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MASS SPECTROMETRY OF ORGANIC COMPOUNDS IN THE GROUP V ELEMENTS—I:

STRAIGHT CHAIN ALIPHATIC DERIVATIVES

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Abstract—Comparative investigations of the mass spectra of EH_2, Me_2EH, Et_2EH(E = N, P); Me_3E, Et_3E(E = N, P, As, Sb, Bi). $(n\text{-}Pr)_3E$(E = Sb, Bi); $(n\text{-}Bu)_3E$(E = P, As); $(n\text{-}C_5H_{11})_3As$ and $(n\text{-}C_6H_{13})_3As$ as well as Et_2AsBr have been carried out. Deuteroanalogues, metastable transitions and low voltage spectra were used for elucidation of the fragmentation paths. The mass spectra of $MeN(CH_2)_2$ and $CD_3N(CH_2)_2$ were studied to analyse the structure of the fragments. The main degradation path of amines, i.e. α-cleavage, was shown to be untypical for P, As, Sb and Bi derivatives.

DATA on the mass spectra of the aliphatic derivatives of the tricoordinative group V elements are mainly limited to N and P compounds,[1 to 6] and are often contradictory. Thus, in the case of trimethylamine, the ion at *m/e* 41 was considered to be $[C_3H_5]^{+\cdot}$.[4] According to high resolution mass spectra it was shown to be a doublet, however, namely $[C_2H_3N]^{+\cdot}$ (89%) and $[C_3H_5]^{+\cdot}$ (11%).[7] Extremely contradictory data have been presented for methylphosphine,[1,2] probably[8] owing to the use of differing experimental techniques.

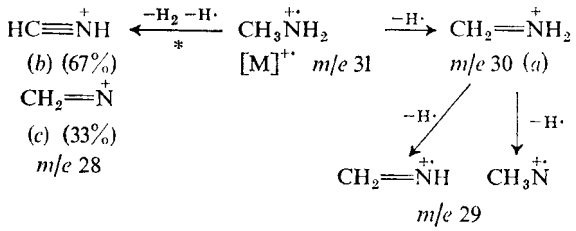
The mass spectra of cyclic phosphines $(CH_2)_2PH$[9] and $(CH_2)_4PH$[10] have also been described. There are even less data on the mass spectra of the compounds of other group V elements. We have briefly described the spectra of Me_3E(E = N, P, As, Sb, Bi);[3] ionization potentials of arsines,[11] and ionization and appearance potentials of the ions in the spectrum of Me_3Sb have been reported.[12] We have recently studied the breakdown of Et_3E(E = N, P, As, Sb) under both electron-impact and photoionization. Ionization and appearance potentials of the ions in the spectrum of Et_3Sb have also been reported.[13]

To compare the breakdown of amines and phosphines the following compounds have been studied: $(CH_2)_4EH$(E = N, P),[11] $Ph_2ECH_2EPh_2$ and $(Ph_2ECH_2)_2$ (E = N, P, As),[14] Me_3E,[3] and Et_3E[6] (E = N, P, As, Sb, Bi). We explained[3] a decrease in intensity of the cleavage ions and products typical of amines in the case of P, As, Sb, Bi as being due to a higher inversion barrier in these compounds. The latter prevents stabilisation which is maximised in a trigonal configuration. The difference between the appearance potential of $Et_2\overset{+}{E}{=}CH_2$ and ionization potential of Et_3E is 1·17 eV higher in the case of phosphorus than nitrogen. This corresponds to the difference in the inversion barriers of the phosphorus and nitrogen compounds.[6]

The mass spectra of the following compounds have been determined in order to compare the bahaviour under electron-impact as well as for a detailed study of the individual fragmentation patterns: $MeNH_2$, $MeND_2$, CD_3NH_2, $MePH_2$, $MePD_2$, Me_2NH, Me_2ND, $MeNHCD_3$, Me_2PH, Me_2PD, Me_3E(E = N, P, As, Sb,

Bi), $MeN(CH_2)_2$, $CD_3N(CH_2)_2$, Et_2NH, Et_2ND, Et_2PH, Et_2PD, Et_2AsBr, Et_3E(E = N, P, As, Sb, Bi), (n-C_3H_7)E(E = Sb, Bi), (n-C_4H_9)$_3$E(E = P, AS) (n-C_5H_{11})$_3$As and (n-C_6H_{13})As.

The general fragmentation scheme for CH_3NH_2 may be represented as follows:



SCHEME 1

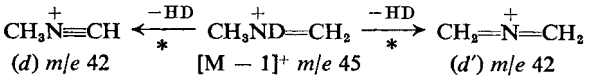
The $[M - 1]^+$ m/e 30 ion shifts to m/e 32 in the spectra of both CH_3ND_2 and CD_3NH_2.

The m/e 28 peak is shifted to m/e 29 ($DC{\equiv}\overset{+}{N}H$) and m/e 30 ($D_2C{=}\overset{+}{N}$) in the spectrum of CD_3NH_2; on this basis the ratio of b and c given in Scheme 1 was determined. An increase of the fragment c in the spectrum of CD_3NH_2 when compared with $MeNH_2$ appears to be an isotopic effect.

