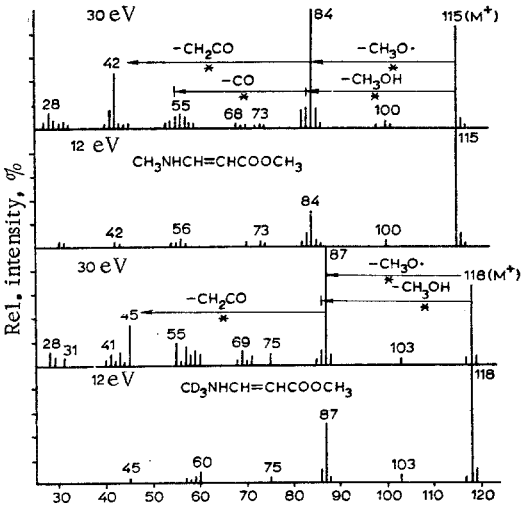


Fig. 4

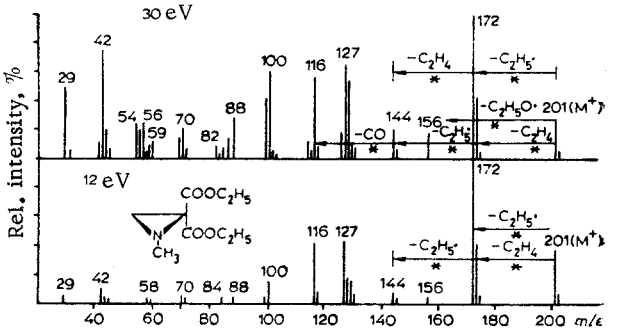


Fig. 5

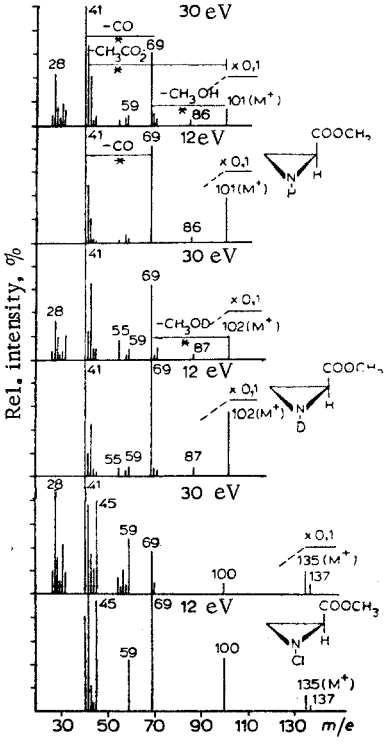
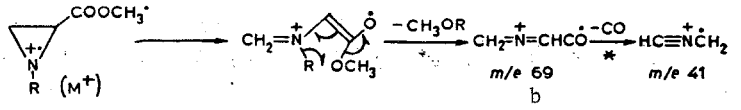
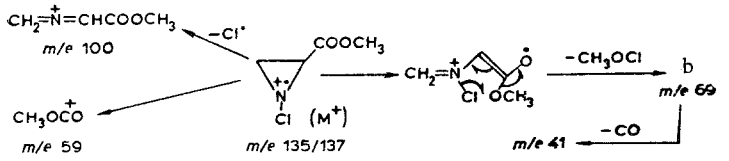


Fig. 6



XII R = H, *m/e* 101 ; XIII R = D, *m/e* 102

Similar fragmentation and splitting out of Cl· from the molecular ion are observed when R = Cl (XIV) (Fig. 6):