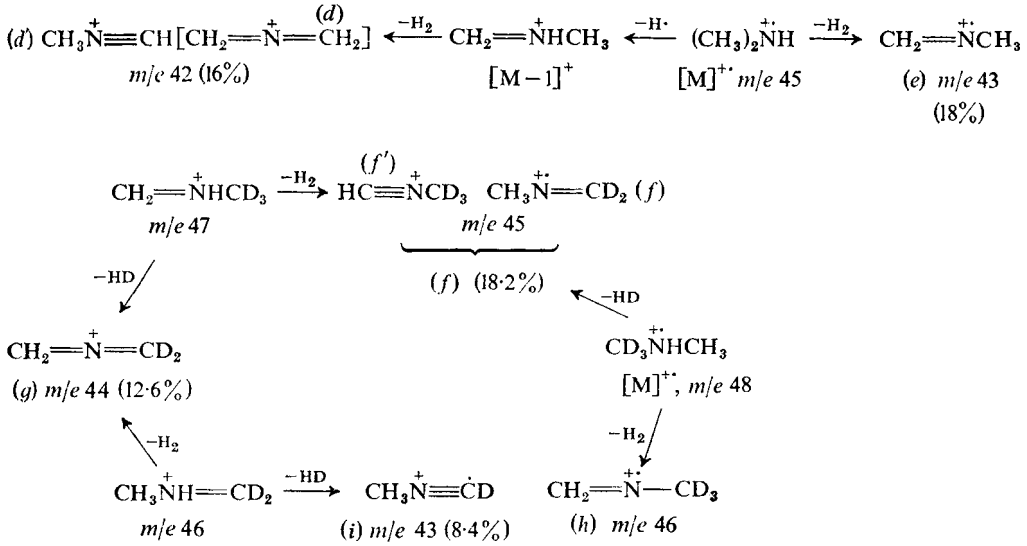
In the spectrum of Me_2NH the fragment due to α-cleavage is also the most abundant. The ion at m/e 44 $[M - 1]^+$ shifts to m/e 45 in the spectrum of Me_2ND and to m/e 46 and 47 in the spectrum of $MeNHCD_3$. The intensity ratio m/e 46: m/e 47 is 0·65 (after allowing for the contribution of the $CD_3\overset{+\cdot}{N}{\equiv}CH_2$ ion at m/e 46 which corresponds to the ion at m/e 43 in the spectrum of the undeuterated sample, see below). This ratio reflects an isotopic effect, the extent of which sharply increases with a decrease in the electron voltage.[16] In the low voltage spectrum this ratio is 6. The probability of C—H bond cleavage is thus six times as high as that of C—D bond cleavage.

The peak at m/e 43 ($[M - 2]^{+\cdot}$) is due to loss of a hydrogen molecule from $[M]^{+\cdot}$. This fragment has the structure e (see Scheme 2), since it does not shift in the spectrum of the N-d_1 compound, where one step expulsion of HD from $[M]^{+\cdot}$ is confirmed by a metastable ion.

The $[M - 3]^+$ ion at m/e 42 is formed from the $[M - 1]^+$ ion by expulsion of a hydrogen molecule; this is confirmed by a metastable transition. The peak at m/e 42 does not shift in the spectrum of the N-d_1 compound, i.e. one hydrogen atom is lost from a nitrogen atom, the expulsion of the second one is possible from both methyl and methylene groups.



The peak at m/e 42 is shifted in the spectrum of the deuteroanalogue-d_3 to m/e 43, 44 and 45, the formation of which is illustrated by the following schemes:



SCHEME 2

Since the ions *i* and *g* in the labelled compound have the same structure as *d'* and *d* in the unlabelled compound, and the ion *f'* (contributing to the ion intensity at *m/e* 45 in the labelled compound) also has the same structure as *d'* we may write

$$\frac{(i) + (f')}{(g)} = \frac{(d')}{(d)}$$

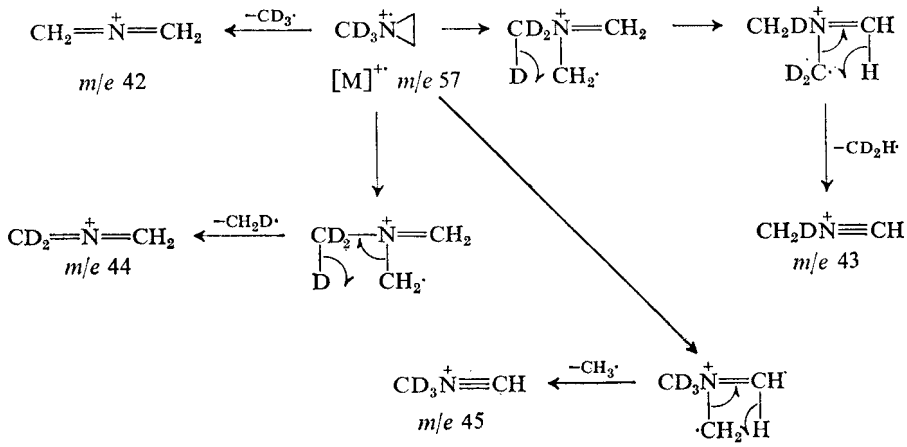
where the brackets denote the intensity of the ions. To evaluate *f'* we assumed that the same isotopic effect (6·0) holds true in the formation of *f* and *h* as in the formation of the $[M - H]^+$ and $[M - D]^+$ ions. If this is the case we can write