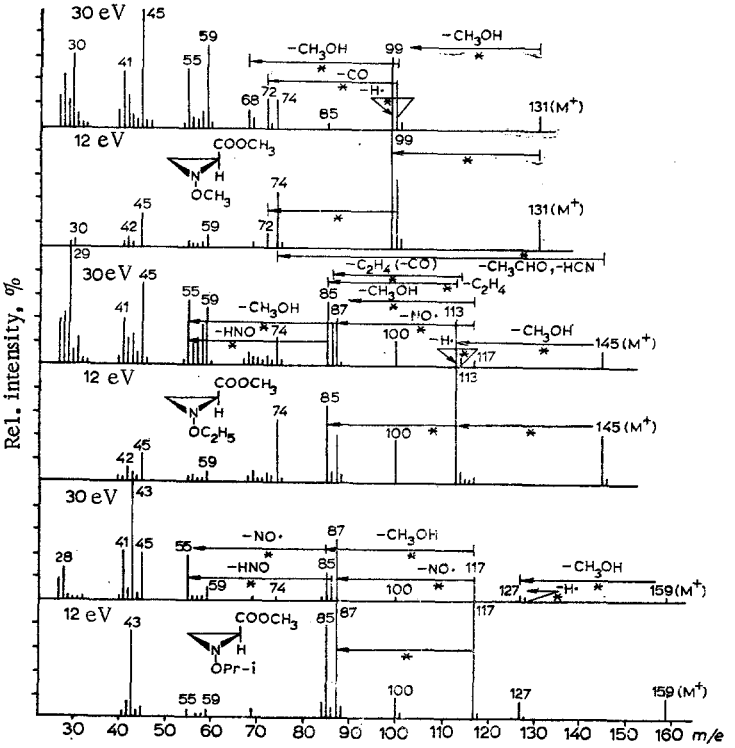

Rel. intensity, %
30 eV
12 eV
30eV
12 eV
30 eV
12 eV
m/e

Fig. 7

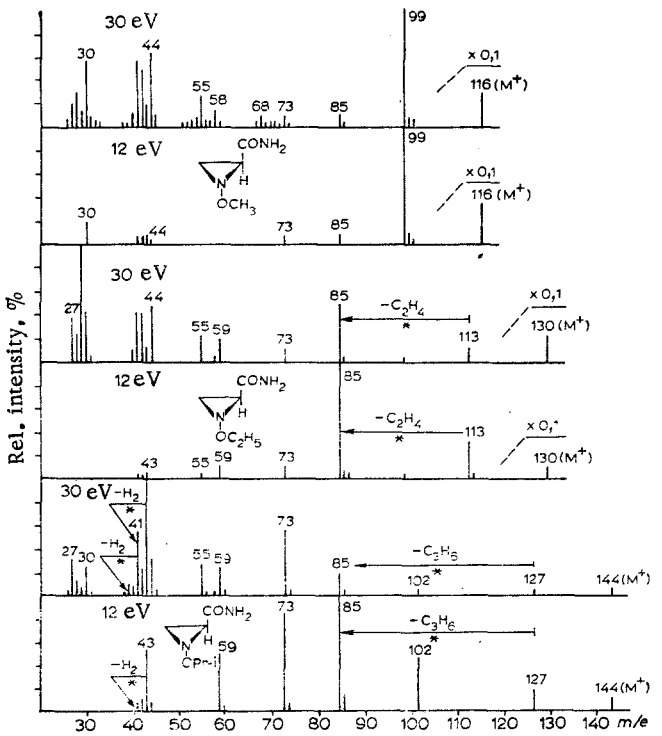

Rel. intensity, %
30 eV
12 eV
30 eV
12eV
30 eV-H2
12 eV
m/e

Fig. 8

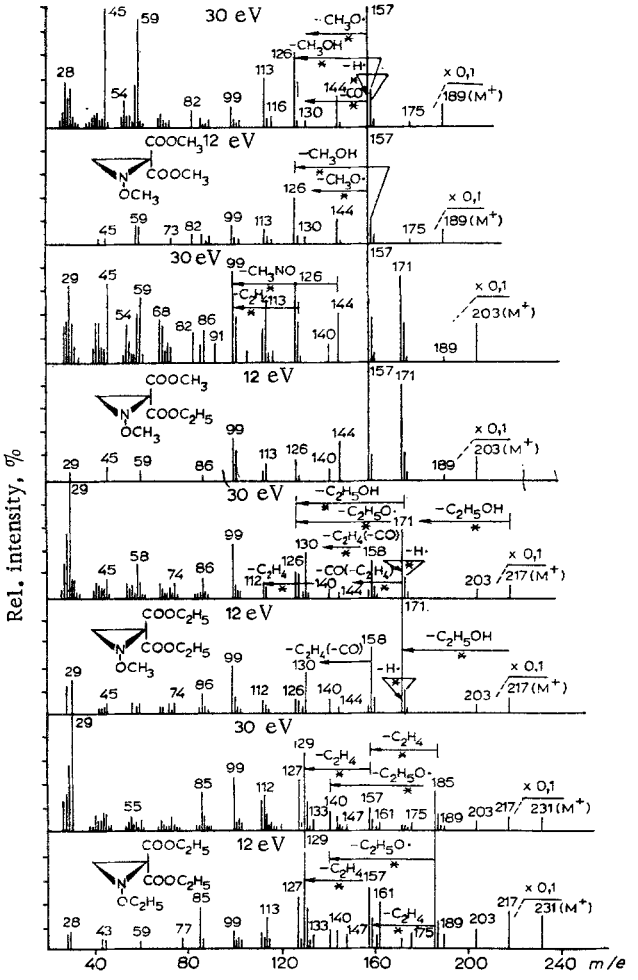


Fig. 9

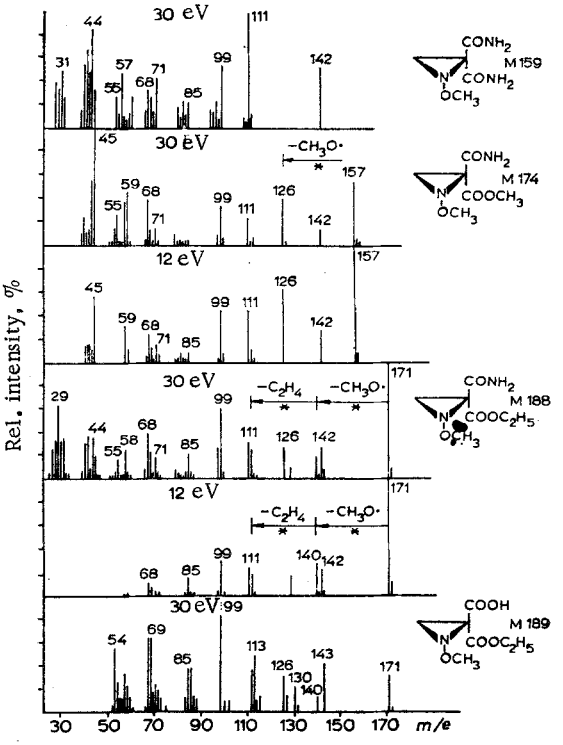
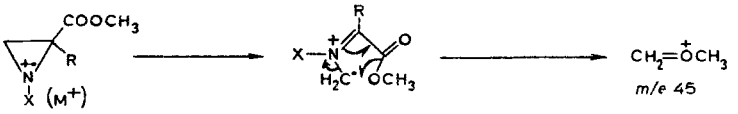


Fig. 10

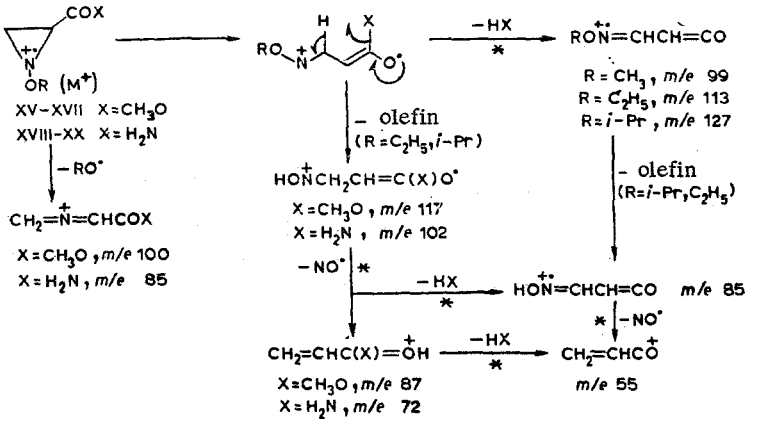
A common rearrangement process, which can be represented from the open form of the molecular ion in the following manner, is observed for the methyl esters (IV, IX, and X) of N-alkylaziridine-2-carboxylic acids (Figs. 2 and 3), the N-chloro- (XIV) (Fig. 6) and N-alkoxy (XV-XVII) (Fig. 7) analogs, and N-alkoxyaziridine-2,2-dicarboxylic acid derivatives XXI and XXII (Fig. 9) and XXVII (Fig. 10):



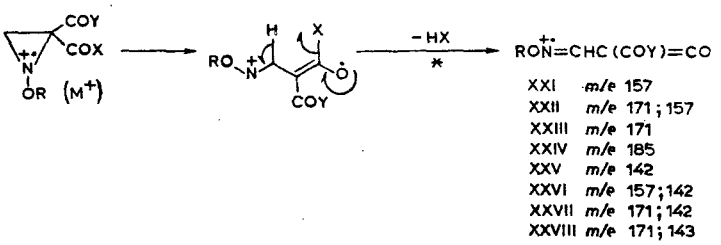
IV, IX, X, XIV-XVII R=H; XXI R=CH_3OOC; XXII R=C_2H_5OOC; XXVII R=$CONH_2$

According to the high-resolution spectrum of X (Fig. 3), the ion with m/e 45 is due completely to the $C_2H_5O^+$ ion. This scheme is also confirmed by the fact that when X = Me, the peak with m/e 45 in the spectrum of $COOCD_3$ deutero analog VI is shifted completely to m/e 48, whereas it is not shifted in the spectrum of $N-CD_3$ deuterium analog V (Fig. 2).

The rearrangement fragmentation of N-alkoxyaziridine-2-carboxylic acid derivatives proceeds with splitting out of the element of alcohol in the case of esters XV-XVII (Fig. 7) and of ammonia in the case of amides XVIII-XX (Fig. 8; the peak with m/e 73 for XIX and XX is corrected to m/e 72).



The chief fragmentation of N-alkoxyaziridine-2,2-dicarboxylic acid derivatives XXI–XXVIII is realized similarly (Figs. 9 and 10) with predominant splitting out of EtOH in mixed ester XXII (Fig. 9) and monoester XXVIII and of NH_3 in monoamides XXVI and XXVII (Fig. 10).



Thus it was shown in the case of the investigated amino acid esters that the character of the fragmentation of the heterocycles, which is similar for seven-, six-, five-, and four-membered compounds, changes radically on passing to three-membered rings.

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