$$\frac{(g) + (i) + (f')}{(f)} = \frac{6(f)}{(e)}$$

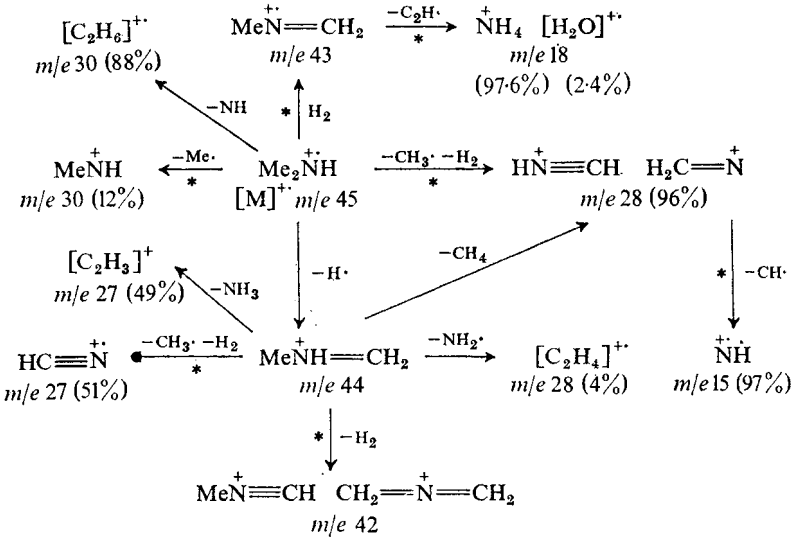
which allows the determination of the intensity of *f'* (12%) and hence the evaluation of the ratio *(d')/(d)*.[1 to 6] This argument is not affected if complete hydrogen randomisation occurs. From the mass spectrum of $CD_3{\cdot}N(CH_2)_2$ [16] it is clear that the loss of methyl occurs with some hydrogen migration (12%).* This result suggests that a possible error due to hydrogen migration in the determination of the ratio of the structures of the fragment *m/e* 42 from dimethylamine should therefore be rather small.

Randomisation in $MeN(CH_2)_2$ similarly effects the formation of the ion at *m/e* 15 which shifts to *m/e* 16, 17 and 18 in the spectrum of CD_3N◁. The fragmentation scheme for Me_2NH is also confirmed by the determination of the percentage of the ions making up the peaks at *m/e* 30, 28, 27, 18 and 15 (represented as a percentage of the total in parenthesis in Scheme 4), carried out by high resolution mass spectrometry.

* Such randomisation is being studied in detail by us with $^{13}CH_3$—$N(CH_2)_2$ and $^{13}CD_3$—$N(CH_2)_2$.



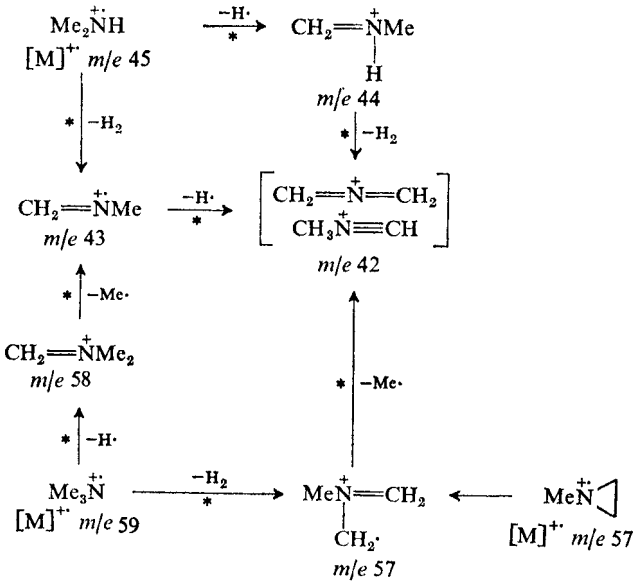
SCHEME 3



SCHEME 4

The peak at *m/e* 28 is a doublet, ($[H_2CN]^+$ (96%) and $[C_2H_4]^+$). Since the peak at *m/e* 28 shifts to *m/e* 29 by 79% in the spectrum of the deuteroanalogue-d_1 a suggestion may be put forward that this part of the nitrogen containing ion at *m/e* 28 corresponds to $[HC{\equiv}NH]^+$, whereas the non-shifted part corresponds to the structure $[H_2C{=}N]^+$. In the case of CH_3NHCD_3 one step formation of the corresponding fragment $[CD_2{=}N]^+$ (*m/e* 30) from the molecular ion is confirmed by a metastable peak.

The main fragmentation path of methylamines (Scheme 5) consists of formation of the α-cleavage ion $[M - 1]^+$ (Figs. 1 to 5) which is the most abundant ion in all cases. The fragmentation path discussed above leading to the *m/e* 42 ion is a higher energy process, being suppressed by decreasing the electron voltage.



SCHEME 5

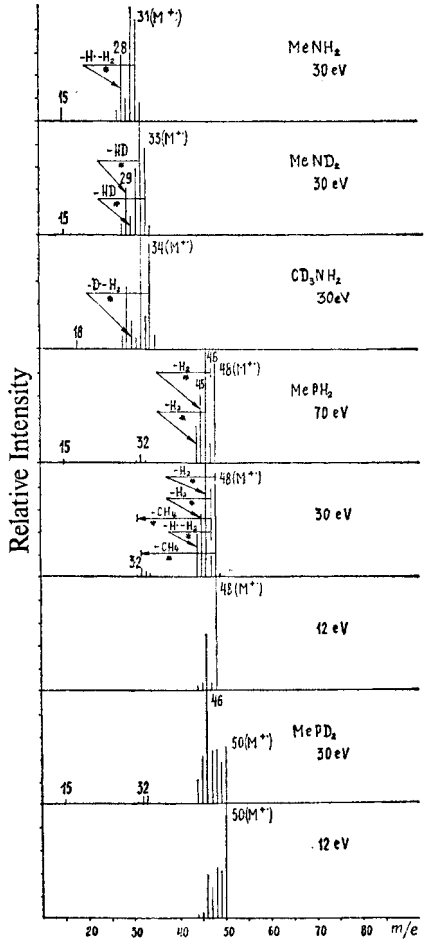


FIG. 1

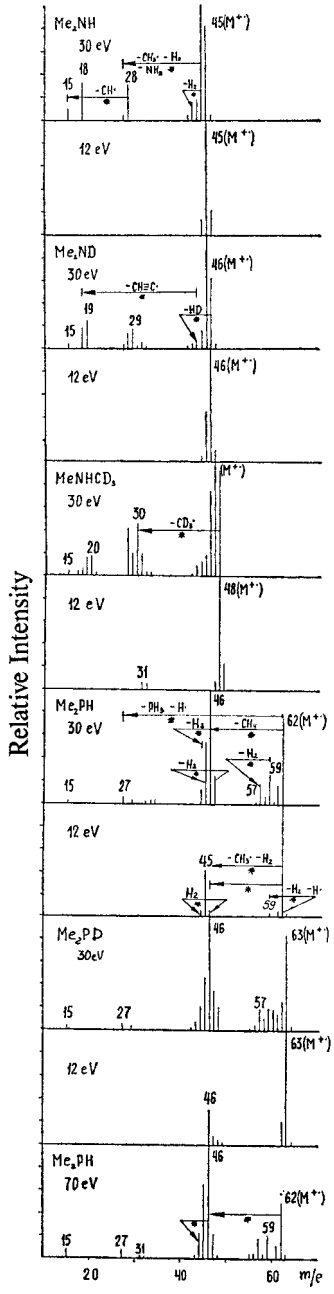

Me2NH
30 eV
45(M+·)
18
28
15
-CH3· - H2
-NH3
-CH·
-H2
12 eV
45(M+·)
Me2ND
30 eV
46(M+·)
-CH=C·
19
29
15
-HD
12 eV
46(M+·)
MeNHCD3
30 eV
(M+·)
30
-CD3·
15
20
12 eV
48(M+·)
31
Me2PH
30 eV
46
-PH2· - H·
-H2
-CH3·
62(M+·)
-H2
-H2
59
15
27
57
12 eV
45
-CH3· - H2
H2
-H2 -H·
59
Me2PD
30eV
46
63(M+·)
15
27
57
12 eV
63(M+·)
46
Me2PH
70eV
46
62(M+·)
59
15
27
31
20
40
60
m/e
Relative Intensity

FIG. 2

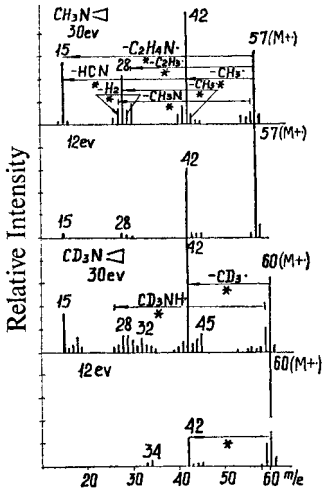


FIG. 3

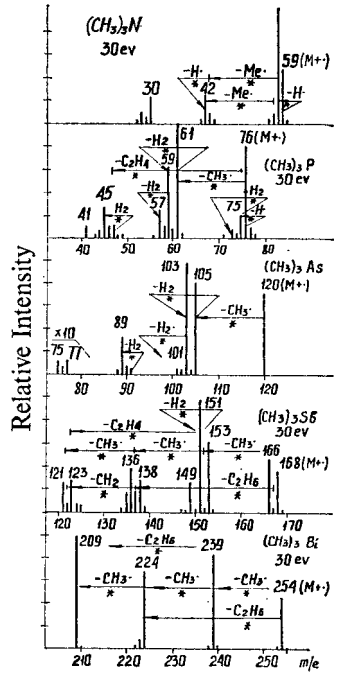


FIG. 4

The formula of the fragmentions in the spectrum of trimethylamine are known by mass measurement.[7] The cyclic structure of the *m/e* 57 fragment proposed in Ref. 7 appears to be wrong, however. In the case of 1-methylaziridine an abundant molecular ion peak is observed which if the ring opened corresponds to the $[M - H_2]^{+\cdot}$ ion in trimethylamine. Stabilisation of the $[M - 1]^+$ ion is hindered in the aziridine due to a lower electron donating power of ethyleneimine nitrogen. For this reason

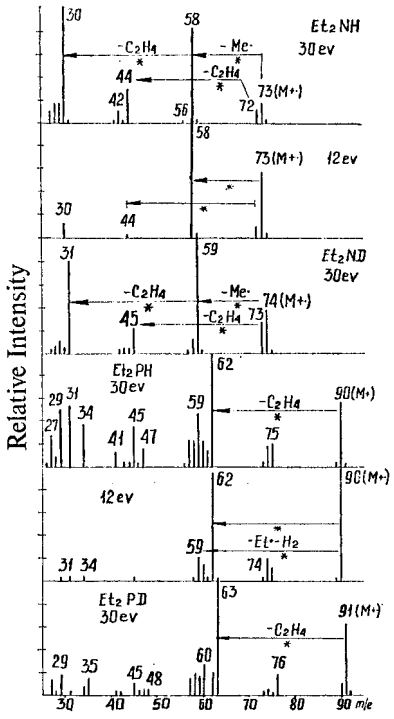


FIG. 5

the ion at *m/e* 42, which is less important for trimethylamine, becomes the most important ion in this particular case.

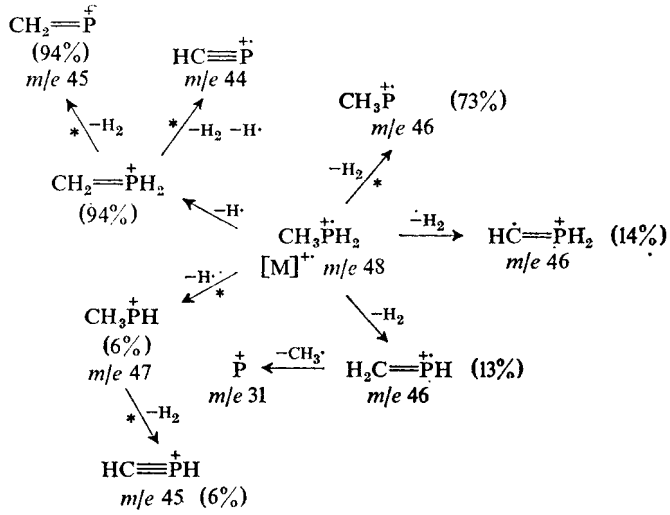
In the case of $MePH_2$* the main fragmentation path consists of expulsion of a hydrogen molecule from the molecular ion. In the spectrum of $Me{\cdot}PD_2$ the *m/e* 46 peak is negligibly shifted. One step formation of the *m/e* 46 ion from the molecular ion is confirmed by the metastable transition (there is also the doubly charged ion at *m/e* 23 (2·7%) which apparently corresponds to $[CH_3P]^{++}$).

The general fragmentation scheme for methylphosphine is depicted in Scheme 6.

When comparing $MeNH_2$ and $MePH_2$ it should be noted that there is an abundant molecular peak in both spectra. The base peak in the spectrum of $MeNH_2$ corresponds to the α-cleavage ion at *m/e* 30, however, whereas the *m/e* 46 fragment ($\overset{+}{P}CH_3$) is the most abundant one in the spectrum of $MePH_2$, the intensity of the α-cleavage ion at *m/e* 47 being only 16%. The ion at *m/e* 46 is also the most abundant one in the spectrum of Me_2PH; in the case of dimethylphosphine-d_1 it shifts by only 75%. Its one step formation from the molecular ion due to CH_4 expulsion is confirmed by a metastable peak. [At 70 eV there is the corresponding doubly charged *m/e* 23 ion (0·026%).]

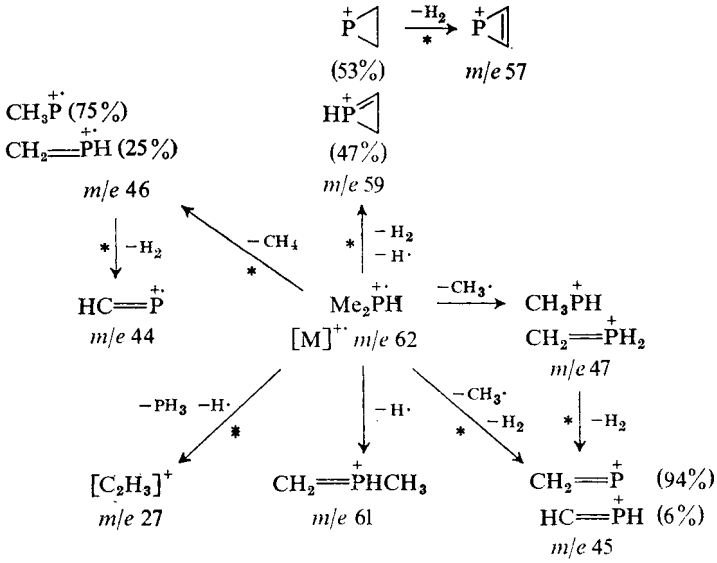
In the spectrum of Me_2PD the peak at *m/e* 59 is shifted to *m/e* 60, its one step formation from the molecular ion being confirmed by a metastable peak.

* The spectrum differs drastically from that described,[1] which seems to be a mixture with dimethyl ether and agrees in the main with the spectrum of dimethyl ether,[2] except for sharp disagreement in the intensity of the peak at *m/e* 15.



SCHEME 6

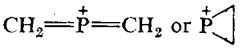
The general fragmentation scheme for dimethylphosphine may be represented as follows:



SCHEME 7

When comparing the spectra of Me_2NH and Me_2PH one can see that the amine α-cleavage ion in $MeNH_2$ is higher than in Me_2NH, whereas the α-cleavage ion in Me_2PH is lower than in $MePH_2$. It should be noted that the fragments $[CH_3P]^+$ (100%), $[CH_2{=}P]^+$ (56%) and $[HC{\equiv}P]^{+\cdot}$ (14%) are predominant in the spectrum of Me_2PH, while the corresponding fragments $[CH_2{=}N]^+$ (32%) and $[CH{\equiv}N]^{+\cdot}$ (4%) in the spectrum of Me_2NH are less abundant, and $[CH_3N]^{+\cdot}$ (*m/e* 29) is absent.

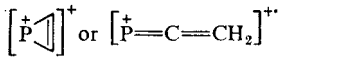
The *m/e* 59 peak is, however, only shifted 47% in the spectrum of dimethylphosphine-d_1. Hence, there are two ion structures:

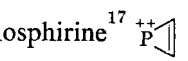
(a) $CH_2{=}\overset{+}{P}{=}CH_2$ or 

and

(b) 

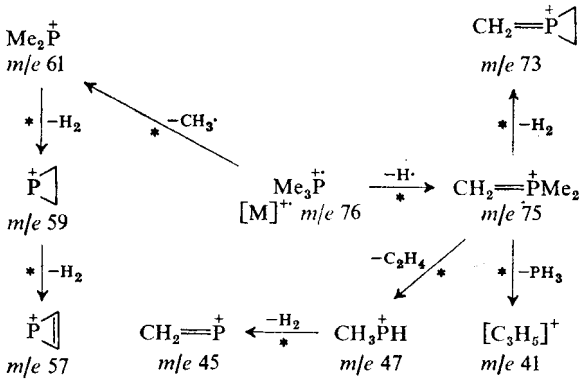
or $[\overset{+}{P}H{-}CH{=}CH_2]^+$. The ion at *m/e* 57 is formed from the *m/e* 59 ion due to expulsion of a hydrogen molecule and is not shifted in the spectrum of the deteroanalogue. Two structures may be ascribed to this, namely



The doubly charged ion *m/e* 28·5 (0·52%) may either correspond to the aromatic system of phosphirine[17]  or have the structure $\overset{+}{P}{-}CH{=}\overset{+}{C}H$.

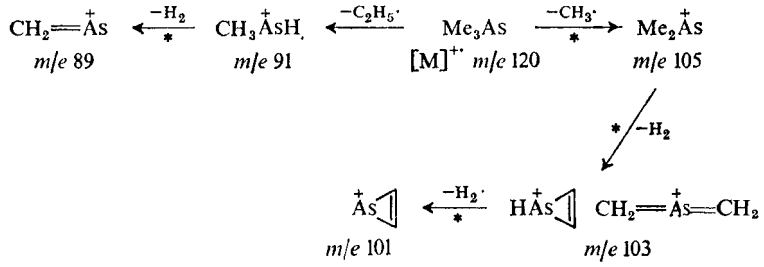
In the trimethyl derivatives of the group V elements a marked decrease in the intensity of the molecular ion is observed when passing from P to Bi. The decrease of the α-cleavage ion in trimethyl derivatives of P, As, Sb and Bi has previously been discussed.[3]

The $[M - Me]^+$ ion at *m/e* 61 is the base peak in the spectrum of Me_3P. A successive twofold expulsion of H_2 from the ion at *m/e* 61 results in the ions at *m/e* 59 and 57. The general fragmentation scheme of Me_3P may be represented as follows:



SCHEME 8

The expulsion of the methyl radical followed by twofold elimination of the hydrogen molecule is observed in the spectrum of trimethylarsine, giving the most abundant peak, as well as in that of trimethylphosphine. The main fragmentation paths for trimethylarsine are given in Scheme 9.



SCHEME 9

The main fragmentation path for ethyl derivatives of P, As, Sb, Bi consists of elimination of ethylene via a 4-membered transition state. In contrast to the corresponding amines this fragmentation proceeds from the ion radical rather than from the ion. The α-cleavage ions and their decomposition products for phosphines (*m/e* 103, 75, 47) are of low intensity and decrease significantly when the energy of the ionizing electrons is 12 eV. As in the case of methyl derivatives[3,6] the trend towards elimination of the substituents with the rupture of the E—C bond increases when passing from P to Bi. The main fragmentation paths are confirmed by the corresponding metastable peaks as well as the spectra of deuteroanalogues (Figs. 6 to 8 and Scheme 10).

To examine the fragmentation paths of $[Et_2As]^+$ the mass spectrum of Et_2AsBr (Fig. 8) was determined since an easy formation of $[M - Br]^+$ was expected. This turned out not to be the case, however; the main fragmentation paths are given in Scheme 11.

The α-cleavage fragmentation predominates when amines have long-chain hydrocarbon substituents. Hydrogen migration to the nitrogen atom in the rearrangement of the α-cleavage ion occurs with equal probability from all positions of the chain except the α-position.[18]

In contrast, very abundant hydrocarbon ions are observed in the spectra of P- and As-derivatives (Figs. 9 and 10). The distinctive feature of the fragmentation patterns of these compounds is exemplified by $(n\text{-}C_4H_9)_3P$ (Scheme 12). Although the five-membered transition state for the C_4H_8 elimination is not proven, it is supported as follows: 1. Consecutive eliminations of C_3H_6 units are observed in all cases and are the most intense ions at 12 eV in the spectra of arsines $(n\text{-}C_4H_9)_3As$; $[M - C_3H_6]^{+\cdot}$, *m/e* 204; $(n\text{-}C_5H_{11})_3As$: $[M - C_3H_6]^{+\cdot}$, *m/e* 246; $(n\text{-}C_6H_{13})_3As$: $[M - 3C_3H_6]^{+\cdot}$, *m/e* 204 (Fig. 11). 2. The characteristic *k* type ion $[(n\text{-}C_4H_9)_3As$: $[Me_3As]^{+\cdot}$, *m/e* 120] as well as homologous ones $[(n\text{-}C_5H_{11})As$: $[Et_3As]^{+\cdot}$; *m/e* 162] and $[(n\text{-}C_6H_{13})_3As$: $[Pr_3As]^{+\cdot}$, *m/e* 204] are observed in the spectra (Fig. 10).

The tendency to elimination of the entire substituent is observed in Sb- and Bi-derivatives; however, processes of C_3H_6 elimination are also seen. The following general conclusions can be drawn from the spectra considered. The intensity of the molecular peak decreases when passing from P to Bi and also decreases with elongation of the chain of the substituent. An increase in the trend towards E—C bond ruptures is observed when passing from P to Bi.

The rearrangement processes accompanied by elimination of an olefine (or

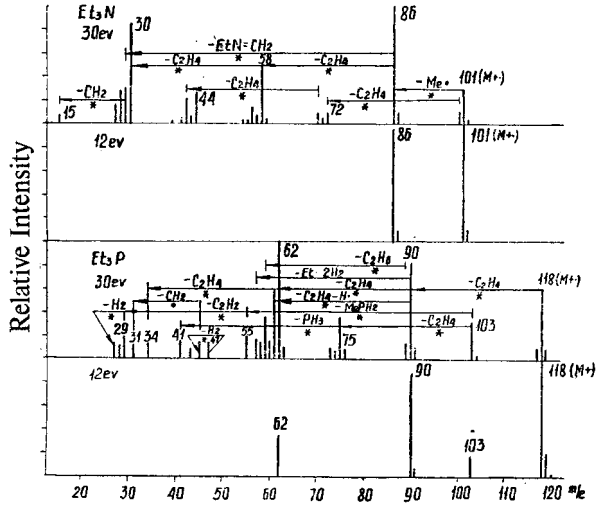


FIG. 6

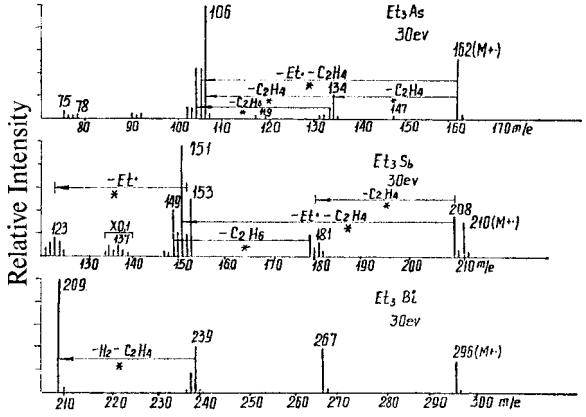


FIG. 7

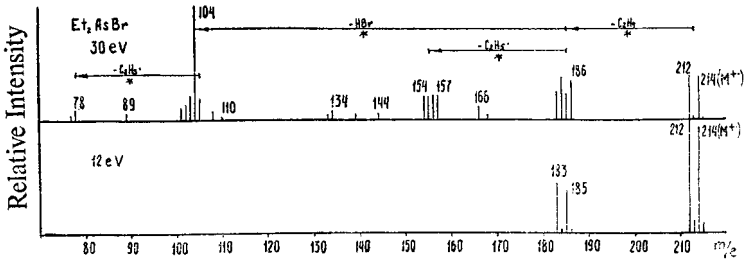
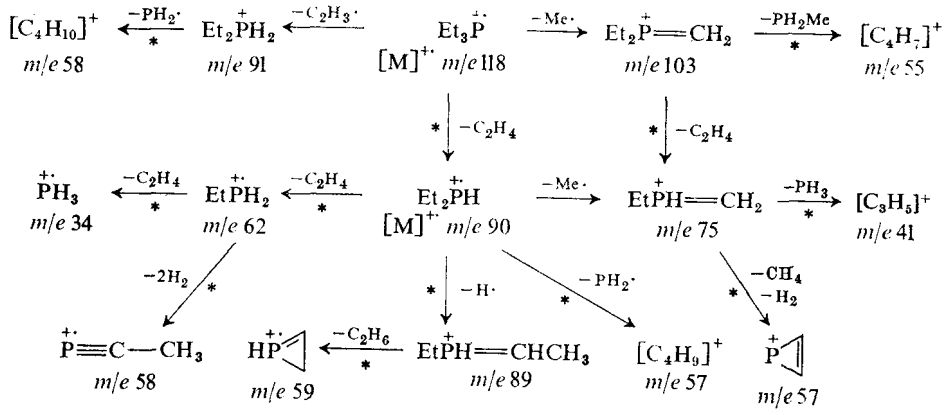
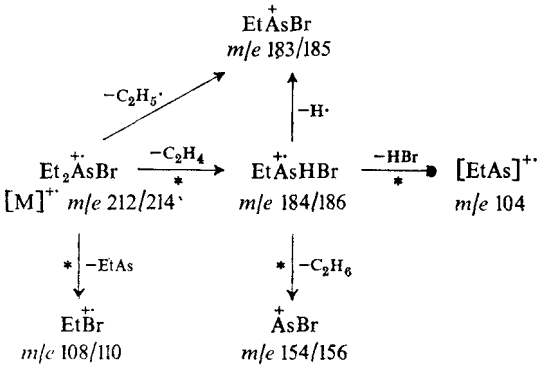


FIG. 8



SCHEME 10



SCHEME 11

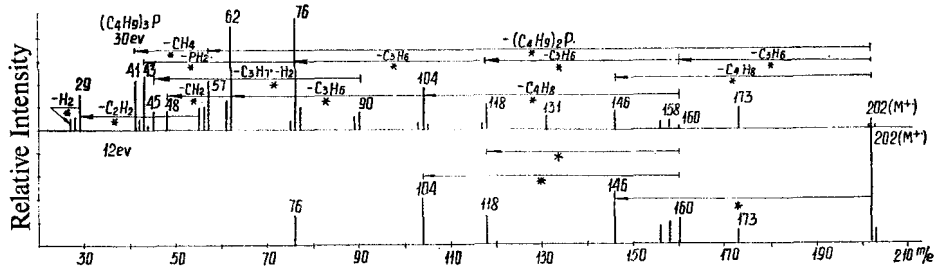


FIG. 9

cycloalkane) due to the rupture of the E—C bond and migration of hydrogen or an alkyl group are characteristic of P, As, Sb derivatives.

In contrast to amines (and quite surprisingly to the compounds of the group IV elements,[19] the odd electron fragments are more abundant in the spectra of P, As, Sb, Bi derivatives.

The α-cleavage fragmentation is insignificant in the derivatives of P and is practically absent from the spectra of As, Sb and Bi derivatives. This main difference in

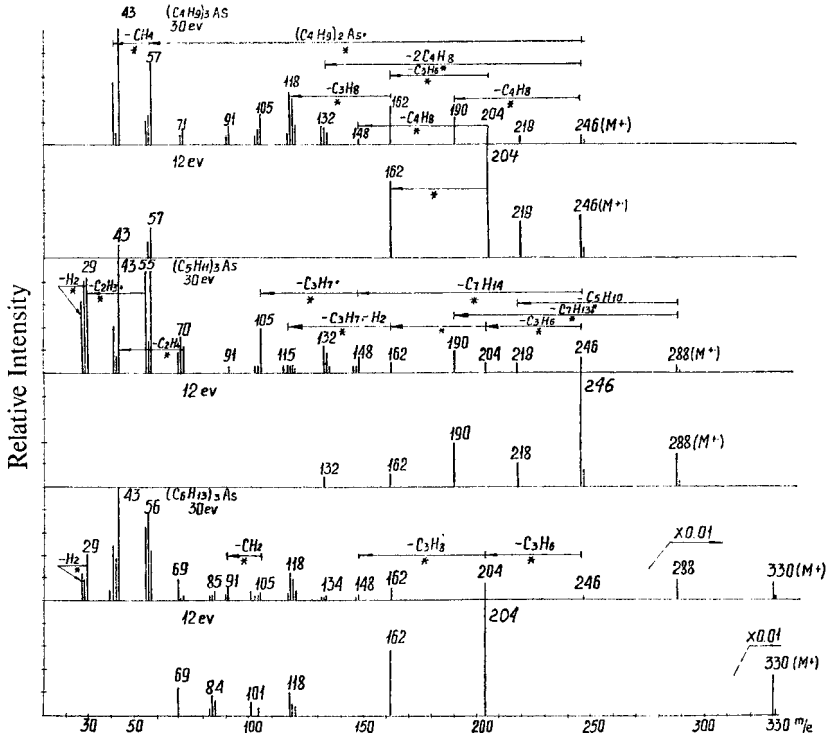
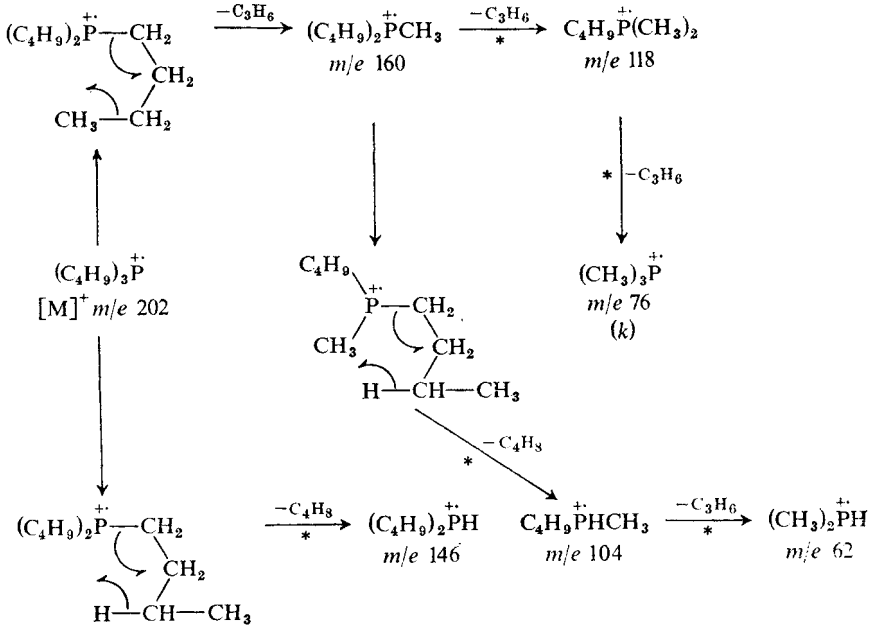


FIG. 10



SCHEME 12

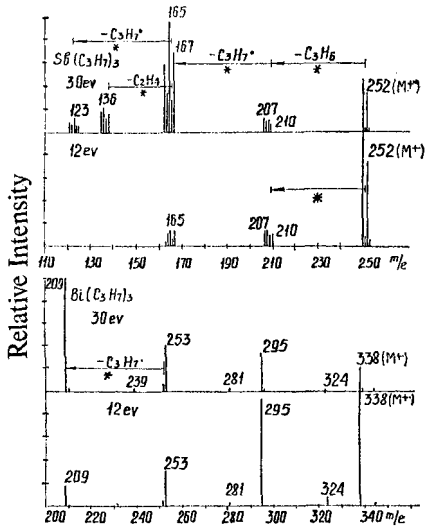


FIG. 11

the fragmentation when passing down inside the group is due to an increase in the configurational stability of the element and to a decrease in the ability to effectively stabilise the α-cleavage ion, respectively.

EXPERIMENTAL

The spectra were taken on an MX-1303 mass spectrometer using the heated inlet system at 30 and 12 eV. To reveal the doubly charged ions the spectra were taken at 70 and 100 eV.

Deuteration of R_2EH and REH_2 was carried out directly in the instrument by repeated introduction of D_2O.

The synthesis of CD_3NHCH_3 was accomplished according to the scheme:

$$Ph{-}CH{=}NMe \xrightarrow[CH_3CN]{CD_3J} Ph{-}CH{=}\overset{+}{N}\begin{matrix}Me\\ \diagup\\ \\ \diagdown\\ J^- \quad CD_3\end{matrix} \xrightarrow[OH^-]{H_2O} CD_3NHCH_3$$

All compounds studied were purified by distillation just before taking the spectra and the samples were sealed *in vacuo*.

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